UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL

ESCOLA DE ENGENHARIA

DEPARTAMENTO DE ENGENHARIA QUÍMICA

PROGRAMA DE PÓS-GRADUAÇÃO EM ENGENHARIA QUÍMICA

PROPOSTA DE UMA TECNOLOGIA AMBIENTALMENTE SUSTENTÁVEL PARA O TRATAMENTO DE EFLUENTES DE INDÚSTRIAS GALVÂNICAS CONTENDO Cr(VI)

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Porto Alegre, 2015

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Tese submetida ao Programa de Pós-Graduação em Engenharia Química da UFRGS como um dos requisitos à obtenção do grau de Doutor em Engenharia Química.

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À Comissão Examinadora, abaixo assinada, aprova a Tese "Proposta de uma Tecnologia Ambientalmente Sustentável para o Tratamento de Efluentes de Indústrias Galvânicas Contendo Cr(VI)", elaborada por Tiele Caprioli Machado, como requisito parcial para obtenção do Grau de Doutor em Engenharia Química.

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Resumo

O cromo hexavalente – Cr(VI) – presente nos efluentes das indústrias galvânicas, entre outras, é tóxico para maioria dos micro-organismos e potencialmente danoso para a saúde humana. No presente trabalho se estuda a redução de Cr(VI) pelos processos fotoquímicos com álcoois e fotocatálise heterogênea, primeiramente em um reator batelada, com objetivo de obter o melhor processo para aplicação industrial. Na sequência, foram realizados experimentos com efluente industrial, contendo Cr(VI), proveniente de uma indústria galvânica. Após, foram projetados e construídos dois reatores contínuos, o reator em forma de espiral e o reator tubular (radiação artificial e luz solar), com intuito de viabilizar a aplicação industrial do melhor processo de redução de Cr(VI). As reações de redução fotocatalítica de Cr(VI), sob radiação UV, alcançaram reduções totais de Cr(VI) de 66,5% e 56,7% para os catalisadores TiO_2 e ZnO, respectivamente, indicando que o catalisador TiO_2 foi mais eficiente que o catalisador ZnO. As reações de redução fotoquímica de Cr(VI) com etanol apresentaram altos valores de redução total de Cr(VI), sendo que as reações sob radiação UV (96,1%) foram mais eficientes que as reações sob radiação visível (48,1%). Na redução fotocatalítica de Cr(VI) com TiO_2, na presença de etanol, sob radiação UV, foi observada uma redução de Cr(VI) de 92,9% maior do que a redução obtida nas reações fotocatalíticas com TiO_2 sob radiação UV (66,5%), evidenciando o efeito sinérgico entre a oxidação do etanol e a redução do Cr(VI). Quando usados com efluente industrial, estes processos mostraram-se eficientes e obtiveram altos valores de redução total de Cr(VI), possibilitando o uso destes tratamentos para remoção de Cr(VI) presente em efluentes de indústrias galvânicas. Entretanto, dentre estes processos estudados, o mais indicado para aplicação industrial foi a fotoquímica com etanol sob radiação UV, pois dispensa o uso de processos de separação do catalisador e apresenta menores custos com reagentes, sendo o etanol de baixo custo, não tóxico e de fácil aquisição. O reator contínuo espiral, projetado e construído, mostrou-se mais eficiente do que o reator batelada, apresentando uma eficiência fotônica de 2,5% comparada a 1,4% para o reator batelada. Ainda, este reator mostrou-se eficiente quando usado com efluente industrial, apresentando uma redução total de Cr(VI) de 51,8%, em 6 horas de reação, sendo sua configuração considerada suscetível para um *scale-up*. Assim, um reator tubular (radiação artificial e luz solar) foi projetado e construído em escala semi-piloto. Este reator apresentou uma remediação de Cr(VI), presente no efluente industrial, de 86,7% em 6 horas de reação sob luz solar e mostrou uma eficiência fotônica maior do que o reator contínuo espiral. Ainda, o reator tubular apresentou eficiência fotônica similar quando usado com lâmpadas (5,6%) ou luz solar (5,5%), porém as reações sob luz solar mostraram uma maior redução total de Cr(VI) quando comparadas com as reações sob radiação artificial. Assim, o reator tubular, projetado e construído, mostrou-se eficiente quando aplicado para o tratamento de efluente industrial contendo Cr(VI), pelo processo de redução fotoquímica. Além disso, o uso do reator tubular solar minimiza a quantidade de energia elétrica necessária para a reação, reduzindo não somente os custos do processo, como também se tornando uma tecnologia ambientalmente sustentável.

Palavras-chaves: cromo hexavalente, fotocatálise, fotoquímica, efluente industrial, reatores, tecnologia ambientalmente sustentável.

Abstract

Hexavalent chromium – Cr(VI) – present in wastewater discharge of galvanic industries is toxic to most microorganisms and potentially harmful to human health. In this work were studied Cr(VI) reduction by heterogeneous photocatalysis and photochemistry with alcohols processes, firstly in a batch reactor, in order to obtain the best process for industrial application. Subsequently, experiments were conducted using real wastewater from an electroplating plant. In order to feasible the industrial application of best Cr(VI) reduction process were designed and built two continuous reactors, the spiral shaped reactor and the tubular reactor (artificial radiation and sunlight). The photocatalytic reduction reaction of Cr(VI) under UV radiation achieved total Cr(VI) reduction of 66.5% and 56.7% for TiO_2 and ZnO catalysts, respectively, indicating that the TiO_2 catalyst was more efficient than ZnO catalyst. The photochemical reduction reaction of Cr(VI) with ethanol presented high values of total Cr(VI) reduction, and the reactions under UV radiation (96.10%) were more efficient than the reactions under visible radiation (48.1%). In the photocatalytic reduction reaction of Cr(VI) with TiO_2 in the presence of ethanol under UV radiation was observed a Cr(VI) reduction of 92.9% greater than the reduction obtained in the photocatalytic reactions with TiO_2 under UV radiation (66.5%), demonstrating the synergistic effect between ethanol oxidation and Cr(VI) reduction. When used with real wastewater these processes proved to be efficient and showed high values of total Cr(VI) reduction, enabling the use of these treatments for removal of Cr(VI) present in wastewater discharge of galvanic industries. However, among these processes studied, the most suitable for industrial application appears to be photochemistry with ethanol under UV radiation, because it does not require catalyst separation processes and presents lower reagent costs, since ethanol is inexpensive, non-toxic and easy to purchase. The spiral shaped reactor, which was designed and built, showed more efficient than the batch reactor, presenting a photonic efficiency of 2.5% compared to 1.4% for the batch reactor. Additionally, this reactor was effective when applied to real wastewater, presenting a total Cr(VI) reduction of 51.8% in 6 hours of reaction, and its configuration is suitable for scale up. Thus, a tubular reactor (artificial radiation and sunlight) was designed and built in semi-pilot scale. This reactor presented a Cr(VI) remediation of 86.7% in 6 hours of reaction under sunlight and showed a photonic efficiency higher than spiral shaped reactor. Additionally, the tubular reactor presented similar photonic efficiency when used with either lamps (5.6%) or sunlight (5.5%), however the reactions under sunlight showed a greater total Cr(VI) reduction when compared to the reactions under artificial radiation. Therefore, the tubular reactor, which was designed and built, proved to be efficient when applied to treatment of real wastewater containing Cr(VI) by photochemical reduction process. Furthermore, the use of a solar tubular reactor minimizes the amount of electricity required for the reaction, which not only reduces process costs, but also makes the technology more environmentally sustainable.

Keywords: hexavalent chromium, photocatalysis, photochemistry, wastewater, reactors, environmentally sustainable technology.

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INTRODUÇÃO

O cromo hexavalente é um metal tóxico para maioria dos micro-organismos e potencialmente danoso para a saúde humana. A forma hexavalente do cromo é altamente solúvel, o que possibilita a contaminação de lençóis freáticos e outras fontes de água potável, sendo mais estável que a trivalente. Além disso, o cromo hexavalente é 100 vezes mais tóxico que o trivalente (MOHAPATRA *et al.*, 2005; DAS *et al.*, 2006; XU *et al.*, 2006; YANG e CHAN, 2009; CHAKRABARTI *et al.*, 2009). A presença de metais pesados no meio ambiente deve-se, principalmente, à descarga inadequada de efluentes industriais, estando as empresas de curtimento de couro, tintas, corantes, materiais fotográficos, galvanoplastia, mineração, metalúrgicas e eletrônicas, entre as possíveis fontes de cromo (SCHRANK *et al.*, 2002; MOHAPATRA *et al.*, 2005; CHAKRABARTI *et al.*, 2009).

A galvanoplastia é um processo químico no qual são depositadas finas camadas de um metal sobre superfícies de corpos metálicos ou não, por meios químicos ou eletroquímicos, a partir de soluções aquosas que contêm metais, tais como, o cromo, o níquel, o cobre, o zinco, o cádmio, entre outros, seguidos de enxágues com água para limpeza (COSTA, 1998). A indústria de galvanização é caracterizada pelo excessivo consumo de água e energia e pela grande geração de efluentes líquidos contendo metais pesados, tais como, cobre, níquel e cromo. Estes efluentes provêm, principalmente, do descarte das águas de enxágue das peças retiradas dos banhos eletroquímicos.

O tratamento convencional para águas residuais contendo Cr(VI) é a redução a Cr(III) com sulfito de sódio ou metabissulfito. Este método, no entanto, apresenta alguns problemas: exige um excesso de produtos químicos para garantir a conversão completa do Cr(VI), ocorre a formação de lama e liberação de dióxido de enxofre. Desta maneira, estudos vêm sendo direcionados ao desenvolvimento de tecnologias mais limpas para remediação de efluentes

contendo cromo, entre eles, a fotocatálise heterogênea e a fotoquímica com álcoois (CHAKRABARTI *et al.*, 2009).

Os processos de fotocatálise heterogênea ocorrem quando uma energia luminosa incide sobre um semicondutor, com comprimento de onda igual ou maior que a energia de *band-gap* deste semicondutor, gerando pares elétron/lacuna que podem sofrer subsequentes reações de oxidação e redução com algumas espécies, as quais podem estar adsorvidas na superfície do semicondutor, gerando os produtos necessários da oxidação/redução (CHATTERJEE e DASGUPTA, 2005). Alguns semicondutores utilizados, na reação de redução fotocatalítica de Cr(VI), são TiO_2 (KU e JUNG, 2001; SCHRANK *et al.*, 2002; CHO *et al.*, 2004; TUPRAKAY e LIENGCHARERNSIT, 2005; XU *et al.*, 2006; JIANG *et al.*, 2006), ZnO (KHALIL *et al.*, 1998; CHAKRABARTI *et al.*, 2009), CdS (WANG *et al.*, 1992), ZrO_2/TiO_2 (COLÓN *et al.*, 2002), ZnO/TiO_2 (KU *et al.*, 2011), $CuFe_2O_4/CdS$ (NASRALLAH *et al.*, 2011), TiO_2/Au (PANDIKUMAR e RAMARAJ, 2012), TiO_2/WO_3 (YANG *et al.*, 2010).

Nos processos fotoquímicos estudam-se as reações químicas e alterações físicas que resultam das interações entre matéria e luz ultravioleta ou visível. A absorção da luz ultravioleta ou visível pela matéria pode excitar elétrons para níveis de energia mais altos, gerando espécies eletronicamente excitadas. Esta excitação eletrônica pode ocasionar mudanças químicas, como a degradação/redução de moléculas (WARDLE, 2009). A redução fotoquímica de Cr(VI), na presença de compostos orgânicos e sob radiação UV ou visível, tem sido estudada. Na literatura são encontrados alguns trabalhos sobre a redução fotoquímica de Cr(VI) por álcoois (MYTYCH *et al.*, 2003), fenol e seus derivados halogenados (MYTYCH e STASICKA, 2004) e glicerol (YURKOW *et al.*, 2002).

Neste contexto, o principal objetivo desta tese de doutorado é desenvolver uma tecnologia sustentável, baseada nos processos de fotocatálise heterogênea e fotoquímica com álcoois, para o tratamento de efluentes contendo cromo hexavalente, provenientes de uma indústria galvânica. Para alcançar este objetivo é indispensável o projeto de um reator e seu *scale-up*. Especificamente pretende-se:

i) investigar as reações de fotocatálise heterogênea e fotoquímica com álcoois para redução de cromo hexavalente, usando um reator batelada e uma solução sintética de Cr(VI);

ii) realizar experimentos com efluente industrial, proveniente de uma indústria galvânica;

iii) projetar e construir reatores, em maior escala, para viabilizar a aplicação industrial do melhor processo de redução de cromo hexavalente.

Este trabalho está estruturado em capítulos. O Capítulo I apresenta os embasamentos teóricos pertinentes à análise dos resultados. Os Capítulos II, III, IV e V descrevem as metodologias utilizadas na condução dos experimentos e os resultados obtidos; estes capítulos estão apresentados na forma de artigos científicos que foram publicados, aceitos e/ou submetidos para publicação. As considerações finais sobre o tema desta tese estão apresentadas no Capítulo VI. Ao final, nos apêndices, são apresentadas informações que complementam o trabalho.

Esta tese foi desenvolvida no Laboratório de Catálise e Reatores (LARET) do Departamento de Engenharia Química (DEQUI) da Universidade Federal do Rio Grande do Sul (UFRGS).

CAPÍTULO I – REVISÃO BIBLIOGRÁFICA

Neste capítulo serão apresentadas informações encontradas na literatura a respeito da Redução de Cromo Hexavalente por Fotocatálise Heterogênea e Fotoquímica com Álcoois, bem como informações sobre o Cromo Hexavalente. Ainda, será apresentada uma revisão bibliográfica sobre Reatores e sobre a Indústria de Galvanoplastia.

1 Cromo Hexavalente

A presença de metais pesados em corpos aquáticos é um sério problema ambiental. A maior fonte de metais pesados é o descarte inadequado de efluentes industriais (KU e JUNG, 2001; MOHAPATRA *et al.*, 2005; DAS *et al.*, 2006). Estes íons metálicos geralmente são persistentes no meio ambiente e suas concentrações estão aumentando nas cadeias alimentares para níveis tóxicos (SCHRANK *et al.*, 2002; DAS *et al.*, 2006). Dentre estes poluentes inorgânicos encontra-se o cromo, metal largamente usado no curtimento de couro e indústrias de tintas, corantes, materiais fotográficos, galvanoplastia, mineração, metalúrgicas e eletrônicas (SCHRANK *et al.*, 2002; MOHAPATRA *et al.*, 2005; CHAKRABARTI *et al.*, 2009).

A Tabela 1.1 apresenta a concentração máxima permitida de cromo hexavalente nos efluentes industriais, que são lançados em corpos d´águas superficiais, para alguns países da América.

O cromo ocorre na natureza em dois estados de oxidação, Cr^{+3} e Cr^{+6} ou Cr(III) e Cr(VI). O cromo hexavalente é tóxico para a maioria dos organismos, sendo carcinogênico e mutagênico para os animais, podendo causar irritação e corrosão na pele humana. Além disso, esta forma de cromo está geralmente associada com o desenvolvimento de várias doenças crônicas, incluindo danos a órgãos, como o fígado, congestões pulmonares, dermatites, vômitos, severa diarreia,

perfuração do septo nasal e aborto (MOHAPATRA *et al.*, 2005; DAS *et al.*, 2006; BARRERA-DÍAZ *et al.*, 2012).

Tabela 1. 1: Critérios de regulamentação internacional, adaptado de Barrera-Díaz et al. (2012).

País	Cr(VI) (mg L^{-1})
Brasil*	0,1
Canadá	0,05
Estados Unidos	0,1
México	0,05

* Resolução nº 430 de 13/05/2011 - CONAMA

O Cr(VI) é altamente solúvel, o que possibilita a contaminação de lençóis freáticos e outras fontes de água potável, sendo mais estável que o trivalente. A forma hexavalente do cromo é 100 vezes mais tóxica que a trivalente (MOHAPATRA *et al.*, 2005; DAS *et al.*, 2006; XU *et al.*, 2006; YANG e CHAN, 2009; CHAKRABARTI *et al.*, 2009). Por outro lado, o cromo trivalente é facilmente precipitado e não apresenta toxicidade, sendo considerado um elemento essencial para o metabolismo humano, em níveis controlados (KIM *et al.*, 2002; MOHAPATRA *et al.*, 2005).

De acordo com Barrera-Díaz et al. (2012), as espécies de Cr(VI) em solução aquosa são $Cr_2O_7^{2-}$, CrO_4^{2-}, H_2CrO_4 e $HCrO_4^{1-}$, a distribuição relativa destas espécies depende do pH da solução, da concentração de Cr(VI) e do potencial redox. No entanto, mesmo variando o pH da solução, o Cr(VI) não exibe nenhuma espécie insolúvel, sendo este estado de oxidação do cromo passível de alteração tanto na água quanto no solo. Por outro lado, o estado trivalente do cromo forma espécies insolúveis, $Cr(OH)_3$, na faixa de pH da solução entre 5,5 e 12,5. Assim, para formar uma espécie de cromo na fase sólida, facilitando a separação em meios aquosos, é necessário mudar o estado de oxidação da mesma.

Ku e Jung (2001) também estudaram o efeito do pH da solução sobre a distribuição das espécies de Cr(VI) em solução aquosa e propuseram as seguintes reações:

$$H_2CrO_4 \leftrightarrow H^+ + HCrO_4^{1-} \tag{1.1}$$

$$HCrO_4^{1-} \leftrightarrow H^+ + CrO_4^{2-} \tag{1.2}$$

$$2HCrO_4^{1-} \leftrightarrow Cr_2O_7^{2-} + H_2O \qquad\qquad\qquad (1.3)$$
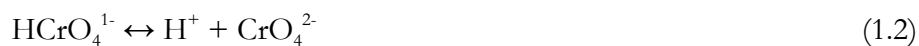
e o balanço de massa das reações das espécies de Cr(VI), utilizando as constantes de dissociação adequadas foi calculado e mostrado na Figura 1.1. Os autores observaram que, a molécula de ácido crômico neutra, H_2CrO_4, foi a espécie dominante para valores de pH menores que 2,0, enquanto que as concentrações das espécies de carga negativa, $HCrO_4^{1-}$, CrO_4^{2-} e $Cr_2O_7^{2-}$, foram dominantes para valores de pH maiores que 2,0.
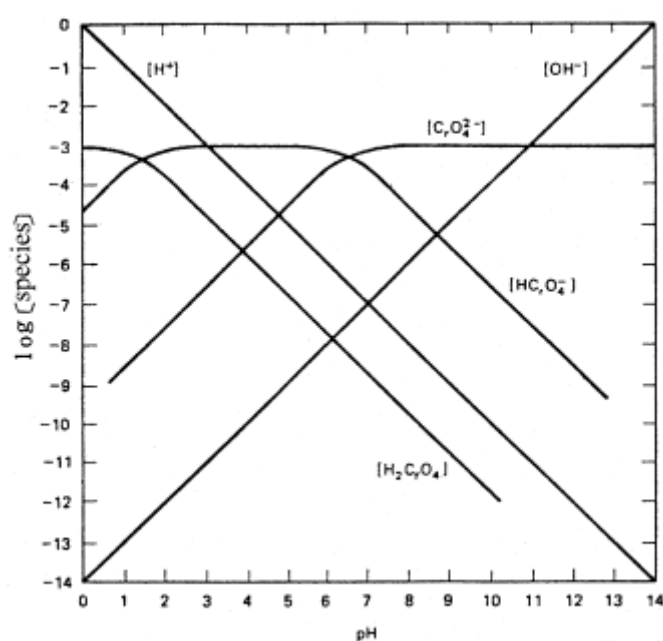
Figura 1. 1: Distribuição das espécies de Cr(VI) em solução aquosa como função do pH da solução. (KU e JUNG, 2001)

Os métodos geralmente utilizados para o tratamento de efluentes industriais contendo cromo hexavalente são precipitação química, osmose reversa, troca iônica, flotação, eletrólise, adsorção, coagulação-precipitação (KU e JUNG, 2001; MOHAPATRA *et al.*, 2005; CHAKRABARTI *et al.*, 2009). Contudo, estes métodos de tratamento requerem altos gastos com energia ou uso de grandes quantidades de produtos químicos (MOHAPATRA *et al.*, 2005). Neste contexto, a fotocatálise heterogênea e a fotoquímica com álcoois surgem como alternativas de tecnologias mais limpa para remediação de cromo hexavalente presente em efluentes industriais.

2 Indústria de Galvanoplastia

A galvanização consiste em um processo de revestimento da superfície de uma peça, geralmente metálica, por outro metal, visando a alterações de algumas de suas características, tais como cor, brilho, rigidez e resistência à corrosão. Na galvanização por deposição eletrolítica, as peças são mergulhadas em um banho composto por sais do metal, que as revestirá, além de aditivos que permitem uma melhor aderência do metal à sua superfície (LADEIRA E PEREIRA, 2008).

Os objetivos da utilização do tratamento de superfície, por meios químicos ou eletroquímicos, são a proteção à corrosão, acabamentos decorativos e acabamentos funcionais. Como principais razões para a utilização da eletrodeposição galvânica sobre peças metálicas, pode-se destacar: prevenir a corrosão do material base, promover resistência ao desgaste e a incidência de manchas, mudar o coeficiente de atrito, mudar as propriedades elétricas superficiais, alterar o comportamento superficial com relação aos agentes pigmentantes, prevenir a carbonização, alterar dimensões e melhor aparência (PASQUALINI, 2004).

O processo de galvanização, basicamente, envolve uma sequência de banhos consistindo de etapas de pré-tratamento, de revestimento e de conversão de superfície. Entre estas etapas, a peça sofre um processo de lavagem. Desta forma, são originados efluentes líquidos, emissões gasosas e resíduos sólidos que necessitam de tratamento específico (CPRH, 2001). No fluxograma apresentado pela Figura 1.2, são mostrados os pontos de geração de poluente de um processo típico.

Como observado no fluxograma da Figura 1.2, a indústria de galvanização é caracterizada pelo excessivo consumo de água e energia, pela geração de efluentes líquidos contendo metais pesados e emissões gasosas, oriundas das perdas por evaporação dos banhos aquecidos, além dos resíduos sólidos gerados no preparo dos materiais a serem galvanizado.
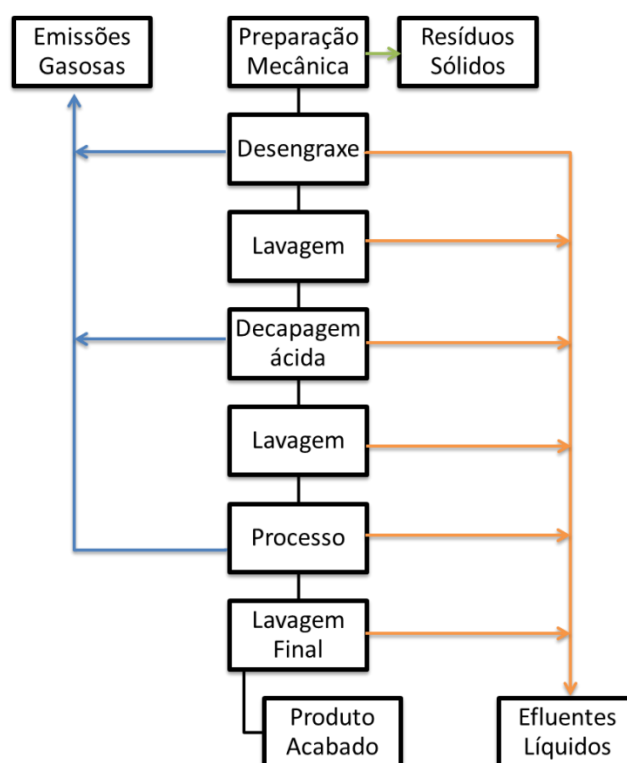
Figura 1. 2: Fluxograma de um processo de galvanoplastia, adaptado de CPRH (2001).

2.1 Efluentes líquidos

Os efluentes líquidos gerados na indústria galvânica provêm das operações de limpeza de peças brutas, das soluções perdidas ou arrastadas durante o processo, do eventual descarte dos banhos, das águas de lavagem do piso e, principalmente, do descarte das águas de enxágue das peças retiradas dos banhos eletroquímicos. A elevada carga tóxica dos efluentes líquidos gerados no processo de galvanoplastia é composta, principalmente, por sais de cianeto e metais pesados como cobre, níquel e cromo, entre outros, que podem estar presentes nas formas solúvel e insolúvel (PACHECO, 2002).

No Brasil, a legislação federal Resolução nº 430, de 13 de maio de 2011 do Conselho Nacional do Meio Ambiente – CONAMA dispõe sobre as condições e padrões de lançamento de efluentes, complementa e altera a Resolução nº 357, de 17 de março de 2005, do Conselho Nacional do Meio Ambiente – CONAMA. Assim, normatiza seu Artigo 3:

"... os efluentes de qualquer fonte poluidora somente poderão ser lançados diretamente nos corpos receptores após o devido tratamento e desde que obedeçam as condições, padrões e exigências dispostos nesta Resolução e em outras normas aplicáveis."

Segundo esta Resolução, os valores máximos dos parâmetros inorgânicos de lançamento de efluentes tais como: os íons metálicos cromo, cobre, zinco, níquel e estanho são: 0,1 mg L^{-1} para o cromo hexavalente, 1,0 mg L^{-1} para o cobre dissolvido, 5,0 mg L^{-1} para o zinco total, 2,0 mg L^{-1} para o níquel total e 4,0 mg L^{-1} para estanho total.

O efluente contaminado com cromo é de coloração amarela (cor de ferrugem) e com pH ácido. Para retirar o cromo do efluente é necessário reduzí-lo para cromo trivalente e, posteriormente, precipitá-lo na forma de hidróxido. A redução de cromatos pode ser feita em meio ácido, por reação com hidrogenossulfito de sódio ($NaHSO_3$) ou metabissulfito de sódio ($Na_2S_2O_5$) podendo também ser obtida em meio neutro e alcalino, por reação com hipossulfito de sódio ($Na_2S_2O_4$). A vantagem de se usar hipossulfito torna-se maior quando os efluentes apresentarem pH próximo ao neutro ou mesmo alcalino, pois dispensa-se a acidificação, e posterior gasto de álcali para neutralização, que seria necessária com o uso do hidrogenossulfito e metabissulfito de sódio. A desvantagem do hipossulfito está em seu custo mais elevado e em sua menor estabilidade à degradação, principalmente após sua diluição em água (CPRH, 2001).

Para reduzir o cromo hexavalente em meio ácido, segundo CPRH (2001), primeiramente deve-se ajustar o pH do efluente para 1,5 – 2,0 com ácido sulfúrico, após adiciona-se o redutor de cromo (metabissulfito 10 à 20%) até observar a mudança de coloração de amarelo para azul esverdeado. Na sequência, eleva-se o pH com solução de soda para 6,5 – 7,0 e, após, adiciona-se solução de cal química para aumentar o pH até 8,0 – 8,5. Sempre mantendo a agitação do tanque de tratamento do efluente. Além disto, deve-se adicionar uma solução de polieletrólito 0,05%, observando a formação dos flocos. Por fim, após a decantação do lodo, descartar o mesmo para o leito de secagem ou filtro prensa e descartar a água clarificada pelo filtro de segurança ou caixa de areia.

3 Redução de Cromo Hexavalente por Fotocatálise Heterogênea

A redução fotocatalítica de Cr(VI), na presença de um material semicondutor e sob radiação UV ou visível, tem sido largamente estudada. Esta foto-redução ocorre em baixos valores de pH, pois a reação consome prótons. Os catalisadores usados são TiO_2 (KU e JUNG, 2001; SCHRANK *et al.*, 2002; CHO *et al.*, 2004; TUPRAKAY e LIENGCHARERNSIT, 2005; XU *et al.*, 2006; JIANG *et al.*, 2006), ZnO (DOMÉNECH e MUNOZ, 1987; KHALIL *et al.*,

1998; CHAKRABARTI *et al.*, 2009), CdS (WANG *et al.*, 1992), titânia pilarizada com fosfato de zircônio e fosfato de titânio (DAS *et al.*, 2006), titânia modificada com sulfato (MOHAPATRA *et al.*, 2005), sistema ZrO_2/TiO_2 (COLÓN *et al.*, 2002), ZnO/TiO_2 (KU *et al.*, 2011[a]), NiO/TiO_2 acoplados (KU *et al.*, 2011[b]), sistema $CuFe_2O_4/CdS$ (NASRALLAH *et al.*, 2011), TiO_2/Au (PANDIKUMAR e RAMARAJ, 2012), nanotubos de titânia modificado com nanopartículas de ouro (PANDIKUMAR e RAMARAJ, 2013), mistura de partículas metálicas (RIVERO-HUGUET e MARSHALL, 2009), ZnO sensibilizado com corante (YANG e CHAN, 2009), nanotubos de TiO_2 dopados com WO_3 (YANG *et al.*, 2010), fotocatalisador magnético (IDRIS *et al.*, 2010), entre outros.

Na Tabela 1.2 são apresentados alguns trabalhos sobre a redução fotocatalítica de Cr(VI) encontrados na literatura.

Tabela 1. 2: Relação dos trabalhos encontrados na literatura sobre a redução fotocatalítica de Cr(VI).

Referência	Catalisador	Contaminante	Fonte de Cr(VI)	Volume reacional	Tipo de radiação
Ku e Jung (2001)	TiO_2	Cr(VI)	---	2200 mL	UV: lâmpada fluorescente 15 W
Schrank et al. (2002)	TiO_2	Cr(VI) e corante	$K_2Cr_2O_7$	300 mL	UV: lâmpada de mercúrio 150 W
Cho et al. (2004)	Surfactante-TiO_2	Cr(VI) e CCl_4	$Na_2Cr_2O_7.2H_2O$	30 mL	Visível: lâmpada de xenônio 300 ou 450 W
Tuprakay e Liengcharernsit (2005)	TiO_2 imobilizado	Cr(VI)	$K_2Cr_2O_7$	40 mL	UV: lâmpada de mercúrio 125 W
Xu et al. (2006)	TiO_2	Cr(VI) e éter metil-ter-butílico	$K_2Cr_2O_7$	150 mL	UV: lâmpada fluorescente 8 W
Jiang et al. (2006)	TiO_2 e SO_4^{2-}/TiO_2	Cr(VI)	---	500 mL	UV: lâmpada de mercúrio 500 W
Doménech e Munoz (1987)	ZnO	Cr(VI)	---	40 mL	UV: lâmpada de mercúrio 125 W
Khalil et al. (1998)	ZnO	Cr(VI)	CrO_3	135 mL	UV: lâmpada de mercúrio 100 W
Chakrabarti et al. (2009)	ZnO	Cr(VI)	$K_2Cr_2O_7$	2000 mL	UV: lâmpada de mercúrio 125 W
Wang et al. (1992)	CdS	Cr(VI)	$K_2Cr_2O_7$	20 mL	Visível: lâmpada de halogênio-

					tungstênio 250 W
Das et al. (2006)	TiO_2 /fosfato de zircônio e fosfato de titânio	Cr(VI)	$K_2Cr_2O_7$	---	Luz solar
Mohapatra et al. (2005)	TiO_2 modificada com sulfato	Cr(VI)	$K_2Cr_2O_7$	25 mL	Luz solar
Colón et al. (2002)	ZrO_2/TiO_2	Cr(VI) e ácido salicílico	$K_2Cr_2O_7$	---	UV: lâmpada de mercúrio 400 W
Ku et al. (2011)[a]	ZnO/TiO_2	Cr(VI)	---	200 mL	UV: lâmpada de mercúrio 10 W
Ku et al. (2011)[b]	NiO/TiO_2 acoplados	Cr(VI)	$K_2Cr_2O_7$	1000 mL	UV: lâmpada de mercúrio 100 W
Nasrallah et al. (2011)	Sistema $CuFe_2O_4/CdS$	Cr(VI)	$K_2Cr_2O_7$	50 mL	Visível: lâmpada de tungstênio 200 W
Pandikumar e Ramaraj (2012)	TiO_2/Au	Cr(VI) e corante azul de metileno	$K_2Cr_2O_7$	---	Visível: lâmpada de xenônio 450 W
Pandikumar e Ramaraj (2013)	Nanotubos de TiO_2 / nanopartículas de ouro	Cr(VI)	$K_2Cr_2O_7$	---	Visível: lâmpada de xenônio 450 W
Yang e Chan (2009)	ZnO sensibilizado com corante	Cr(VI)	$K_2Cr_2O_7$	500 mL	Lâmpadas fluorescentes ou luz visível 18 W
Yang et al. (2010)	Nanotubos de TiO_2 dopados com WO_3	Cr(VI) e ácido cítrico	---	20 mL	Lâmpada de mercúrio e lâmpada de xenônio
Idris et al. (2010)	Fotocatalisador magnético	Cr(VI)	$K_2Cr_2O_7$	100 mL	Luz solar

3.1 Reações envolvidas

O caminho proposto para a reação de redução de Cr(VI) para Cr(III), em meio aquoso, na presença de um fotocatalisador é apresentada a seguir. Inicialmente, a solução de Cr(VI) contendo catalisador é iluminada, possuindo esta luz uma energia de fóton maior que a energia de *band-gap* do semicondutor. Durante o processo de fotocatálise primeiramente ocorre, na ausência de radiação, a adsorção do metal na superfície do catalisador, sendo este um processo reversível.

Após, na presença de radiação, os pares elétron/lacuna são gerados na superfície do catalisador, onde a lacuna é responsável pela oxidação e o elétron é responsável pela redução:

$$Semicondutor + hv \rightarrow e^- + h^+ \qquad (1.4)$$

De acordo com Ku e Jung (2001) e Schrank et al. (2002), a reação de redução fotocatalítica de Cr(VI) depende do pH da solução.

Para soluções ácidas:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \leftrightarrow 2Cr^{3+} + 7H_2O \qquad (1.5)$$

Para soluções alcalinas:

$$Cr_2O_7^{2-} + 14H_2O + 3e^- \leftrightarrow Cr(OH)_3 + 5OH^- \qquad (1.6)$$
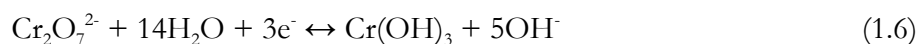
Sendo os experimentos realizados em pH 2,0, somente as espécies CrO_4^{2-} e $Cr_2O_7^{2-}$ podem existir, assim, considerando a espécie CrO_4^{2-}, Das et al. (2006) propuseram a seguinte reação de redução de Cr(VI) para Cr(III) com a oxidação da água, na ausência de outros agentes redutores:

$$CrO_4^{2-} + 8H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O \qquad (1.7)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (1.8)$$

Logo,

$$4CrO_4^{2-} + 20H^+ \rightarrow 4Cr^{3+} + 10H_2O + 3O_2 \qquad (1.9)$$
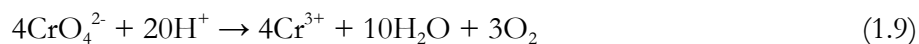
Considerando a doação de um elétron por vez, espécies de Cr(V) são formados no primeiro estágio da redução de Cr(VI):

$$CrO_4^{2-} + e^- \rightarrow CrO_4^{3-} \qquad (1.10)$$

Sucessivos estágios de redução por um elétron formarão espécies de Cr(IV) e depois Cr(III).

Chakrabarti et al. (2009) propuseram outro mecanismo para foto-redução do Cr(VI). Após a geração dos pares elétron/lacuna na superfície do catalisador, ocorre a formação de H_2O_2 através da reação de duas espécies livres na solução, possibilitando a redução homogênea de Cr(VI), desde que não exista significativa adsorção de Cr(VI) na superfície do catalisador. O oxigênio dissolvido atua como escravizador de elétron, gerando H_2O_2, o qual reduz o Cr(VI) como mostra a equação a seguir:

$$O_2 + H^+ + SC(e^-) \rightarrow H_2O_2 \qquad (1.11)$$

Uma reação de redução paralela ocorre, devido à adsorção do metanol, gerando radicais metóxi sobre a lacuna escravizada:

$$CH_3OH + SC(h^+) \rightarrow CH_3O\bullet \qquad (1.12)$$

As reações de redução de Cr(VI) para Cr(III), com peróxido de hidrogênio e radicais metóxi, são apresentadas a seguir. A reação homogênea de redução de Cr(VI) por H_2O_2 foto-gerado é responsável pelo fornecimento de elétrons para o cromo hexavalente em solução. Apesar da forte capacidade de oxidação do peróxido de hidrogênio, ele atua como redutor (E_0 = +0,68 V) quando com agentes oxidantes fortes como o cloro (E_0 = 1,77 V), o permanganato de potássio (E_0 = 1,52 V) e o dicromato de potássio (E_0 = 1,33 V).

$$Cr(VI) + H_2O_2 + H^+ \rightarrow Cr(III) + H_2O + O_2 \qquad (1.13)$$

$$Cr(VI) + CH_3O\bullet \rightarrow Cr(III) + produtos \qquad (1.14)$$
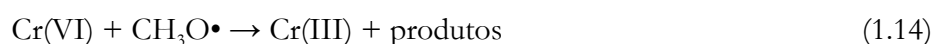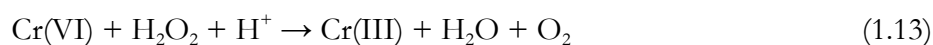
De acordo com Wang et al. (1992) a redução de Cr(VI) para Cr(III) é um processo termodinamicamente espontâneo, porém com baixa velocidade de reação, sendo que o $Cr_2O_7^{2-}$ mostrou-se muito estável em solução ácida na ausência de fotocatalisador.

$$2Cr_2O_7^{2-} + 16H^+ \rightarrow 4Cr^{3+} + 8H_2O + O_2 \qquad \Delta G°_{298} = -1158\ kJ \qquad (1.15)$$
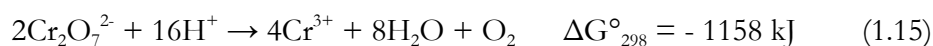
4 Redução de Cromo Hexavalente por Fotoquímica com Álcoois

A redução fotoquímica de Cr(VI), na presença de compostos orgânicos e sob radiação UV ou visível, tem sido estudada. Na literatura são encontrados alguns trabalhos sobre a redução fotoquímica de Cr(VI) por álcoois (MYTYCH *et al.*, 2003), fenol e seus derivados halogenados (MYTYCH e STASICKA, 2004) e glicerol (YURKOW *et al.*, 2002).

Mytych et al. (2003) investigaram a redução fotoquímica de Cr(VI) mediada por álcoois alifáticos sobre condições próximas as ambientais. Os autores analisaram os efeitos da natureza do álcool, da concentração inicial de álcool, do pH da solução e da presença de oxigênio. A taxa da reação mostrou-se dependente da natureza do álcool diminuindo na seguinte ordem: 1-butanol > 2-butanol >> 2-propanol > etanol >> metanol > 2-metil-2-propanol. Além da natureza do álcool, a taxa da redução mostrou-se sensível ao pH da solução, a presença de oxigênio molecular e a concentração de álcool, mas insensível a temperatura entre 283 e 303 K. Ainda, análises no espectro de tempo-resolvido foram usadas para acompanhar a geração das espécies transientes do cromo Cr(V), Cr(IV) e Cr(II) e os radicais $R_1R_2CHOH\bullet^+$. Uma interação indireta entre o cromato(VI) e um doador de elétron foi apresentada como precondição para foto-redução via transferência de elétron fotoinduzida (TEF). Assim, os autores identificaram dois caminhos para TEF: transferência intermolecular de um elétron e transferência intramolecular de dois elétrons.

Mytych e Stasicka (2004) investigaram a redução fotoquímica de Cr(VI) em soluções contendo fenol ou monohalogenofenol (4-bromofenol, 4-clorofenol e 3-clorofenol) sobre condições próximas as ambientais. Os autores estudaram os efeitos do comprimento de onda da radiação, pH da solução e oxigênio molecular. Os resultados mostraram que o cromato(VI) no estado excitado é reduzido pelo fenol no seu estado fundamental via transferência de elétron fotoinduzida (TEF). Ainda, foi observada que a oxidação do fenol ocorre via geração de radicais $C_6H_5O\bullet$, e que, condições ácidas e anóxicas favorecem a foto-redução do Cr(VI), enquanto que soluções oxigenadas alcalinas são preferíveis para foto-oxidação do fenol seguida de redução térmica de Cr(VI). Além disso, o sistema constituído de cromato(VI) e fenol apresentou uma sinergia entre a fotodegradação da substância fenólica e a foto-redução do Cr(VI).

Yurkow et al. (2002) estudaram redução fotoquímica de Cr(VI), na forma de dicromato de potássio, para Cr(III) em soluções aquosas contendo glicerol. Os autores observaram que a

reação ocorre rapidamente durante a irradiação com luz solar não filtrada ou fonte de luz emitindo UVA. Ainda, a redução fotoquímica de Cr(VI) mostrou-se dependente do pH, não ocorrendo em soluções diluídas de hidróxido de sódio, entretanto, em soluções acidificadas, a redução ocorreu em taxas elevadas e em concentrações mais baixas de glicerol. Além disso, a reação mostrou-se dependente dos grupos de álcool não substituídos do glicerol. Com este trabalho os autores concluíram que o glicerol ou os polióis relacionados podem ser utilizados para remediação do cromo hexavalente presente no meio ambiente.

4.1 Reações envolvidas

De acordo com Mytych et al. (2003) o cromato(VI) sozinho é fotoquimicamente inativo em todas as suas formas existentes em solução aquosa, a fotoredução do cromato(VI) por álcoois tem sido interpretada em termos de reatividade fotoquímica dos ésteres cromato(VI). As reações térmicas de Cr(VI) com álcool, em meio ácido, foram largamente estudadas e vários caminhos da reação foram propostos. O mecanismo mais aceito compreende a redução de dois-elétrons de Cr(VI) gerando aldeído ou cetona e espécies de Cr(IV). A formação do éster cromato(VI) é assumida como condição necessária para ocorrer as reações redox ou fotoredox.

$$HCrO_4^{1-} + ROH \leftrightarrow ROCrO_3^{1-} + H_2O \qquad\qquad (1.16)$$

$$ROCrO_3^{1-} + hv \rightarrow Cr(IV) + \text{aldeído/cetona} \qquad\qquad (1.17)$$

$$Cr(IV) + Cr(VI) \rightarrow 2Cr(V) \qquad\qquad (1.18)$$

$$3Cr(V) \rightarrow 2Cr(VI) + Cr(III) \qquad\qquad (1.19)$$

$$Cr(V) + ROH \rightarrow Cr(III) + \text{aldeído/cetona} \qquad\qquad (1.20)$$
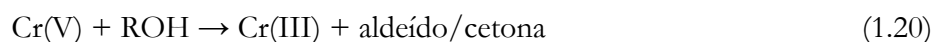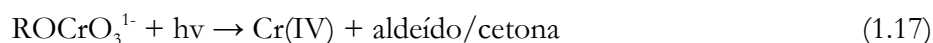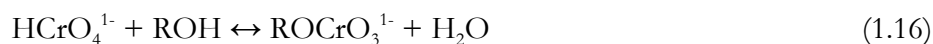
O destino da espécie Cr(V) gerada depende fortemente do meio: sólido ou matrizes orgânicas ou em baixas temperaturas sua formação pode ser facilmente observada. Em outros casos, o Cr(V) é rapidamente reduzido para espécies de Cr(III) e/ou é passível de sofrer uma nova oxidação, sendo portanto oxidado para Cr(VI) (Equações (1.19) e (1.20)).

5 Reatores

É de suma importância a escolha da forma e do tipo de reator para o processo fotocatalítico e/ou fotoquímico, sendo a viabilidade e a eficiência do mesmo dependentes da geometria, do tipo de fluxo e da distribuição da luz. Esta última é determinada através de fatores como: tipo de lâmpada, geometria do sistema reator-lâmpada, propriedades óticas do meio, natureza das paredes do reator, além do posicionamento apropriado das fontes de irradiação, de modo a maximizar o rendimento do processo (ALEXIADIS e MAZZARINO, 2005).

Encontra-se na literatura uma grande quantidade de reatores utilizados em ensaios de degradação/redução fotoquímica e fotocatalítica. Em laboratório, os sistemas reacionais são, geralmente, com reatores de pequeno volume, do tipo batelada completamente misturados, com fontes de radiação de baixa energia e com concentrações e temperaturas muito bem controladas (TEIXEIRA e JARDIM, 2004). Na Tabela 1.3 são apresentados alguns reatores encontrados na literatura.

Tabela 1. 3: Relação dos reatores fotoquímicos e fotocatalíticos encontrados na literatura.

Referência	Catalisador	Configuração do catalisador	Forma do reator	Volume reacional	Tipo de radiação
Dijkstra et al. (2001)	TiO_2	Suspensão, imobilizado e leito recheado	Tubular	124 mL	Lâmpada Philips UV-A 15 W
Chan et al. (2003)	TiO_2	Imobilizado	9 placas em cascata	7000 mL	Luz solar
Grzechulska e Morawski (2003)	TiO_2	Imobilizado	Retangular do tipo labirinto	700 mL	Lâmpadas Philips UV-A 140 W
Tuprakay e Liengcharernsit (2005)	TiO_2	Imobilizado	Bandejas circulares	40 mL	Lâmpada Philips UV 125 W
Duarte et al. (2005)	TiO_2 Fenton	Suspensão	Tubular	12 L	Luz solar
Krýsa et al. (2006)	TiO_2	Imobilizado	Bandejas retangulares	---	Lâmpadas UV 11 W
Silva (2007)	TiO_2	Imobilizado	Retangular do tipo labirinto	4300 mL	Lâmpadas UV 10 W
Grieken et al. (2009)	TiO_2	Suspensão, imobilizado e	Anular	1000 mL	Lâmpadas Philips UV-A

			leito fixo		0,7 W
McCullagh et al. (2010)	TiO_2	Suspensão	3 vasos rotativos em série	12 L	Lâmpadas Philips UV 36 W
Pereira et al. (2011)	TiO_2	Suspensão	4 tubos conectados em série	15 L	Luz solar
Shahrezaei et al. (2012)	TiO_2	Suspensão	Cilindro com a parte inferior cônica	1200 mL	Lâmpada mercúrio UV 400 W
Kim et al. (2013)	TiO_2	Imobilizado	Vaso tubular rotacional	1000 mL	Lâmpada xenônio 1000 W
Kumar e Bansal (2013)	TiO_2	Imobilizado	Anular	1000 mL	Lâmpada mercúrio UV

Dentre os reatores citados na Tabela 1.3, os reatores tubulares solares usados por Duarte et al. (2005) e Pereira et al. (2011) mostraram-se os mais promissores para aplicação no tratamento de efluentes industriais, devido à sua capacidade de tratamento e uso da luz solar como fonte de fótons, minimizando os gastos energéticos intrínsecos ao processo.

Os reatores fotoquímicos solares, utilizados por Duarte et al. (2005) e Pereira et al. (2011), são do tipo CPC ("compound parabolic concentrator"). De maneira geral estes autores propuseram um reator constituído de tubos de vidro borossilicato ligados em série e distribuídos sobre uma estrutura metálica. A superfície refletora é construída empregando-se chapas de alumínio anodizado, curvadas no formato de involutas e é montada com uma inclinação específica, de acordo com a latitude local. Estes reatores são dotados de tanques de armazenamento, bombas centrífugas, medidores de vazão e válvulas de controle. Fotos do reator proposto por Duarte et al. (2005) e do reator proposto por Pereira et al. (2011) são apresentadas nas Figuras 1.3 e 1.4, respectivamente.

Figura 1. 3: Reator fotoquímico solar do tipo CPC proposto por Duarte et al. (2005).

Figura 1. 4: Planta piloto de um reator solar do tipo CPC proposta por Pereira et al. (2011).

INTRODUÇÃO AOS CAPÍTULOS II, III, IV E V

Os Capítulos II, III, IV e V estão apresentados em forma de artigos científicos, seguindo as normas propostas pelo Programa de Pós-Graduação em Engenharia Química (PPGEQ).

Estes capítulos apresentam os materiais e métodos utilizados no desenvolvimento de cada artigo, juntamente com os resultados obtidos e as conclusões pertinentes a cada etapa de trabalho.

O primeiro artigo (Capítulo II – "Photocatalytic Reduction of Hexavalent Chromium on TiO_2 and ZnO Suspensions") aborda o estudo da redução fotocatalítica de Cr(VI) sob radiação UV usando os catalisadores comerciais, TiO_2 e ZnO. Estes experimentos foram realizados em um reator batelada e com catalisador em suspensão. Um planejamento de experimentos foi utilizado para otimizar o pH inicial da solução, a concentração de catalisador e a concentração inicial de Cr(VI) para cada semicondutor e suas atividade fotocatalíticas foram comparadas. Este artigo foi aceito para publicação no periódico ***Journal of Chemistry and Chemical Engineering*** em junho de 2015.

O segundo artigo (Capítulo III – "Reduction of Hexavalent Chromium: Photocatalysis and Photochemistry and its Application in Wastewater Remediation") apresenta o estudo da redução fotoquímica de Cr(VI) com etanol sob radiação UV e visível, e da redução fotocatalítica de Cr(VI) com TiO_2 na presença de etanol, sob radiação UV. Os efeitos do pH inicial da solução, da quantidade de etanol, da concentração de catalisador e da concentração inicial de Cr(VI) foram avaliados através de um planejamento de experimentos e todos os ensaios foram realizados em um reator batelada. Ainda, foram realizados testes com efluente industrial proveniente de uma indústria galvânica. Este artigo está publicado no periódico ***Water Science & Technology***, 70.1, 55-61, 2014. Doi: 10.2166/wst.2014.193.

O terceiro artigo (Capítulo IV – "Wastewater Remediation using a Spiral Shaped Reactor for Photochemical Reduction of Hexavalent Chromium") aborda o projeto e a construção de um reator contínuo em forma de espiral feito de vidro borossilicato e sua aplicação na redução fotoquímica de Cr(VI). Um planejamento de experimentos foi usado para investigar a influencia da quantidade de etanol e da concentração inicial de cromo hexavalente na redução total de Cr(VI). Ainda, foram realizados testes com efluente industrial proveniente de uma indústria galvânica. Este artigo está publicado e foi selecionado para ser capa do periódico **Photochemical & Photobiological Sciences**, 14, 501-505, 2015. Doi: 10.1039/c4pp00263f.

O quarto artigo (Capítulo V – "Proposal for Environmentally Sustainable Technology for the Treatment of Wastewater Containing Cr(VI): Design and Construction of a Solar Tubular Reactor") propõe uma tecnologia alternativa para o tratamento de efluentes contendo Cr(VI) oriundos de indústria galvânica, baseada na redução fotoquímica de Cr(VI) por álcoois sob radiação UV, a qual é ambientalmente sustentável e economicamente viável. Um reator tubular, que opera sob radiação artificial e sob luz solar, em escala semi-piloto foi projetado e construído. Experimentos foram realizados no reator tubular usando-se uma solução sintética de Cr(VI) ou um efluente industrial, tanto sob luz solar como iluminado por lâmpadas. Este artigo foi submetido para publicação no periódico **Chemical Engineering Research and Design** em novembro de 2015.

CAPÍTULO II – ARTIGO 1

PHOTOCATALYTIC REDUCTION OF HEXAVALENT CHROMIUM ON TiO$_2$ AND ZNO SUSPENSIONS

Photocatalytic Reduction of Hexavalent Chromium on TiO_2 and ZnO Suspensions

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ABSTRACT

Photocatalytic reduction of hexavalent chromium under UV radiation was studied using TiO_2 and ZnO, both in their commercial forms, as catalysts. The experiments were carried out in a glass batch reactor with temperature control and the catalyst in suspension under UV radiation. The effects of the initial pH, the catalyst concentration and the initial concentration of hexavalent chromium were evaluated for each catalyst through an experimental design. The experimental results showed that, for both catalysts, the total reduction of Cr(VI) increases as the catalyst amount increases, decreases as the initial pH of the solution increases and decreases as the initial Cr(VI) concentration increases. Furthermore, TiO_2 catalyst was more efficient than ZnO catalyst, presenting a Cr(VI) reduction of 66.5%.

Keywords: hexavalent chromium, photocatalysis, TiO_2, ZnO

1 Introduction

Increasing concerns on various environmental contaminations has stimulated vital development of various treatment technologies (KU *et al.*, 2011). Semiconductor photocatalysis, as an economical and efficient method in the treatment of drinking water and industrial wastewater, has attracted more and more attention nowadays mainly because of the relatively mild reaction conditions required to the satisfactory decomposition of refractory pollutants. A number of toxic organic or inorganic compounds could be transformed into non-toxic or biodegradable species (XU *et al.*, 2006; KU *et al.*, 2011). The heterogeneous photocatalytic processes occur when light energy falls on a semiconductor, with a wavelength equal to or greater than the band-gap energy of the semiconductor, generating electron/hole pairs that can undergo subsequent reactions of oxidation and reduction in some species, which can then be adsorbed on the semiconductor surface, generating the necessary products of oxidation/reduction (CHATTERJEE and DASGUPTA, 2005).

The application of photocatalytic reduction process using semiconductors is reported to effectively reduce various heavy metals in aqueous solutions to less-toxic states. The presence of heavy metals in aquatic bodies has been known to cause pollution problems. The major source of heavy metals is the improper discharge of various industrial wastewaters (KU and JUNG, 2001). These metal ions are generally non-degradable. They have got infinite life times and build up their concentrations in food chains to toxic levels. Among these inorganic pollutants chromium is an important industrial metal that is considered a priority pollutant since it is toxic to most organisms (DAS *et al.*, 2006).

Chromium occurs in nature in two oxidation states, Cr^{+3} and Cr^{+6} or Cr(III) and Cr(VI). Hexavalent chromium is toxic to most organisms, as it is carcinogenic and mutagenic to animals and can cause irritation and corrosion to human skin. In the environment, Cr(VI), which is more stable than trivalent, is highly soluble, making the contamination of groundwater and drinking water sources possible. The hexavalent form of chromium is 100 times more toxic than trivalent chromium (MOHAPATRA *et al.*, 2005; DAS *et al.*, 2006; XU *et al.*, 2006; YANG and CHAN, 2009; CHAKRABARTI *et al.*, 2009). On the other hand, trivalent chromium is easily precipitated and non-toxic and is considered an essential element in the human metabolism at controlled levels (KIM *et al.*, 2002; MOHAPATRA *et al.*, 2005).

In academic literature there are several studies of photocatalytic reduction of Cr(VI) with TiO$_2$ (KU and JUNG, 2001; SCHRANK *et al.*, 2002; CHO *et al.*, 2004; TUPRAKAY and LIENGCHARERNSIT, 2005; XU *et al.*, 2006 ; JIANG *et al.*, 2006) and ZnO (KHALIL *et al.*, 1998; CHAKRABARTI *et al.*, 2009). However, there is no systematic study that analyzes the effect of each parameter of the reaction, as well as, the interaction between them. Nor has a study been published comparing the performance of the catalysts, each in its appropriate conditions for maximum reduction.

So in the present work, we have studied the photocatalytic reduction of hexavalent chromium under ultraviolet radiation, using TiO$_2$ and ZnO, both commercial catalysts. The response surface methodology was used to optimize the initial pH, amount of catalyst and initial concentration of hexavalent chromium for each semiconductor and their efficiency to reduce chromium was compared.

2 Materials and Methods

Materials: Potassium dichromate (Fmaia) was used as it was received and deionized, and distilled water was used to prepare the solutions. One of the catalysts used was zinc oxide (ZnO) from Merck with a purity of 99% and a specific surface area of about 5 m^2 g^{-1}. Titanium dioxide (TiO$_2$) from Degussa P-25, 80% anatase and 20% rutile, was also used, with a specific area of 50 m^2 g^{-1} and an average particle size of 20 nm.

Analytical methods: The concentration of potassium dichromate in solution was determined by measurement of absorbance at a wavelength of 348 nm (MOHAPATRA *et al.*, 2005; DAS *et al.*, 2006; NASRALLAH *et al.*, 2011) using a UV-vis spectrophotometer (Varian Cary 100).

2.1 Experiments of photocatalytic reduction

The experiments were carried out in a batch reactor irradiated with a modified mercury vapor lamp (Philips HPL-N 125 W) emitting only UV-A (365 nm) with an incident irradiance of 5.8 mW cm^{-2} as determined at the start of each experiment by a radiometer (Cole-Parmer Instrument, Radiometer Series 9811). The agitation of the reaction mixture was maintained using a magnetic stirrer and the temperature was monitored using a K-type thermocouple. The hexavalent chromium solution was prepared from potassium dichromate (K$_2$Cr$_2$O$_7$) and kept

under vigorous magnetic stirring for approximately 1 hour. The catalyst powder was added to 150 mL aqueous Cr(VI) solution. The reduction tests were divided into two steps: one in the dark (1 hour), presenting adsorption-desorption equilibrium of the metal on the catalyst surface without radiation, and the other the reaction (1 hour), which was conducted with UV radiation. The progress of the photocatalytic reduction reaction of Cr(VI) was monitored by collecting samples at fixed intervals 0, 15, 30, 45 and 60 min. The collected samples were then centrifuged, filtered and stored in amber glass bottles.

2.2 Methodology of response surface

The statistical model of a circumscribed central composite design (CCCD) was used in order to optimize the photocatalytic reduction reaction of Cr(VI) with TiO_2 or ZnO under UV radiation. This model consists of three types of points: 2^n (n = 3) cube points (factorial design points), 6 axial points and 3 central points, resulting in a total of 17 experiments. The distance of axial points from the center points (α) was fixed at 1.68 depending upon the number of factors chosen for the experiment. The variables (factors) used in the study were the initial pH (X_1), amount of catalyst (X_2) and, initial Cr(VI) concentration (X_3). The response factor was defined as the total reduction of Cr(VI) after 1 hour of reaction under UV radiation. This methodology has been previously described for photochemical reduction of Cr(VI) with ethanol (MACHADO *et al.*, 2015). The real values of the process variables (factors), their variation limits, and number were selected based on the preliminary experiments. The coded values along with real values of the factors are shown in Table 2.1.

Table 2. 1: Real and coded levels of the independent variables.

Factors	Real values of coded levels				
	-α	-1	0	+1	+α
	TiO_2				
Initial pH of the solution (X_1)	2	3	4.5	6	7
Amount of TiO_2 (g L^{-1}) (X_2)	0.4	0.8	1.4	2.0	2.4
Cr(VI) concentration (mg L^{-1}) (X_3)	13	20	30	40	47
	ZnO				
Initial pH of the solution (X_1)	2.6	4	6	8	9.4
Amount of ZnO (g L^{-1}) (X_2)	0.4	0.8	1.4	2.0	2.4
Cr(VI) concentration (mg L^{-1}) (X_3)	13	20	30	40	47

The data were analyzed using the Statistica 10 software, which provided the polynomial associated with the system photocatalytic reduction reaction of Cr(VI) and the response surfaces. The model was statistically validated with the same software using the analysis of variance

(ANOVA). The quality of the fit for the polynomial model was expressed by the coefficient of determination (R^2). Model terms were selected or rejected based on the probability value within 95% confidence interval (or 5% significance level).

3 Results and Discussion

3.1 Optimization of the photocatalytic reduction reaction

The experimental conditions in which the photocatalytic reduction of hexavalent chromium occurs at a higher speed were determined by using a design of experiments; details are outlined in section 2.2. The variables studied were: the catalyst amount in the suspension, the initial pH of the solution, and the initial Cr(VI) concentration. In this work we used a constant operating temperature of 30 °C, since it is known that the rate of photocatalytic reduction of Cr(VI) is insensitive to temperature variations. Previous research reported that the activation energy is only 3.6 kJ mol^{-1}, and that for temperature variation from 25 to 88 °C there is a 25% increase in reaction rate (CHAKRABARTI *et al.*, 2009).

Tables 2.2 and 2.3 show the experiments of photocatalytic reduction of Cr(VI) under UV radiation carried out with TiO_2 and ZnO catalysts in suspension, respectively. The response factor (Y) was defined as the percentage of total reduction of Cr(VI) after 1 hour of reaction. In Tables, the consistency of the statistical model is validated by the calculated values shown in the last column, where high agreement with the experimental ones is shown.

Table 2. 2: Circumscribed central composite design of experiments along with observed and predicted values of response for photocatalytic reduction reaction of Cr(VI) with TiO_2 catalyst.

Run	Coded levels of variables			Actual levels of variables			Response (% total reduction)	
	x_1	x_2	x_3	X_1	X_2	X_3	$Y_{observed}$	$Y_{predicted}$
1	-1	-1	-1	3	0.8	20	49.8	47.6
2	1	-1	-1	6	0.8	20	19.3	21.4
3	-1	1	-1	3	2.0	20	66.5	65.2
4	1	1	-1	6	2.0	20	39.2	39.0
5	-1	-1	1	3	0.8	40	26.6	23.4
6	1	-1	1	6	0.8	40	8.0	7.2
7	-1	1	1	3	2.0	40	31.8	27.8
8	1	1	1	6	2.0	40	12.9	11.6
9	- α	0	0	2	1.4	30	47.3	52.2
10	+ α	0	0	7	1.4	30	17.6	16.5

11	0	- α	0	4.5	0.4	30	11.5	12.3
12	0	+ α	0	4.5	2.4	30	28.2	30.8
13	0	0	- α	4.5	1.4	13	56.0	55.5
14	0	0	+ α	4.5	1.4	47	7.7	12.1
15	0	0	0	4.5	1.4	30	21.9	21.6
16	0	0	0	4.5	1.4	30	23.1	21.6
17	0	0	0	4.5	1.4	30	20.0	21.6

Table 2. 3: Circumscribed central composite design of experiments along with observed and predicted values of response for photocatalytic reduction reaction of Cr(VI) with ZnO catalyst.

Run	Coded levels of variables			Actual levels of variables			Response (% total reduction)	
	x_1	x_2	x_3	X_1	X_2	X_3	$Y_{observed}$	$Y_{predicted}$
1	-1	-1	-1	4	0.8	20	36.0	36.1
2	1	-1	-1	8	0.8	20	28.8	28.9
3	-1	1	-1	4	2.0	20	48.8	50.9
4	1	1	-1	8	2.0	20	44.9	43.7
5	-1	-1	1	4	0.8	40	23.7	18.5
6	1	-1	1	8	0.8	40	10.7	11.3
7	-1	1	1	4	2.0	40	26.4	24.9
8	1	1	1	8	2.0	40	19.2	17.7
9	- α	0	0	2.6	1.4	30	29.8	30.8
10	+ α	0	0	9.4	1.4	30	19.6	18.6
11	0	- α	0	6	0.4	30	13.4	15.8
12	0	+ α	0	6	2.4	30	32.4	33.6
13	0	0	- α	6	1.4	13	56.7	55.2
14	0	0	+ α	6	1.4	47	15.3	18.5
15	0	0	0	6	1.4	30	23.5	24.7
16	0	0	0	6	1.4	30	24.6	24.7
17	0	0	0	6	1.4	30	26.5	24.7

For the reactions with TiO_2, the polynomial (Eq. (1)), obtained from the multivariate analysis, indicates that the initial pH and initial Cr(VI) concentration are the main variable that affects the extent of Cr(VI) reduction, showing first order and quadratic interactions. Whereas, for the reactions with ZnO, the polynomial (Eq. (2)) indicates that the initial Cr(VI) concentration is the main variable that affects this reaction. Moreover, these polynomials presented coefficient of determination of 0.9804 and 0.9743, respectively, indicating a good fit between the experimental data and the statistical model. In these polynomials, the values in parenthesis represent the standard deviation for each coefficient, and x_1, x_2 and x_3 represent the coded values of the initial pH, catalyst amount and, initial Cr(VI) concentration, respectively.

$$Y_{TiO_2}(\%) = 21.6\ (\pm1.5) - 10.6x_1(\pm0.9) + 4.5x_1^2(\pm1.0) + 5.5x_2(\pm0.9) - 12.9x_3(\pm0.9) + 4.3x_3^2(\pm1.0) + 2.5x_1.x_3(\pm1.2) - 3.3x_2.x_3(\pm1.2) \tag{1}$$

$$Y_{ZnO}(\%) = 24.7(\pm0.8) - 3.6x_1(\pm0.7) + 5.3x_2(\pm0.7) - 10.9x_3(\pm0.7) + 4.3x_3^2(\pm0.7) - 2.1x_2.x_3(\pm0.9) \tag{2}$$

In addition, for both catalyst, the linear coefficients of the effects of pH and Cr(VI) concentration were negative, indicating that the lower the initial pH of the solution and the initial Cr(VI) concentration, the higher the total Cr(VI) reduction. Additionally, the coefficient for the linear effect of amount of catalyst is positive, indicating that the higher the amount of catalyst, the higher the total Cr(VI) reduction. It is observed that the higher total reductions achieved were 66.5 and 56.7% for TiO$_2$ and ZnO catalysts, respectively, indicating that the TiO$_2$ catalyst was significantly better than ZnO for photocatalytic reduction reaction of Cr(VI). These conclusions are evident in Figures 2.1 and 2.2, which depicts the response surfaces for the experimental data obtained.
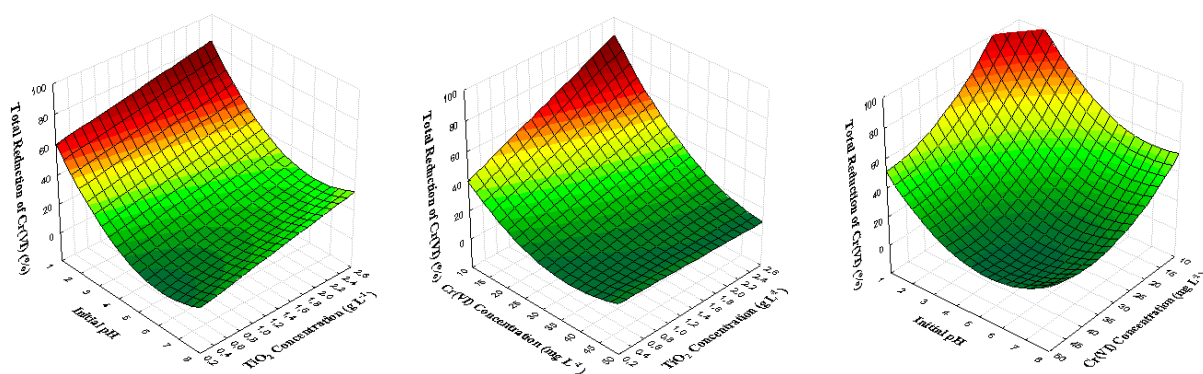
Figure 2. 1: Response surfaces showing the percentage of Cr(VI) reduction with TiO₂ catalyst (a) Initial Cr(VI) concentration = 30 mg L⁻¹, (b) Initial pH of the solution = 4.5 and (c) Catalyst concentration = 1.4 g L⁻¹.
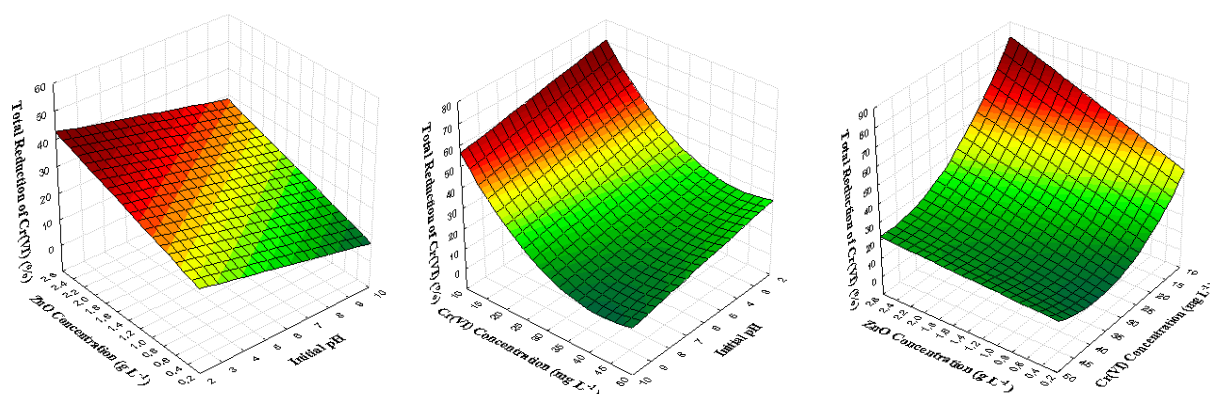
Figure 2. 2: Response surfaces showing the percentage of Cr(VI) reduction with ZnO catalyst (a) Initial Cr(VI) concentration = 30 mg L⁻¹, (b) Catalyst concentration = 1.4 g L⁻¹ and (c) Initial pH of the solution = 6.0.

For the reactions with TiO_2 observed a significant interaction between the initial pH of the solution and the initial Cr(VI) concentration. The initial pH of the solution determines the charges to the catalyst surface as well as the ionization state of the substrate, which affects the amount adsorbed and hence the total reduction. The interaction term between catalyst concentration and initial Cr(VI) concentration was also significant, as was to be expected.

For the reactions with ZnO, the initial pH of the solution did not have a significant effect on total reduction, leading to experiments during which the pH was monitored throughout the reaction. It was noted that the photocatalysis reactions with ZnO ended with a similar final pH, at approximately 7.0, regardless of the initial pH of the solution, thus explaining the lower effect of the solution's pH for reactions carried out with this catalyst. This behavior of photocatalytic reactions using ZnO as catalyst was also observed by Hermes et al. (2015) for photocatalytic oxidation of glycerol over ZnO.

Furthermore, increasing pH during photocatalytic reduction reaction of Cr (VI) with ZnO justifies the reduction of reaction efficiency compared to the reaction carried out with TiO_2 catalyst which does not alter the final pH of the solution. In addition, ZnO catalyst from Merck presents a specific surface area (5 m^2 g^{-1}), which is lower than TiO_2 catalyst from Degussa (50 m^2 g^{-1}).

3.2 Complementary tests

The results obtained in the experiment indicate that the TiO_2 catalyst provides better performance in the photocatalytic reduction of Cr(VI). Thus, additional tests of Cr(VI) reduction with TiO_2 were performed to experimentally prove the behavior of the interest variables and extend the range of analysis of the parameters in the experimental design.

Experiments were conducted in the absence of UV radiation to verify the adsorption of Cr(VI) on the catalyst surface. Adsorption equilibrium was established when 5.9% of hexavalent chromium was adsorbed. To quantify the contribution of photolysis, experiments in which only the Cr(VI) solution was subjected to UV radiation were also carried out. The reaction under UV showed no Cr(VI) reduction, thus, the contribution of photolysis can be negligible (MOHAPATRA *et al.*, 2005; CHAKRABARTI *et al.*, 2009).

The effect of the catalyst amount on Cr(VI) reduction was studied using TiO_2 concentrations between 0.8 g L^{-1} and 8 g L^{-1} at pH 3, and the results can be seen in Figure 2.3. The operating temperature, the initial Cr(VI) concentration, and UV radiation were kept constant in these experiments.
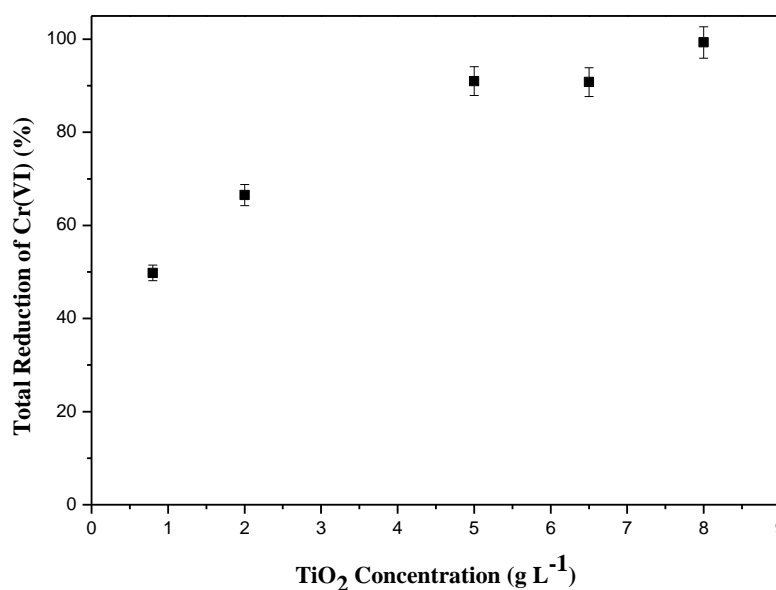
Figure 2. 3: Effect of the catalyst amount on total reduction of Cr(VI) ($C_{Cr(VI)}$ = 20 mg L^{-1}, T = 30 °C, pH = 3 and 5.8 mW cm^{-2}).

It was observed that by increasing catalyst amount up to 5 g L^{-1}, a significant increase in total reduction of Cr(VI) occurred, as was expected; beyond this value, the slope of the line tangent to the curve tends to zero. With the increase of the catalyst mass, there is a larger illuminated area, which favors the reagent reduction. However, simultaneously, the suspension becomes increasingly opaque, so that at any given time a portion of the catalyst particles is no longer illuminated, although there are excess photons. Similar behaviors were observed in the literature (KHALIL *et al.*, 1998; MOHAPATRA *et al.*, 2005; DAS *et al.*, 2006; CHAKRABARTI *et al.*, 2009).

The photocatalytic reduction reaction of Cr(VI) is strongly dependent on the solution's pH. Thus, experiments were performed in which the initial pH was changed within the range of 3 and 10, with a fixed catalyst amount. Other parameters, such as operating temperature, UV radiation intensity and initial Cr(VI) concentration were also kept constant. Figure 2.4 shows the results obtained in these experiments.
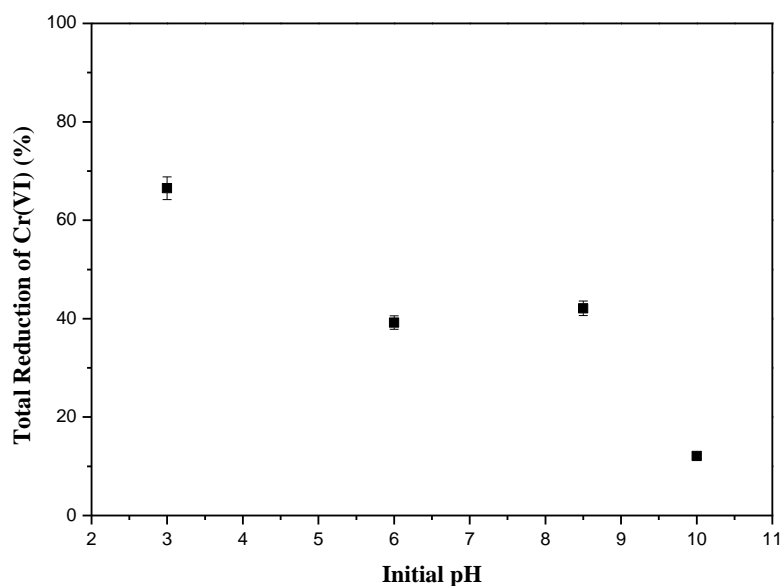
Figure 2. 4: Effect of the initial pH of the solution on total reduction of Cr(VI) ($C_{Cr(VI)}$ = 20 mg L^{-1}, T = 30 °C, C_{TiO2} = 2.0 g L^{-1} and 5.8 mW cm^{-2}).

This figure indicates that the total reduction of Cr(VI) decreases with an increase in the solution's initial pH. The pH affects the semiconductor's surface charges and the ionization state of the substrate, and hence its adsorption. The dominant species of Cr(VI) at pH 2 is $HCrO_4^{-1}$, and the increase of the solution's pH will shift the $HCrO_4^{-1}$ concentration to form CrO_4^{-1} and $Cr_2O_7^{-2}$ species. As the point of zero charge for the TiO_2 catalyst is at pH 7.52 (KU and JUNG, 2001), with pH above this value, the semiconductor surface becomes negative and repels dichromate ions (KU and JUNG, 2001; MOHAPATRA *et al.*, 2005).

The influence of the initial Cr(VI) concentration on the photocatalytic reduction reaction was determined from tests with initial concentrations of 10, 20, 30 and 40 mg L^{-1}. Other parameters such as temperature, UV radiation intensity, catalyst amount and pH were kept constant in all these experiments. The results are shown in Figure 2.5.

It can be observed from Figure 2.5 that by reducing the initial Cr(VI) concentration, greater total reduction of this species occurs. With increasingly higher substrate concentrations, there is an increase in absorbance of the Cr(VI) solution, and a greater fraction of the radiation is intercepted before reaching the catalyst surface, causing a decrease in the efficiency of the photocatalytic reaction. Similar results have been found for photocatalytic reduction of Cr(VI) (KU and JUNG, 2001; DAS *et al.*, 2006; CHAKRABARTI *et al.*, 2009).
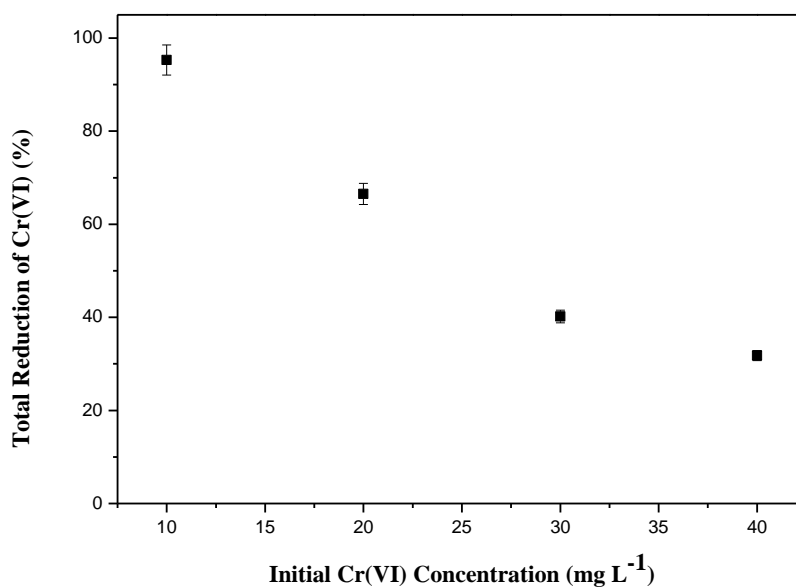
Figure 2. 5: Effect of the initial Cr(VI) concentration on total reduction of Cr(VI) (C_{TiO2} = 2.0 g L^{-1}, T = 30 °C, pH = 3 and 5.8 mW cm^{-2}).

4 Conclusion

Photocatalytic reduction of hexavalent chromium on TiO_2 and ZnO suspensions was studied in this work. The results obtained showed that, for both catalysts, the photocatalytic reduction of Cr(VI) under UV radiation is dependent upon the catalyst amount, the initial pH of the solution, and the initial substrate concentration. Further, the total reduction of Cr(VI) increases with an increase in catalyst amount and decreases with an increase in the initial pH of the solution and initial Cr(VI) concentration. Additionally, the higher total reductions achieved were 66.5 and 56.7% for TiO_2 and ZnO catalysts, respectively, indicating that the TiO_2 catalyst was more efficient than ZnO catalyst for the reduction reaction of Cr(VI).

5 Acknowledgements

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CAPÍTULO III – ARTIGO 2

REDUCTION OF HEXAVALENT CHROMIUM: PHOTOCATALYSIS AND PHOTOCHEMISTRY AND ITS APPLICATION IN WASTEWATER REMEDIATION

Reduction of Hexavalent Chromium: Photocatalysis and Photochemistry and its Application in Wastewater Remediation

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ABSTRACT

Hexavalent chromium present in wastewater discharge of galvanic industries is toxic to most microorganisms and potentially harmful to human health. This work examines the photochemical reduction of Cr(VI) with ethanol under UV and visible radiation, and photocatalytic reduction of Cr(VI) with TiO_2 in the presence of ethanol under UV radiation. By means of different experimental designs, this study investigates the influence of the initial pH, ethanol amount, catalyst concentration and initial Cr(VI) concentration on total Cr(VI) reduction. The results obtained showed that photochemistry with ethanol under UV radiation (96.10%) was more efficient than photochemistry with ethanol under visible light (48.07%). Furthermore, photocatalysis with TiO_2 in the presence of ethanol under UV radiation showed high values of total Cr(VI) reduction, 94.15%, under the optimal conditions established by the experimental design. Finally, experiments were carried out with wastewater discharge from an electroplating plant in its original concentration, and higher values of total Cr(VI) reduction were observed.

Keywords: hexavalent chromium, photocatalysis, photochemistry, wastewater

1 Introduction

Hexavalent chromium -Cr(VI)- is toxic to most microorganisms and potentially harmful to human health. In the environment, Cr(VI), which is more stable than trivalent chromium, is highly soluble, making the contamination of groundwater and drinking water sources a possibility. The hexavalent form of chromium is 100 times more toxic than the trivalent (MOHAPATRA *et al.*, 2005; DAS *et al.*, 2006; XU *et al.*, 2006; YANG and CHAN, 2009).

A possible source of chromium is the improper discharge of wastewaters from electroplating plants. The conventional treatment for these wastewaters is reduction with sodium sulphite or metabisulphite. This method, however, requires an excessive amount of chemicals to ensure that the complete conversion of Cr(VI) and the formation of sludge or the release of sulfur dioxide occurs. Studies have been directed to developing cleaner technologies capable of dealing with wastewater containing chromium. Among these are heterogeneous photocatalysis and photochemistry with alcohols (CHAKRABARTI *et al.*, 2009).

Literature shows few studies on the photochemical reduction of Cr(VI) by alcohols (MYTYCH *et al.*, 2003), phenol and its halogen derivatives (MYTYCH and STASICKA, 2004), and glycerol (YURKOW *et al.*, 2002). In these studies, only Mytych et al. (2003) used ethanol in the photochemical reduction reaction of Cr(VI) , and the work is limited to the effects of the alcohol concentration. Also, a comparison between photochemical reduction reactions of Cr(VI) with ethanol under UV radiation and visible light was not found in literature. Furthermore, there are several studies on the photocatalytic reduction of Cr(VI) with TiO_2 (KU and JUNG, 2001; SCHRANK *et al.*, 2002; CHO *et al.*, 2004; TUPRAKAY and LIENGCHARERNSIT, 2005; XU *et al.*, 2006; JIANG *et al.*, 2006). However, the ethanol effect on the photocatalytic reduction of Cr(VI) with TiO_2 under UV radiation was studied only by Ku and Jung (2001) and in this study the authors analyzed the ethanol effect, leaving out other variables that affect the reaction rate.

There is no systematic and comparative study that analyzes the effect of the solution's pH, catalyst concentration, initial Cr(VI) concentration and ethanol amount on the photocatalytic reduction of Cr(VI) with TiO_2 in the presence of ethanol under UV radiation. The same happens with photochemical reduction of Cr(VI) with ethanol under UV and visible radiation. Furthermore, the application of sustainable treatments such as photochemistry and

heterogeneous photocatalysis to remediate Cr(VI) present in wastewater discharges of electroplating industries has not been found in the literature.

This work aims to fill this information gap and, thus, the reduction of Cr(VI) by photochemistry with alcohols under UV and visible radiation, and photocatalysis with TiO_2 in the presence of ethanol under UV radiation were investigated. To evaluate Cr(VI) reduction by photochemistry with ethanol, two experimental designs (UV and visible) were used in which the influence of initial pH, ethanol amount and initial Cr(VI) concentration were investigated. Subsequently, tests of photocatalytic reduction of Cr(VI) with TiO_2 in the presence of ethanol under UV radiation were carried out and the effects of the initial pH, ethanol amount, catalyst concentration and initial Cr(VI) concentration were evaluated through an experimental design. Finally, experiments were conducted using raw wastewater from an electroplating plant.

2 Materials and Methods

Materials: Deionized and distilled water and potassium dichromate (Fmaia), as it was received, were used to prepare the solutions. Absolute ethyl alcohol (Nuclear) was used in the reactions of photochemical reduction of Cr(VI) and a titanium dioxide (TiO_2) catalyst from Degussa P-25, 80% anatase and 20% rutile with a specific area of 50 m^2 g^{-1} and an average particle size of 20 nm was used in the reactions of photocatalytic reduction of Cr(VI).

2.1 Experiments of Cr(VI) reduction

The experiments were carried out in a batch reactor irradiated with a mercury vapor lamp (Philips HPL-N 125 Watt) in its original shape for visible light, or modified to emit in the UV region by removing the inner covering of the bulb. Agitation of the reaction medium was conducted by a magnetic stirrer, and the temperature was monitored by using a K-type thermocouple connected to a digital display. The irradiation chamber consisted of a wooden box, internally lined with aluminum foil, and a syringe-catheter system was used to collect liquid samples at specific intervals. Lamp radiation was adjusted by changing the distance between the lamp and the solution, and measured at the beginning of each test using a radiometer (Cole-Parmer Instrument, Series 9811 Radiometer) for UV radiation and a solarimeter (Kimo® Instruments) for visible radiation.

The synthetic Cr(VI) solution was prepared by using potassium dichromate ($K_2Cr_2O_7$), at concentrations ranging from 10 to 50 mg L^{-1}, and kept under vigorous magnetic stirring for approximately 1 hour. For the photochemical reduction reactions with ethanol, a known volume of alcohol was added to 150 mL of the aqueous Cr(VI) solution and the solution's pH was adjusted. These reactions, under UV and visible radiation, occurred in 1 hour, and the progress of the photochemical reduction reaction of Cr(VI) was monitored by collecting samples at fixed intervals (0, 15, 30, 45 and 60 minutes). Subsequently, the Cr(VI) content was analyzed quantitatively by measuring the absorbance at 348 nm using Cary 100 (Varian) Spectrophotometer (MOHAPATRA *et al.*, 2005; DAS *et al.*, 2006; NASRALLAH *et al.*, 2011). A calibration curve was used to relate the Cr(VI) concentration in the samples collected during the tests to its absorbance at a wavelength of maximum absorption (348 nm), according to the Lambert-Beer Law.

For the photocatalytic reduction reactions of Cr(VI) with TiO_2 in the presence of ethanol under UV radiation, catalyst powder was added to 150 mL of aqueous Cr(VI) solution to produce a suspension of known concentration, and the solution's pH was adjusted. The reduction tests were divided into two steps: one in the dark (1 hour), in which adsorption-desorption equilibrium of the metal on the catalyst surface occurs without radiation, and the other (1 hour) with UV radiation. The progress of the photocatalytic reduction reaction of Cr(VI) was monitored by collecting samples at fixed intervals (0, 15, 30, 45 and 60 minutes). Subsequently, the samples were centrifuged during 15 minutes, filtered with an ester mixture membrane (0.2 μm) and stored in amber glass bottles, and then analyzed in a spectrophotometer.

For the tests carried out with raw wastewater, samples were diluted with distilled and deionized water to obtain the same chromium concentration as under the best conditions of the experimental design (20 mg L^{-1}). Experiments were also carried out with raw wastewater in its original Cr(VI) concentration, which was 1100 mg L^{-1}. These tests followed the same methodology as used for the synthetic Cr(VI) solution.

2.2 Methodology of response surface

The statistical model of a circumscribed central composite design (CCC) was used in order to optimize ethanol amount, initial pH of the solution and initial Cr(VI) concentration for photochemical reduction reactions of Cr(VI) with ethanol under UV and visible radiation. This model consists of a factorial design with 2^n (n = 3) experiments, 6 star points and 3 central

points, resulting in a total of 17 experiments for each radiation. For the photocatalytic reduction reactions of Cr(VI) with TiO_2 in the presence of ethanol under UV radiation, the independent variables were: ethanol amount, catalyst concentration, initial pH of the solution, and initial Cr(VI) concentration. This model of a factorial design with 2^n (n = 4) experiments, 8 star points and 3 central points, resulted in a total of 27 experiments.

The response factor, for all of the experimental designs, was defined as the total Cr(VI) reduction after 1 hour of reaction. Data were analyzed using the Statistica 10 software and the model was statistically validated using ANOVA (confidence interval 95%).

3 Results and Discussion

3.1 Optimization of the photochemical reduction reaction of Cr(VI) with ethanol

Table 3.1 shows the experiments of the photochemical reduction of Cr(VI) with ethyl alcohol under UV and visible radiation. The numbers in parentheses represent the coded variables, and the response factor (Y) was defined as the percentage of total Cr(VI) reduction after 1 hour of reaction.

Table 3. 1: Factorial experimental design for photochemical reduction reaction of Cr(VI) with ethanol under UV and visible radiation.

Tests	Initial pH of the solution	Initial Cr(VI) concentration $(mg\ L^{-1})$	Ethanol amount (%) $(v_{ethanol}/v_{total})$	Total reduction (%) $(Y_{exp.})$ UV radiation	Total reduction (%) $(Y_{exp.})$ Visible radiation
1	2 (-1)	20 (-1)	1.5 (-1)	55.51	15.65
2	3.5 (1)	20 (-1)	1.5 (-1)	28.89	4.74
3	2 (-1)	40 (1)	1.5 (-1)	44.24	13.09
4	3.5 (1)	40 (1)	1.5 (-1)	19.35	5.61
5	2 (-1)	20 (-1)	5 (1)	96.10	48.07
6	3.5 (1)	20 (-1)	5 (1)	34.79	13.68
7	2 (-1)	40 (1)	5 (1)	94.88	39.91
8	3.5(1)	40 (1)	5 (1)	12.72	7.42
9	1.5 (-1.68)	30 (0)	3.25 (0)	89.55	34.02
10	4 (1.68)	30 (0)	3.25 (0)	0.00	0.45
11	2.75 (0)	13 (-1.68)	3.25 (0)	86.03	29.78
12	2.75 (0)	47 (1.68)	3.25 (0)	64.97	18.84
13	2.75 (0)	30 (0)	0.31 (-1.68)	9.29	2.49
14	2.75 (0)	30 (0)	6.2 (1.68)	94.48	45.22
15	2.75 (0)	30 (0)	3.25 (0)	71.36	28.26

| 16 | 2.75 (0) | 30 (0) | 3.25 (0) | 73.98 | 27.44 |
| 17 | 2.75 (0) | 30 (0) | 3.25 (0) | 71.65 | 27.06 |

The polynomial (Equations 1 and 2) obtained from the multivariable analysis showed a correlation coefficient (R^2) of 0.9431 for reactions using UV radiation, and 0.9527 for reactions using visible radiation, indicating a good fit between the experimental data and the statistical model. In the polynomial equations, the values in parentheses represent standard deviation for each coefficient and x, y e z represent the coded values of the initial pH, initial Cr(VI) concentration and ethanol amount, respectively.

$$Y_{UV\_radition} (\%) = 72.3(\pm 3.8) - 25.3x\,(\pm 2.6) - 11.5x^2\,(\pm 2.6) - 5.8y\,(\pm 2.6) + 17.1z\,(\pm 2.6) - 9.0z^2$$
$$(\pm 2.6) - 11.5x.z\,(\pm 3.4) \tag{1}$$

$$Y_{Visible\_radiation} (\%) = 24.0(\pm 1.3) - 10.4x\,(\pm 1.1) - 3.4x^2\,(\pm 1.1) - 2.5y\,(\pm 1.1) + 10.4z\,(\pm 1.1) - 6.1x.z$$
$$(\pm 1.4) \tag{2}$$

The initial pH of the solution and the ethanol amount are the main variables affecting the reaction, with linear and quadratic interactions. In addition, for both photochemical reactions (UV and visible), the coefficients of the linear effects of pH and Cr(VI) concentration were negative, indicating that the lower the initial pH of the solution and the initial Cr(VI) concentration, the higher the total Cr(VI) reduction. The coefficient for the linear effect of ethanol amount was positive, so the greater the ethanol amount, the higher the total Cr(VI) reduction. Moreover, the intensity of the coefficients of the polynomial was greater, in all cases, under UV radiation.

This behavior can be seen in Table 3.1, in which test 5, for reactions under UV and visible radiation, with lower initial pH values and Cr(VI) concentration and high ethanol amount, presented the highest total Cr(VI) reduction of 96.10% and 48.07%, respectively. Moreover, it was observed that the photochemical reactions with ethanol under UV radiation obtained higher values of Cr(VI) reduction than the photochemical reactions with ethanol under visible light.

The effect of initial pH has been associated with higher susceptibility of $HCrO_4^-$ to reduction and chromate(VI) ester formation, a necessary condition for redox or photoredox reactions. Equations 3-5 show the Cr(VI) species distribution in aqueous solution as a function of

the solution's pH. The neutral chromic acid molecule, H_2CrO_4, is the predominant species for pH levels below 2.0, while concentrations of negatively-charged $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$ species are predominant for pH levels above 2.0 (KU and JUNG, 2001); and Equations 6-10 show the mechanism of the Cr(VI) reduction reaction by alcohols (MYTYCH *et al.*, 2003).

$$H_2CrO_4 \leftrightarrow H^+ + HCrO_4^- \tag{3}$$

$$HCrO_4^- \leftrightarrow H^+ + CrO_4^{2-} \tag{4}$$

$$2HCrO_4^- \leftrightarrow Cr_2O_7^{2-} + H_2O \tag{5}$$

$$HCrO_4^- + ROH \leftrightarrow ROCrO_3^- + H_2O \tag{6}$$

$$ROCrO_3^- + h\nu \rightarrow Cr(IV) + aldehyde/ketone \tag{7}$$

$$Cr(IV) + Cr(VI) \rightarrow 2Cr(V) \tag{8}$$

$$3Cr(V) \rightarrow 2Cr(VI) + Cr(III) \tag{9}$$

$$Cr(V) + ROH \rightarrow Cr(III) + aldehyde/ketone \tag{10}$$
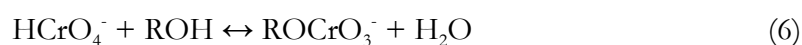
The total Cr(VI) reduction is proportional to the amount of electrons supplied by the alcohol (Equation 6). Therefore, the greater the ethanol amount, the more electrons are provided to reduce the initial Cr(VI) concentration, increasing total Cr(VI) reduction. Conversely, maintaining the ethanol amount at a fixed level and increasing the initial Cr(VI) concentration will decrease total Cr(VI) reduction.

In addition, other tests were conducted in the absence of UV or visible light to verify Cr(VI) reduction in the presence of alcohol. No Cr(VI) reduction was observed in 2 hours, indicating that Cr(VI) reduction occurs only in the presence of light, thus it is considered a photochemical reaction. Similar behavior was observed by Mytych et al. (2003). To quantify the contribution of photolysis, experiments in which only the Cr(VI) solution was subjected to UV radiation/visible radiation were also carried out. The reaction under UV showed no Cr(VI) reduction, while the reaction under visible light showed a total Cr(VI) reduction of 0.4%. Thus,

the contribution of photolysis can be negligible (MOHAPATRA *et al.*, 2005; CHAKRABARTI *et al.*, 2009).

3.2 Optimization of the photocatalytic reduction reaction of Cr(VI) with TiO$_2$ in the presence of ethanol under UV radiation

For the photocatalytic reduction reactions of Cr(VI) with TiO$_2$ in the presence of ethanol under UV radiation, the variables studied were: ethanol amount, catalyst concentration, initial pH of the solution, and initial Cr(VI) concentration. The experimental design and results are shown in Table 3.2. The numbers in parentheses represent the coded variables, and the response factor (Y) was defined as the percentage of total Cr(VI) reduction after 1 hour of reaction.

Table 3. 2: Factorial experimental design for photocatalytic reduction reaction of Cr(VI) with TiO$_2$ in the presence of ethanol under UV radiation.

Tests	Initial pH of the solution	Catalyst concentration (g L^{-1})	Initial Cr(VI) concentration (mg L^{-1})	Ethanol amount (%) ($v_{ethanol}/v_{total}$)	Total reduction (%) ($Y_{exp.}$)
1	3 (-1)	0.8 (-1)	20 (-1)	0.15 (-1)	46.92
2	6 (1)	0.8 (-1)	20 (-1)	0.15 (-1)	32.81
3	3 (-1)	2.0 (1)	20 (-1)	0.15 (-1)	84.85
4	6 (1)	2.0 (1)	20 (-1)	0.15 (-1)	62.18
5	3 (-1)	0.8 (-1)	40 (1)	0.15 (-1)	28.57
6	6 (1)	0.8 (-1)	40 (1)	0.15 (-1)	8.91
7	3 (-1)	2.0 (1)	40 (1)	0.15 (-1)	49.69
8	6 (1)	2.0 (1)	40 (1)	0.15 (-1)	21.73
9	3 (-1)	0.8 (-1)	20 (-1)	0.35 (1)	56.16
10	6 (1)	0.8 (-1)	20 (-1)	0.35 (1)	39.66
11	3 (-1)	2.0 (1)	20 (-1)	0.35 (1)	92.97
12	6 (1)	2.0 (1)	20 (-1)	0.35 (1)	60.35
13	3 (-1)	0.8 (-1)	40 (1)	0.35 (1)	26.24
14	6 (1)	0.8 (-1)	40 (1)	0.35 (1)	14.31
15	3 (-1)	2.0 (1)	40 (1)	0.35 (1)	52.44
16	6 (1)	2.0 (1)	40 (1)	0.35 (1)	20.05
17	1.5 (-2)	1.4 (0)	30 (0)	0.25 (0)	87.37
18	7.5 (2)	1.4 (0)	30 (0)	0.25 (0)	26.51
19	4.5 (0)	0.2 (-2)	30 (0)	0.25 (0)	6.38
20	4.5 (0)	2.6 (2)	30 (0)	0.25 (0)	59.08
21	4.5 (0)	1.4 (0)	10 (-2)	0.25 (0)	94.15
22	4.5 (0)	1.4 (0)	50 (2)	0.25 (0)	13.50
23	4.5 (0)	1.4 (0)	30 (0)	0.05 (-2)	24.62
24	4.5 (0)	1.4 (0)	30 (0)	0.45 (2)	33.45
25	4.5 (0)	1.4 (0)	30 (0)	0.25 (0)	29.00
26	4.5 (0)	1.4 (0)	30 (0)	0.25 (0)	30.54
27	4.5 (0)	1.4 (0)	30 (0)	0.25 (0)	29.51

Equation 11 shows the polynomial obtained from the multivariable analysis. The values in parentheses represent standard deviation for each coefficient and x, y, z and w represent the coded values of the initial pH, initial Cr(VI) concentration, ethanol amount and TiO$_2$ concentration respectively.

$Y(\%) = 30.7(\pm1.4) - 12.5x\ (\pm0.8) + 6.7x^2\ (\pm0.8) + 12.3w\ (\pm0.8) - 17.3y\ (\pm0.8) + 5.9y^2\ (\pm0.8) + 1.8z\ (\pm0.8) - 3.3x.w\ (\pm1.0) - 3.7w.y\ (\pm1.0)$ (11)

The polynomial presents a correlation coefficient (R^2) of 0.9823 and indicates that the initial pH of the solution and the initial Cr(VI) concentration are the main variables that affect the reaction, with linear and quadratic interactions. The linear coefficients of the effects of the initial pH and the Cr(VI) concentration were negative, indicating that the lower the initial pH of the solution and the initial Cr(VI) concentration, the higher the total Cr(VI) reduction. The coefficients for the linear effects of the TiO$_2$ concentration and the ethanol amount are positive, indicating that the higher the TiO$_2$ concentration and the ethanol amount, the higher the total Cr(VI) reduction. As can be seen in Table 3.2, test 21 showed the largest removal of Cr(VI) at 94.15%, with an initial pH of 4.5, an initial Cr(VI) concentration of 10 mg L^{-1}, a TiO$_2$ concentration of 1.4 g L^{-1}, and an ethanol amount of 0.25% (v/v).

The initial pH of the solution is an important parameter, influencing reduction reactions of Cr(VI). The initial pH determines the charges to the catalyst surface as well as the ionization state of the substrate, which affects the amount adsorbed and hence the total reduction. The predominant species of Cr(VI) at pH 2 is HCrO$_4^-$. Thus, an increase in the solution's pH will shift the HCrO$_4^-$ concentration to form CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$ species. As the zero point charge of TiO$_2$ is pH 7.52 (KU and JUNG, 2001), at pH values above the isoelectric point, the semiconductor surface becomes negative and repels dichromate ions (KU and JUNG, 2001; MOHAPATRA et al., 2005). Therefore, the higher the initial pH of the solution, the lower the Cr(VI) reduction.

As observed, by decreasing the initial Cr(VI) concentration, an increase in the total reduction of this species takes place because at higher levels of the substrate's initial concentration, absorbance of Cr(VI) solution is increased and a higher fraction of the UV radiation is intercepted before it reaches the catalyst surface, thereby diminishing the efficiency of

the photocatalytic reaction (KU and JUNG, 2001; DAS *et al.*, 2006; CHAKRABARTI *et al.*, 2009).

The catalyst, when illuminated with energy of wavelength equal to or greater than its band-gap energy, generates electron/hole pairs. These, in turn, reduce the Cr(VI) and oxidize ethanol, which acts as a sacrificial electron donor providing electrons to the reaction medium and prevents the recombining of electron/hole pairs. Greater Cr(VI) reductions were observed with photocatalytic reactions of Cr(VI) with TiO_2 in the presence of ethanol, demonstrating the synergistic effect between ethanol oxidation and Cr(VI) reduction, as can be seen in Figure 3.1.
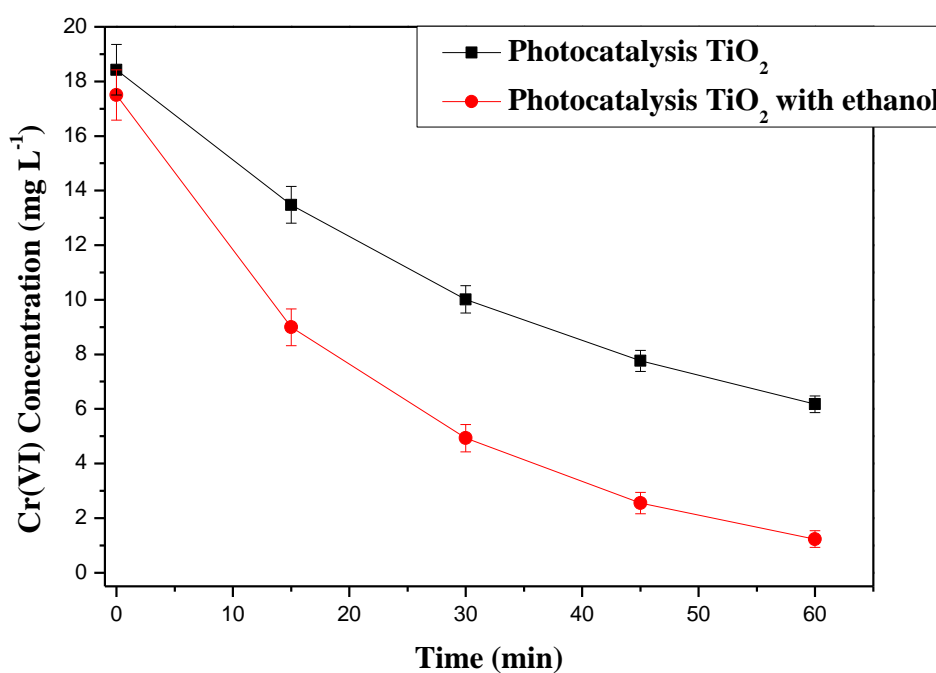
Figure 3. 1: Photocatalytic reduction of Cr(VI) with TiO_2 under UV radiation in the presence and absence of ethanol (C_{TiO2} = 2.0 g L^{-1}, $C_{Cr(VI)}$ = 20 mg L^{-1}, $V_{ethanol}$ = 0.35% (v/v), pH = 3.0, T = 30 °C e 5.8 mW cm^{-2}).

Experiments were conducted in the absence of UV or visible light to verify the adsorption of Cr(VI) on the catalyst surface. An adsorption of 14% was observed in 1 hour, with an initial pH at 3.0, an initial Cr(VI) concentration at 20 mg L^{-1}, catalyst concentrations of 2.0 g L^{-1}, and ethanol amount at 0.35% (v/v).

3.3 Tests with wastewater

In order to verify the application of photochemistry with ethanol and heterogeneous photocatalysis in treating Cr(VI) in raw wastewater discharges from an electroplating plant, tests of total Cr(VI) reduction were initially carried out with diluted wastewater, according to the methodology mentioned above, using the conditions that yielded maximum reduction as indicated by the experimental design. The results obtained were similar to those obtained with the synthetic solution, and significantly improved in the case of photocatalysis with TiO_2, in the presence of ethanol under UV radiation, as observed in Table 3.3.

Table 3. 3: Tests of total Cr(VI) reduction with diluted wastewater.

Source of Cr(VI) solution	Reactions	Total Cr(VI) reduction
Synthetic ($K_2Cr_2O_7$)	Photochemistry Ethanol, UV	96.10%
Diluted wastewater	Photochemistry Ethanol, UV	95.10%
Synthetic ($K_2Cr_2O_7$)	Photochemistry Ethanol, visible	48.07%
Diluted wastewater	Photochemistry Ethanol, visible	44.87%
Synthetic ($K_2Cr_2O_7$)	Photocatalysis TiO_2, UV, with Ethanol	92.97%
Diluted wastewater	Photocatalysis TiO_2, UV, with Ethanol	99.62%

Subsequently, tests of total Cr(VI) reduction were carried out with industrial wastewater in its original concentration (1100 mg L^{-1}), under other experimental conditions, in order to enable the application of these processes in electroplating industries. These tests were conducted to evaluate the ethanol amount and the reaction time required to reduce the Cr(VI) present in concentrate wastewater. The conditions tested for the synthetic solution in photochemistry with ethanol under UV radiation showing 96.10% removal were used to evaluate the ethanol amount and the reaction time. Results indicated the highest total Cr(VI) reduction to be 98.48%, considering an ethanol amount of 40% (v/v) and a reaction time of 6 hours. Thus, these conditions were selected to run photochemical reduction reactions of Cr(VI) with ethanol under visible light and photocatalytic reduction reactions of Cr(VI) with TiO_2, in the presence of ethanol, under UV radiation (Table 3.4).

As can be observed in Table 3.4, all processes were successful in obtaining high removals of total Cr(VI), suggesting their potential to be used for industrial applications. Moreover, the most suitable process is photochemistry with ethanol under UV radiation. Although it does not present the largest total Cr(VI) reduction, it does not require catalyst separation processes and presents lower reagent costs, since ethanol is inexpensive, non-toxic and easy to purchase.

Table 3. 4: Tests of total Cr(VI) reduction with industrial wastewater in its original concentration.

Reactions	Experimental conditions	Total Cr(VI) reduction
Photochemistry Ethanol, UV	$C_{Cr(VI)}$ = 1100 mg L^{-1}, pH = 2.0, $V_{ethanol}$ = 40%, and 5.8 mW cm^{-2} 6 hours of reaction	98.48%
Photochemistry Ethanol, visible	$C_{Cr(VI)}$ = 1100 mg L^{-1}, pH = 2.0, $V_{ethanol}$ = 40%, and 250 W m^{-2} 6 hours of reaction	89.74%
Photocatalysis TiO$_2$, UV, with Ethanol	$C_{Cr(VI)}$ = 1100 mg L^{-1}, pH = 2.0, C_{TiO2} = 2.0 g L^{-1}, $V_{ethanol}$ = 40%, and 5.8 mW cm^{-2} 6 hours of reaction	99.21%

4 Conclusion

Cr(VI) reduction by photocatalysis and photochemistry processes were studied, as well as their application in wastewater remediation. Photochemistry with ethanol under UV radiation was more efficient than photochemistry with ethanol under visible light. Photocatalytic reduction with TiO$_2$ in the presence of ethanol under UV radiation presented high Cr(VI) removals, showing the synergistic effect between ethanol oxidation and Cr(VI) reduction. Furthermore, results obtained with raw wastewater in its original concentration, suggested high values of total Cr(VI) reduction, thus potentially confirming the feasibility of applying these processes to remove hexavalent chromium from wastewater discharges of electroplating industries. Among the processes observed, the most suitable appears to be photochemistry with ethanol under UV radiation.

5 Acknowledgements

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CAPÍTULO IV – ARTIGO 3

WASTEWATER REMEDIATION USING A SPIRAL SHAPED REACTOR FOR PHOTOCHEMICAL REDUCTION OF HEXAVALENT CHROMIUM

Wastewater remediation using a spiral shaped reactor for photochemical reduction of hexavalent chromium

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ABSTRACT

The hexavalent chromium contained in wastewater of some industries is toxic to most microorganisms and potentially harmful to human health. The application of photochemical reduction of Cr(VI) in the treatment of wastewater from the electroplating industry was studied, and a continuous reactor in spiral shape made of borosilicate was designed and constructed (SSR). The statistical model of a circumscribed central composite design (CCCD) was used to investigate the influence of the amount of ethanol and the initial concentration of hexavalent chromium on total Cr(VI) reduction. A total Cr(VI) reduction of 46.0% was achieved under the optimal conditions established by the experimental design, using a synthetic Cr(VI) solution. In addition, the photochemical reduction of Cr(VI) follows pseudo first-order kinetics. The SSR exhibited similar behavior to that of the plug flow reactor (PFR), and presented higher photonic efficiency than the batch reactor. Finally, the designed reactor was effective when applied to real wastewater, showing a total Cr(VI) reduction of 51.8%, and its configuration is suitable for scale up.

Keywords: hexavalent chromium, photochemical reduction, reactor, wastewater

1 Introduction

Heavy metals found in the environment originate mainly from the improper discharge of wastewater (KU and JUNG, 2001), whereas leather tanners, paint and dye factories, producers of photographic material, electroplating companies, mines, and metallurgical and electronic plants are among the possible sources of chromium (SCHRANK *et al.*, 2002; MOHAPATRA *et al.*, 2005; CHAKRABARTI *et al.*, 2009). The electroplating industry is characterized by its excessive consumption of water and energy, and generation of large amounts of wastewater containing heavy metals such as copper, nickel, and chromium. Among these inorganic pollutants, hexavalent chromium is an important industrial metal that is considered a priority pollutant since it is toxic to most organisms (DAS *et al.*, 2006). This form of chromium is carcinogenic and mutagenic to animals and can cause irritation and corrosion to human skin (YANG and CHAN, 2009).

The methods generally employed for hexavalent chromium removal are chemical precipitation, adsorption, reverse osmosis, ion exchange, electrolysis, etc. However, most of these methods require either high energy or large quantities of chemicals (MOHAPATRA *et al.*, 2005; CHAKRABARTI *et al.*, 2009). The problems associated with conventional techniques have been the main reasons behind the attempts to develop alternative clean technologies for chromium remediation (CHAKRABARTI *et al.*, 2009), whereby photochemical reduction is one of these technologies.

Neat chromate(VI) is photochemically inactive, but its effective photoreduction is observed when irradiated in the presence of a sacrificial electron donor (YURKOW *et al.*, 2002; MYTYCH *et al.*, 2003; MYTYCH and STASICKA, 2004; CIESLA *et al.*, 2004). The photochemical reduction of Cr(VI) by alcohols in an acidic medium has been studied, and some pathways have been proposed. The most generally accepted mechanism (Equations (1)-(5)) consists of two-electron reduction of Cr(VI) giving rise to an aldehyde or ketone and a Cr(IV) species. The formation of the chromate(VI) ester is mostly assumed as a necessary condition for redox or photoredox reactions (MYTYCH *et al.*, 2003; CIESLA *et al.*, 2004).

$$HCrO_4^- + ROH \leftrightarrow ROCrO_3^- + H_2O \qquad\qquad (1)$$

$$ROCrO_3^- + h\nu \rightarrow Cr(IV) + \text{aldehyde/ketone} \tag{2}$$

$$Cr(IV) + Cr(VI) \rightarrow 2Cr(V) \tag{3}$$

$$3Cr(V) \rightarrow 2Cr(VI) + Cr(III) \tag{4}$$

and/or

$$Cr(V) + ROH \rightarrow Cr(III) + \text{aldehyde/ketone} \tag{5}$$
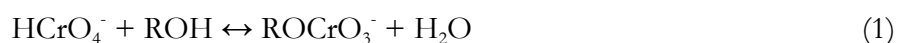
Literature review showed few studies on the photochemical reduction of Cr(VI) by alcohols (MYTYCH *et al.*, 2003), phenol and its halogen derivatives (MYTYCH and STASICKA, 2004), and glycerol (YURKOW *et al.*, 2002). However, there were no systematic and comparative studies that analyze the effect of each parameter of the reaction, nor the interaction between them, for photochemical reduction reactions of Cr(VI) with alcohols under UV and visible radiation. Furthermore, the application of sustainable treatments such as photochemistry with alcohols to remediate Cr(VI) present in wastewater discharges of electroplating industries has not been found in the literature. Therefore, we initiated a research line that aims to fill this gap.

In previous work, we studied Cr(VI) reduction by photochemistry with ethanol under UV and visible radiation; photocatalysis with TiO_2 in the presence of ethanol under UV radiation; and the application of these processes for the treatment of Cr(VI) containing wastewater from the electroplating industry. The experiments were carried out in a glass batch reactor irradiated with a mercury vapor lamp, with controlled temperature and agitation of the reaction medium. We concluded that the most suitable process for industrial application was photochemistry with ethanol under UV radiation, which presented 98.5% of total Cr(VI) reduction for real wastewater (MACHADO *et al.*, 2014). However, the design and construction of a large-scale reactor is essential to the industrial application of the photochemical process.

Thus, the main objective of this work was to design and build a semi-pilot scale reactor in order to enable the industrial application of photochemical reduction of hexavalent chromium in the treatment of wastewater from the electroplating industry. Initially, a spiral shaped reactor (SSR) was designed and built. Subsequently, the influence of the initial Cr(VI) concentration and ethanol amount were investigated using an experimental design, and the designed reactor was compared to the batch reactor used by Machado et al. (2014). Finally, experiments were conducted using real wastewater from an electroplating plant.

2 Experimental Section

Materials: Potassium dichromate (Fmaia) was used as it was received, and deionized and distilled water were used to prepare the solutions. Absolute ethyl alcohol (Nuclear) were used in the reactions of photochemical reduction of Cr(VI). Untreated wastewater containing Cr(VI) were collected directly from a storage tank in the electroplating plant. Information about the real wastewater is presented in Table 4.1.

Table 4. 1: Information about the real wastewater.

Information	Quantity
Hexavalent chromium	$1,100 \text{ mg L}^{-1}$
Color	Orange
pH at 25°C	2.9
COD	$< 5 \text{ mg L}^{-1}$
Total aluminum	3.1 mg L^{-1}
Total copper	179 mg L^{-1}
Total nickel	36.1 mg L^{-1}

2.1 Spiral shaped reactor (SSR)

A continuous reactor in spiral shape made of borosilicate (255 cm long and 1 cm diameter) was designed and built. The reactor was placed inside a stainless steel chamber (19.1 cm internal diameter and 42.4 cm height), containing 12 evenly distributed UV tubular fluorescent lamps (Xelux 8 Watt, 16 mm diameter). The radiation of the lamps was measured (2.5 mW cm^{-2}) at the beginning of each test using a radiometer (Cole-Parmer Instrument, Series 9811 Radiometer), and the total irradiated area was 801.1 cm^2. A centrifugal pump was used in order to circulate a Cr(VI) solution through the reactor and a storage tank, as shown in Figure 4.1. The liquid samples were collected through a syringe-catheter system located in the storage tank. A flow rate of 100 L h^{-1} was measured by a rotameter and a reaction volume of approximately 2,800 mL (spiral reactor, pipes and storage tank) was used.
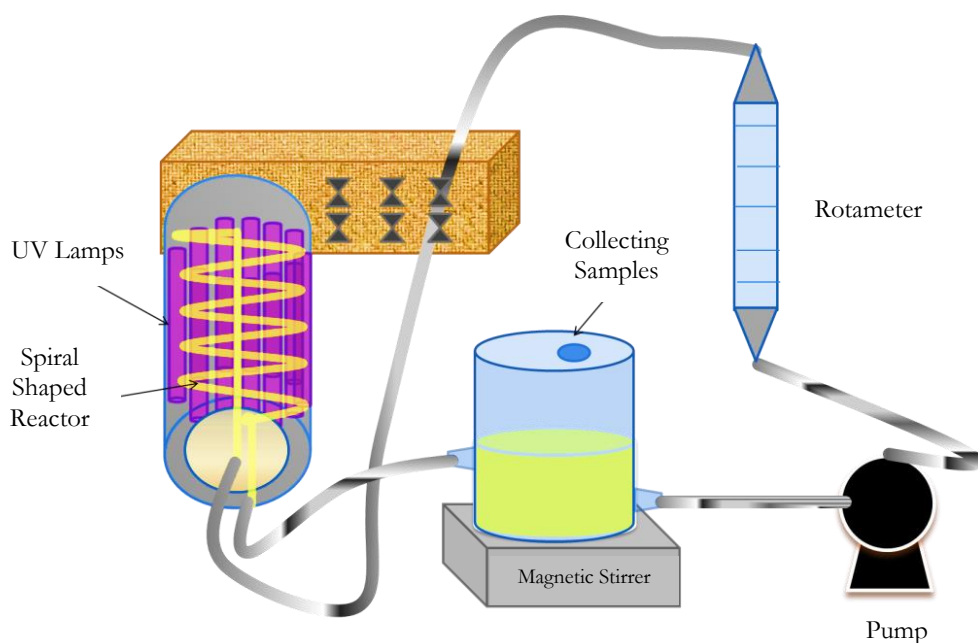
Figure 4. 1: Spiral shaped reactor apparatus.

The synthetic Cr(VI) solution was prepared from potassium dichromate ($K_2Cr_2O_7$) and kept under vigorous magnetic stirring for approximately 1 hour. For the photochemical reduction reactions with ethanol, carried out in the SSR, an aqueous Cr(VI) solution of known concentration (100 mg L^{-1}) was added to the storage tank and diluted with deionized and distilled water in order to obtain the desired initial Cr(VI) concentration (16, 20, 30, 40 and 44 mg L^{-1}). Then, a known volume of ethanol was added to the storage tank, and the solution's pH was adjusted. These reactions occurred in 1 hour and the progress of the photochemical reduction reaction of Cr(VI) was monitored by collecting samples at fixed intervals (0, 15, 30, 45 and 60 minutes). Subsequently, the samples were analyzed using a spectrophotometer (Varian Cary 100) by absorbance measurement at a wavelength of 348 nm (COLÓN *et al.*, 2002; MOHAPATRA *et al.*, 2005; DAS *et al.*, 2006; NASRALLAH *et al.*, 2011).

In the photochemical reduction reactions using real wastewater, the water was added to the storage tank along with a known volume of ethanol. These reactions occurred in 6 hours and the samples were collected at fixed intervals. Subsequently, the samples were diluted and analyzed using a spectrophotometer.

All experiments were carried out maintaining the solution's initial pH and operating temperature constant at 2.0 and 30 °C, respectively. We decided to do so based on literature (MYTYCH *et al.*, 2003; MOHAPATRA *et al.*, 2005; DAS *et al.*, 2006) and our previous results

(MACHADO *et al.*, 2014). An increase in the reaction rate was observed when the acidity increased. This was interpreted in terms of higher susceptibility of $HCrO_4^-$, in comparison to CrO_4^{2-}, to undergo reduction and chromate(VI) ester formation (MYTYCH *et al.*, 2003). Moreover, Mytych et al. (2003) reported that the reaction rate is insensitive to temperature within 283-303 K.

2.2 Methodology of response surface

The statistical model of a circumscribed central composite design (CCCD) was employed for the optimization of photochemical reduction of Cr(VI) with ethanol in SSR. The design consists of three types of points: 2^k cube points (factorial design points), 2k axial points, and N_0 center points. In the present case, three replications at the center point and two numbers of factors (k) were utilized leading to a total of 11 experimental runs. The distance of axial points from the center points (α) was fixed at 1.41, based on the number of factors chosen for the experiment. The variables (factors) used in the study were the initial Cr(VI) concentration (X_1) and ethanol amount (X_2). The percentage of the total reduction (Y) of Cr(VI), as given by the following equation, was considered as the response.

$$Y = \left[\frac{C_0 - C_t}{C_0} \right] \times 100 \qquad (6)$$

where C_0 is the initial Cr(VI) concentration, and C_t is the concentration achieved after the photochemical treatment. The real values of the process variables (factors), their variation limits and number were selected based on the preliminary experiments. The coded values along with real values of the factors are shown in Table 4.2.

Table 4. 2: Real and coded levels of the independent variables.

Factors	Real values of coded levels				
	-α	-1	0	+1	+α
Cr(VI) concentration (mg L^{-1})	16	20	30	40	44
Ethanol amount (%) (v$_{ethanol}$/v$_{total}$)	0.8	1.5	3.25	5.0	5.7

A regression model was proposed, and results were analyzed using Statistica software version 10. The model was statistically validated with the same software using the analysis of variance (ANOVA). The quality of the fit for the polynomial model was expressed by the

coefficient of determination (R^2). Model terms were selected or rejected based on the probability value within a 95% confidence interval (or 5% significance level).

2.3 Calculation of the photonic efficiency (ξ)

The photonic efficiency, ξ, being defined as the ratio of the reaction rate and the incident photon flux (MILLS and LEHUNTE, 1997; SERPONE and EMELINE, 2002; OHTANI, 2010; TOKODE *et al.*, 2012; BOUZID *et al.*, 2014) was calculated, according to Bouzid et al. (2014) to compare the efficiency of spiral shaped and batch reactors.

3 Results and Discussion

3.1 Experiments of photochemical reduction of Cr(VI) with ethanol carried out in a SSR

The SSR flow was analyzed using a tracer injected by pulse. The results showed that the reactor presented similar behavior to that of a plug flow reactor (PFR).

Table 4.3 shows the experimental design used for the photochemical reduction reactions of Cr(VI) with ethanol under UV radiation. Some variables were unaltered in all these tests (flow of 100 L h^{-1}, UV 2.5 mW cm^{-2}, 30°C and initial pH of 2.0). The response factor (Y) was defined as the percentage of total Cr(VI) reduction after 1 hour of reaction.

Table 4. 3: Circumscribed central composite design of experiments along with observed and predicted values of response.

Run	Coded levels of variables		Actual levels of variables		Response (% total reduction)	
	x_1	x_2	X_1	X_2	$Y_{observed}$	$Y_{predicted}$
1	-1	-1	20	1.5	15.9	17.3
2	1	-1	40	1.5	9.3	7.9
3	-1	1	20	5.0	46.0	41.5
4	1	1	40	5.0	34.0	32.1
5	- α	0	16	3.25	30.8	31.3
6	+ α	0	44	3.25	17.2	18.0
7	0	- α	30	0.8	7.3	7.6
8	0	+ α	30	5.7	37.13	41.8
9	0	0	30	3.25	24.5	24.7
10	0	0	30	3.25	24.4	24.7
11	0	0	30	3.25	24.8	24.7

The polynomial (Equation (7)) obtained from the multivariable analysis, with a coefficient of determination (R^2) of 0.9641, indicated a good fit between the experimental data and the statistical model. In the polynomial equation, the values in parentheses represent the standard deviation for each coefficient, and x_1 e x_2 represent the coded values of the initial Cr(VI) concentration and ethanol amount, respectively.

$$Y(\%) = 24.7(\pm0.8) - 4.7x_1 (\pm0.9) + 12.1x_2 (\pm0.9) \qquad (7)$$

Additionally, these reactions proved to be dependent on the initial Cr(VI) concentration and the ethanol amount, with linear interactions. The linear coefficient of the effect of the initial Cr(VI) concentration was negative, indicating that the lower the initial Cr(VI) concentration, the higher the total Cr(VI) reduction, while the effect of the ethanol amount was positive, indicating that the higher the ethanol amount, the higher the total Cr(VI) reduction. As can be seen in Table 4.3, run 3 resulted in the greatest total Cr(VI) reduction at 46.0% with initial Cr(VI) concentration at 20 mg L^{-1} and ethanol amount at 5% (v/v). These conclusions are evident in Figure 4.2, which depicts the response profiles for the experimental data obtained.
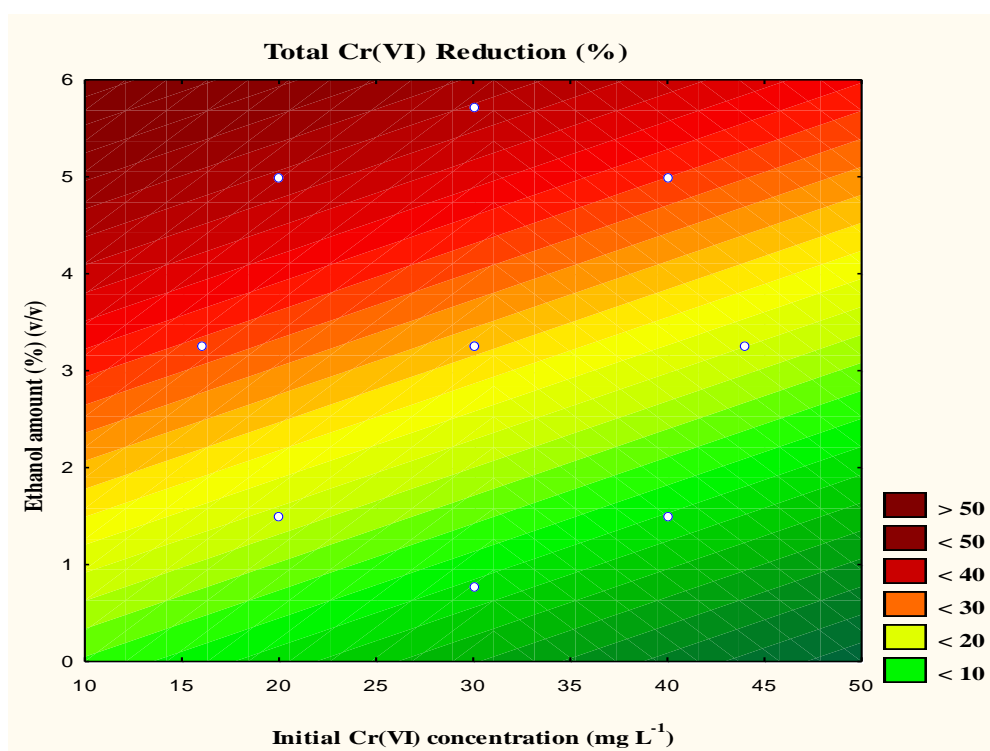
Figure 4. 2: Response profiles showing the percentage of Cr(VI) reduction.

In comparing the results obtained by using the SSR with the results obtained from the batch reactor studied in our previous work (MACHADO *et al.*, 2014), the same behavior as the

parameters evaluated in the statistical model was observed. Table 4.4 presents information about batch reactor and SSR.

Table 4. 4: Specification about the reactors.

Specifications	Batch reactor[a]	SSR
Total Cr(VI) reduction	96.1%	46.0%
Reaction volume	150 mL	2,800 mL
Reaction time	1h	1h
Irradiation	5.8 mW cm^{-2}	2.5 mW cm^{-2}
Irradiated surface area	56.7 cm^2	801.1 cm^2
Photonic efficiency	1.43 %	2.52 %

[a] Reactor used by Machado et al. (2014).

Table 4.4 shows that the batch reactor presented higher total Cr(VI) reduction (96.1%) than the SSR (46.0%) under maximum yield conditions. However, the SSR is more efficient than the batch reactor, presenting a photonic efficiency of 2.52% compared to 1.43% for the batch reactor.

3.2 Kinetics of reduction reaction

Figure 4.3 presents the reaction kinetics of photochemical reduction of Cr (VI), under maximum yield conditions established in the experimental design, considering that this reaction occurs by pseudo first-order kinetics (MYTYCH *et al.*, 2003). In Figure 4.3, a line passing through the origin with a correlation coefficient (R^2) of 0.9991, indicating that the photochemical reduction of Cr(VI) follows pseudo first-order kinetics can be observed. Thus, the specific reaction rate, *k*, for these conditions is equal to 0.0101 min^{-1}.
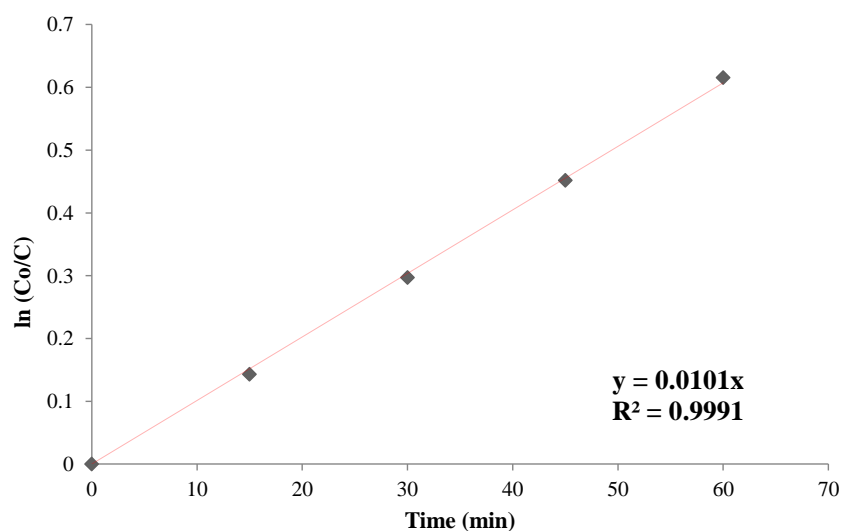
Figure 4. 3: Response Pseudo first-order kinetic to photochemical reduction of Cr(VI) ($C_{Cr(VI)}$ = 20 mg L^{-1}, $V_{ethanol}$ = 5.0% (v/v), pH = 2.0, T = 30 °C, and 2.5 mW cm^{-2}).

3.3 Tests with real wastewater

Tests were performed using real wastewater from the electroplating industry in order to verify the industrial application of the SSR. Experiments were carried out with different ethanol amounts (20 and 40% (v/v)) and 6 hours of reaction. The results are shown in Table 4.5, along with the results obtained for the batch reactor. A total Cr(VI) reduction of 49.2% and 51.8% was observed for an ethanol amount of 20% and 40%, respectively. These values of total reduction were higher than those obtained under the maximum yield conditions established in the experimental design, containing a synthetic Cr(VI) solution (46.0%). Thus, the spiral shaped reactor, which was designed and built, was effective when applied to real wastewater, and its configuration is suitable for scale up.

Table 4. 5: Comparison of total Cr(VI) reduction.

Reactions	Reactor	TR[b] Synthetic	Experimental conditions	TR Wastewater
Photochemistry Ethanol, UV	SSR	46.0%	$C_{Cr(VI)}$ = 1,100 mg L^{-1}, pH = 2.2, $V_{ethanol}$ = 20%, and 2.5 mW cm^{-2} 6 hours of reaction	49.2%
Photochemistry Ethanol, UV	SSR	46.0%	$C_{Cr(VI)}$ = 1,100 mg L^{-1}, pH = 2.2, $V_{ethanol}$ = 40%, and 2.5 mW cm^{-2} 6 hours of reaction	51.8%
Photochemistry Ethanol, UV	Batch[a]	96.1%	$C_{Cr(VI)}$ = 1,100 mg L^{-1}, pH = 2.0, $V_{ethanol}$ = 40%, and 5.8 mW cm^{-2} 6 hours of reaction	98.5%

[a] Results presented by Machado et al. (2014).
[b] Maximum yield conditions established in the experimental designs.

4 Conclusion

The application of photochemical reduction of hexavalent chromium, using a spiral shaped reactor, in wastewater remediation was studied. The results obtained showed that total Cr(VI) reduction increases with an increase in ethanol amount and decreases with an increase in initial Cr(VI) concentration. The spiral shaped reactor (SSR), which was designed and constructed, presented higher photonic efficiency than the batch reactor. The Cr(VI) photochemical reduction follows pseudo first-order kinetics. Furthermore, the SSR was effective when applied to real wastewater, and its configuration is suitable for scale up.

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CAPÍTULO V – ARTIGO 4

PROPOSAL FOR ENVIRONMENTALLY SUSTAINABLE TECHNOLOGY FOR THE TREATMENT OF WASTEWATER CONTAINING Cr(VI): DESIGN AND CONSTRUCTION OF A SOLAR TUBULAR REACTOR

Proposal for Environmentally Sustainable Technology for the Treatment of Wastewater Containing Cr(VI): Design and Construction of a Solar Tubular Reactor

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ABSTRACT

The hexavalent chromium, Cr(VI), which is generated in the electroplating process, is toxic to most organisms and potentially harmful to human health. The method generally used for remediation of wastewater containing Cr(VI) employs chemicals with high toxicity. This work proposes an alternative technology for the treatment of these wastewaters, based on photochemical reduction of Cr(VI) by alcohols under radiation, which is environmentally sustainable and economically viable. Initially, a batch reactor in laboratory scale was used to determine the best experimental conditions and its specific reaction rate was calculated. Based on these results a tubular reactor (artificial radiation and sunlight) was designed and built in semi-pilot scale. Tests were carried out with real wastewater from an electroplating industry containing Cr(VI). Tests conducted under sunlight showed a higher total Cr(VI) reduction than the tests with artificial radiation. The remediation of Cr(VI) from wastewater was 86.7% after 6 hours of reaction under sunlight, indicating the high efficiency of the developed process.

Keywords: solar tubular reactor, environmentally sustainable technology, hexavalent chromium, photochemical reduction, real wastewater

1 Introduction

The presence of heavy metals in water bodies has been known to cause pollution problems. The major source of heavy metals in these bodies is the improper discharge of various industrial wastewaters. One of these heavy metals, hexavalent chromium, is toxic to most organisms, mutagenic and carcinogenic to animals, causing corrosion and irritation to human skin (MOHAPATRA *et al.*, 2005; DAS *et al.*, 2006). The potential sources of chromium include leather tanning, electroplating, paints, dyes, photographic materials, electronic processes, metallurgy and mining (SCHRANK *et al.*, 2002; MOHAPATRA *et al.*, 2005; CHAKRABARTI *et al.*, 2009).

Galvanizing is the process of coating the surface of an object, usually a metal, with other metals in order to confer specific characteristics such as color, gloss, hardness and resistance to corrosion. This process involves a sequence of baths to perform pretreatment, plating and surface conversion, which are alternated by washing. As a result, the electroplating industry is characterized by excessive consumption of water and energy, and the generation of wastewater containing heavy metals (CPRH, 2001; LADEIRA and PEREIRA, 2008).

Wastewater contaminated with hexavalent chromium has an orange color and acid pH. Reduction with sodium sulfite or metabisulfite is a conventional method of treating hexavalent chromium in wastewater. Besides requiring excess chemicals to ensure complete conversion of Cr(VI), the formation of sludge or the release of sulfur dioxide are major problems associated with this method (CHAKRABARTI *et al.*, 2009).

Faced with this reality, our research group has been working to develop an environmentally sustainable alternative technology for the treatment of wastewater containing Cr(VI). Initially, experiments of photocatalytic reduction of Cr(VI) under UV radiation using TiO_2 and ZnO as catalysts were carried out. The TiO_2 catalyst was more efficient than the ZnO catalyst. Subsequently, tests of photochemical reduction of Cr(VI) with ethanol under UV and visible radiation were carried out. The photochemical reaction showed greater Cr(VI) reductions under UV radiation. In addition, experiments of photocatalytic reduction of Cr(VI) with TiO_2 in the presence of ethanol under UV radiation were carried out, which showed high Cr(VI) reductions. Based on the results obtained in these tests, we concluded that the most suitable process for industrial application is photochemistry with ethanol under UV radiation. Although it

does not present the highest Cr(VI) reduction, it does not require catalyst separation processes and presents lower reagent costs, since ethanol is inexpensive, non-toxic and easy to purchase (MACHADO *et al.*, 2014).

As a result, we are working with a photochemical reduction reaction of Cr(VI) with ethanol, under UV radiation, in an acid medium, in order to build a reactor in semi-pilot scale and enable its application in the remediation of Cr(VI) found in the wastewater of electroplating industries. Initial studies were conducted in a batch reactor (0.15 L), before arriving at the semi-pilot scale. It was necessary to study the reaction behavior in an intermediate scale (2.8 L). So we designed and built a spiral shaped reactor (SSR), which allowed us to determine the optimal operating conditions through a design of experiments (MACHADO *et al.*, 2015).

The reactors that have been employed in wastewater decontamination can be classified according to the type of radiation used, that is artificial radiation (mercury vapor lamps, fluorescent, LED, etc.) or solar radiation, and as to how the wastewater circulates through the reactor, that is stirred vessel, current film or tubular. Among these, the solar tubular reactors have proven to be the most promising for application in the treatment of industrial wastewater, due to its configuration, treatment capacity and use of sunlight as a source of photons (MALATO *et al.*, 2002; DUARTE *et al.*, 2005; PEREIRA *et al.*, 2011).

In the present work, details will be presented on the design and construction of a tubular reactor (artificial radiation and sunlight) in semi-pilot scale to be used in the photochemical reduction of Cr(VI) found in the wastewater of electroplating industries.

2 Materials and Methods

Materials. Preliminary tests were carried out with potassium dichromate solutions (Fmaia, used as received) in distilled and deionized water (synthetic Cr(VI) solutions). The reactions were performed with absolute ethyl alcohol (Nuclear) and the pH was adjusted with sulfuric acid (Anidrol). Untreated wastewater containing Cr(VI) was collected directly from a storage tank in an electroplating plant. Information about the real wastewater is presented in Table 5.1. The Rhodamine B dye was used in tests to determine the residence time distribution.

Table 5. 1: Information about the real wastewater.

Information	Quantity
Hexavalent chromium	1,100 mg L^{-1}
Color	Orange
pH at 25°C	2.9
COD	< 5 mg L^{-1}
Total aluminum	3.1 mg L^{-1}
Total copper	179 mg L^{-1}
Total nickel	36.1 mg L^{-1}

Analytical methods. Absorbance measurements of samples containing Cr(VI) were taken in a UV-vis spectrophotometer (Varian Cary 100). Cr(VI) samples presented an absorption range between 315-400 nm with a maximum absorbance at a wavelength of 348 nm, which is in agreement with the literature (MOHAPATRA *et al.*, 2005; DAS *et al.*, 2006; NASRALLAH *et al.*, 2011). In addition, the incident radiation on the tubular reactor (artificial radiation and sunlight) was measured using a radiometer (Cole-Parmer Instruments Co.) with a sensing range between 354-376 nm, with center calibration at 365 nm.

2.1 Tubular reactor (artificial radiation and sunlight)

A tubular reactor (artificial radiation and sunlight) was designed and built in semi-pilot scale and can be seen in Figure 5.1. The reactor's structure was made of galvanized steel and was divided into three levels with a total size of: Height 1.60 m, Length 1.80 m and Depth 1.50 m.

The bottom level is fixed and was used as support for a centrifugal pump, storage tank, valve and hoses. The central part can be tilted at different angles. On this level, 10 borosilicate glass tubes (1.50 m length and 30 mm diameter) were placed and connected in series, resulting in a total volume of 11 L. The top level, which can be removed (sunlight), served as support for 16 mercury vapor lamps (Osram HQL 125 W) evenly distributed and positioned vertically in the reactor (artificial radiation).

The reactor is equipped with a storage tank with a maximum capacity of 20 L to treat the solution. A centrifugal pump Visograf with 27 W power and pumping capacity of 25 L min^{-1} was used to continuously feed the reactor. The volumetric flow rate was controlled by a Conaut rotameter with flow rates between 0.83 and 8.3 L min^{-1}, and a valve was connected between the pump and the rotameter. The medium temperature of the reaction was controlled by a K-type thermocouple, which was connected to a digital display and immersed in the solution in the

storage tank. The liquid samples were collected through a syringe-catheter system located in the storage tank.
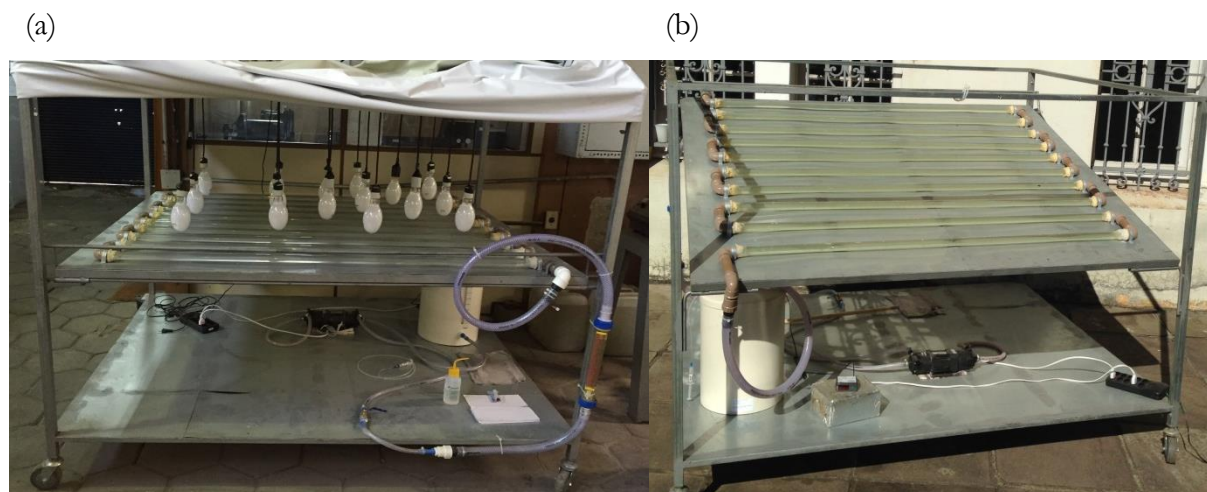
Figure 5. 1: Tubular reactor in operation (a) artificial radiation and (b) sunlight.

2.2 Description of photochemical reduction of Cr(VI) experiments

Experiments with synthetic solutions or real wastewater were carried out under artificial radiation or sunlight. When tests were conducted under sunlight, the reactor top (supporting the mercury vapor lamps) was removed and the central part (borosilicate glass tubes) was adjusted to an angle of 30°, which is equivalent to the latitude of the city of Porto Alegre, so as to ensure better use of incident radiation.

Experiments with synthetic Cr(VI) solution. At the beginning of the reaction, distilled water was added to the storage tank in order to fill the pipes, centrifugal pump and borosilicate glass tubes. Then the pump was turned on, the volumetric flow rate of the reactor was adjusted and the pump remained on for 30 minutes. During this time, the Cr(VI) solution was prepared in a 1000 mL volumetric flask and the solution concentration was calculated in order to obtain the desired initial Cr(VI) concentration of 20 mg L^{-1} for the reaction.

Subsequently, the synthetic solution was added into the storage tank and 30 minutes were waited. After 20 minutes, the initial pH of the solution was adjusted with sulfuric acid (pH = 2.0). Then a previously measured ethanol volume was added to the storage tank so as to obtain a known alcohol amount (5.0% v/v) and 5 minutes were waited. After this, a sample of the solution was collected and the lamps were connected, initiating the photochemical reduction reaction of Cr(VI). The reactions occurred in 1 hour and the progress of the photochemical

reduction reaction of Cr(VI) was monitored by collecting samples at fixed intervals (0, 5, 15, 30, 45 and 60 minutes). Subsequently, the samples were analyzed using a UV-vis spectrophotometer by measuring absorbance at a wavelength of 348 nm.

Experiments with real wastewater. Real wastewater containing hexavalent chromium (1100 mg L^{-1}) was used to conduct tests under the best operating conditions for the tubular reactor (previously determined using the synthetic solution). In these tests, the wastewater was added to the storage tank together with a known ethanol volume. Subsequently, the pump was turned on and the volumetric flow rate of the reactor was adjusted. After 15 minutes, a sample of the solution was collected, the pH was measured and the lamps were connected, initiating the reaction. These reactions occurred in 6 hours and samples were collected at fixed intervals (0, 15, 30, 60, 120, 180, 240, 300 e 360 minutes), which were subsequently diluted and analyzed.

3 Results and Discussion

3.1 Solar tubular reactor design

The tubular reactor was designed based on the hypotheses described below.

a) It was assumed that the mechanism of the photochemical reduction of Cr (VI) by alcohols is as described by Mytych et al. (2003). This mechanism (Equations (1)-(5)) consists of two-electron reduction of Cr(VI) giving rise to an aldehyde or ketone and a Cr(IV) species. The formation of the chromate(VI) ester is mostly assumed as a necessary condition for redox or photoredox reactions. Therefore, equation (2) is considered slow stage being used for the calculation of the reaction rate.

$$HCrO_4^- + ROH \leftrightarrow ROCrO_3^- + H_2O \tag{1}$$

$$ROCrO_3^- + hv \rightarrow Cr(IV) + \text{aldehyde/ketone} \tag{2}$$

$$Cr(IV) + Cr(VI) \rightarrow 2Cr(V) \tag{3}$$

$$3Cr(V) \rightarrow 2Cr(VI) + Cr(III) \tag{4}$$

and/or

Cr(V) + ROH → Cr(III) + aldehyde/ketone   (5)
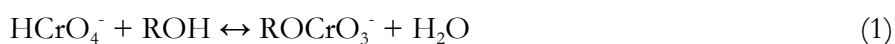
b) The best conditions to carry out the photochemical reduction reaction of Cr (VI) are those determined by MACHADO et al. (2014): initial Cr(VI) concentration of 20 mg L^{-1}, initial pH of 2.0, ethanol amount equal to 5.0% (v/v) and temperature of 30 °C. Under these conditions, the reaction is pseudo first order with respect to the chromium concentration, C_{Cr}, and it presented an experimental specific reaction rate, k_{exp}, of 0.056 min^{-1}.

c) The rate law also depends on the photons concentration in the reactor, C_p, which is constant due to the continuous irradiation medium. This concentration can be calculated knowing the UV irradiation intensity (I, W m^{-2}), the irradiated surface area (A_i, m^2) and the irradiated volume (V_i, L) of the batch reactor. Thus, being k the specific reaction rate:

$$-r_{Cr} = k \, C_{Cr} \, C_p$$

So, for a batch reactor:

$$-\frac{dN_{Cr}}{dt} = (-r_{Cr})V_i$$

Where N_{Cr} is the number of chromium moles present in the reactor and r_{Cr} is the chemical reaction rate, mol L^{-1} min^{-1}, calculated based on the irradiated volume, V_i. In addition, considering the reaction occurs in liquid phase and V is the volume occupied by the reaction mixture:

$$-\frac{V \, dC_{Cr}}{dt} = (k \, C_{Cr} \, C_p)V_i$$

Thus, $k_{exp} = k \, C_p \frac{V_i}{V}$

The irradiated volume fraction of the batch reactor was determined experimentally. For this, a radiometer was positioned under the glass reactor and increasing amounts of solution were added. It was observed that, although the irradiation intensity decreases with the liquid height, there is still incidence of photons in the reactor bottom, so $V_i/V = 1$. Thus, as $I = 58$ W m^{-2}, A_i $= 0.006$ m^2 e $V_i = 0.15$ L:

$$C_p = \frac{I A_i}{V_i} = 3.9 \times 10^{-4} \ ein \ L^{-1} \ min^{-1} \quad \text{and} \quad k = 144.7 \ L \ ein^{-1}$$

Consequently, the specific reaction rate expected for the tubular reactor would be calculated by:

$$k_T = 144.7 \ C_{p_T}$$

Where C_{p_T} is the photons concentration in the tubular reactor.

d) The irradiated surface area is equal to the lateral area of the glass tubes, so a tube diameter of 30 mm was considered appropriate for the tubular reactor design, since the tests with the batch reactor showed that this liquid height allows complete irradiation of the reactor volume. The electroplating industry (partner of this research group) generates approximately 21 L per day of wastewater, and thus the tubular reactor will be designed to operate with recycle.

e) In order to estimate C_{p_T}, the solar irradiation intensity in Porto Alegre was measured and found to be approximately 9 W m^{-2}. Thus, for a plug-flow reactor (PFR), considering an irradiated volume of 1 L and a diameter of 30 mm, the irradiated surface area (cylinder lateral area) will be 0.13 m^2, $C_{p_T} = 2.1 \times 10^{-4} \ ein \ L^{-1} \ min^{-1}$ and $k_T = 0.030 \ min^{-1}$.

f) Tubular reactor design equation, considering a pseudo first order kinetics and a constant volumetric flow rate:

$$V = -\frac{v_0}{k_T} \ln(1-x) \quad \text{or} \quad \tau = -\frac{1}{k_T} \ln(1-x) \quad \text{or} \quad x = 1 - e^{(-\tau k_T)}$$

Where V is the irradiated volume of the tubular reactor, v_o is the volumetric flow rate, x is the fraction converted to Cr(VI) and τ is the space time. Therefore, the space time should be 77 min to 90% conversion. The experimental conditions allowed volumetric flow rates between 0.83 and 8.3 L min^{-1}, whereas the most accurate central value was 4 L min^{-1}, and the calculated total volume of the reactor was 308 L (number of passes x volume of each pass). Considering the available space, the standard size of the borosilicate glass tubes available in the market and other conveniences, the tubular reactor was constructed with 10 tubes of 1.50 m length each, connected in series, resulting in a volume of 11 L per pass.

3.2 Preliminary tests

In order to define the best operating conditions of the tubular reactor, experiments were carried out with different volumetric flow rates and numbers of mercury vapor lamps (UV irradiation intensity). In these tests, a synthetic solution was used and the initial Cr(VI) concentration (20 mg L^{-1}), the initial pH of the solution (2.0), the alcohol amount (5.0% v/v) and temperature (approximately 30 °C) were kept constant. These parameters were established from the design of experiments, which were presented and discussed in other works (MACHADO *et al.*, 2014; MACHADO *et al.*, 2015). Additionally, tests were conducted to determine the reactor macromixing.

3.2.1 Analysis of the reactor macromixing

The tubular reactor flow was analyzed using a tracer injected by pulse (rhodamine B dye). The results showed that the reactor presented similar behavior to that of a plug flow reactor (PFR) for volumetric flow rates equal to or greater than 6.7 L min^{-1} (mean residence time of approximately 2 minutes). Below this volumetric flow rate, several deviations from the ideal flow were observed, such as the formation of air bubbles, stagnant regions, etc.

3.2.2 Determination of volumetric flow rate

The relationship between the volumetric flow rate and the photochemical reduction of Cr(VI) was studied (1.7, 3.3, 5.0, 6.7, 8.3 L min^{-1}), and the reduction achieved after 1 hour of operation was chosen as the response. The results are shown in Figure 5.2. Other parameters such as temperature, irradiation intensity, ethanol volume, chromium concentration and pH were kept constant in all these experiments.
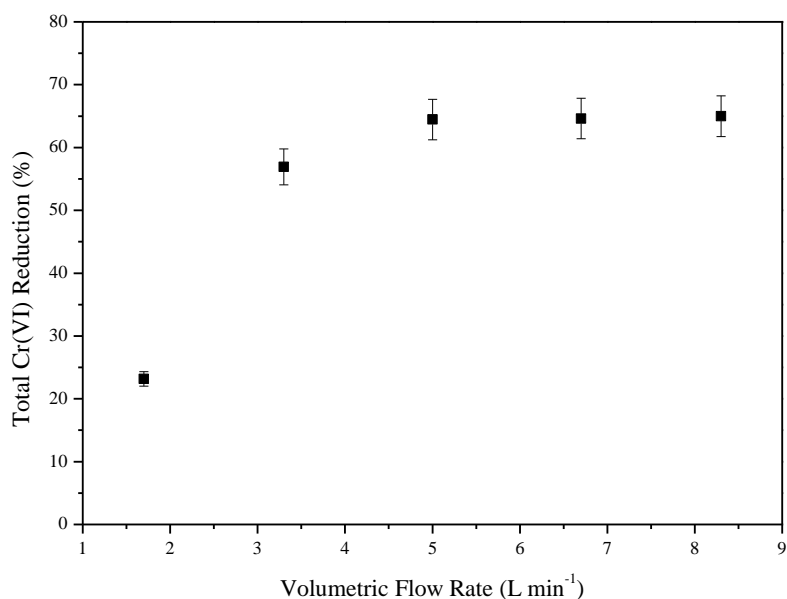
Figure 5. 2: Effect of the volumetric flow rate on total Cr(VI) reduction. ($C_{Cr(VI)}$ = 20 mg L^{-1}, pH = 2.0, $V_{ethanol}$ = 5.0% (v/v), T = 30 °C e I = 4.6 W m^{-2})

It can be observed in Figure 5.2 that as the volumetric flow rate increases, the total Cr(VI) reduction increases up to a volumetric flow rate of 5.0 L min^{-1}. Beyond this value, the total Cr(VI) reduction becomes constant at approximately 64.5%. Thus, the standard volumetric flow rate for the reactor was 6.7 L min^{-1}. These results are compatible with the analysis of the reactor macromixing, and the ideal behavior deviations are responsible for the lower reduction levels obtained at lower volumetric flow rates.

3.2.3 Influence of UV irradiation intensity

The reactor was illuminated with an increasing quantity of lamps, consequently increasing irradiation. The mean values obtained for incident UV radiation on the reactor and photochemical reduction of Cr(VI) achieved after 1 hour of reaction with different amounts of lamps are shown in Figure 5.3.
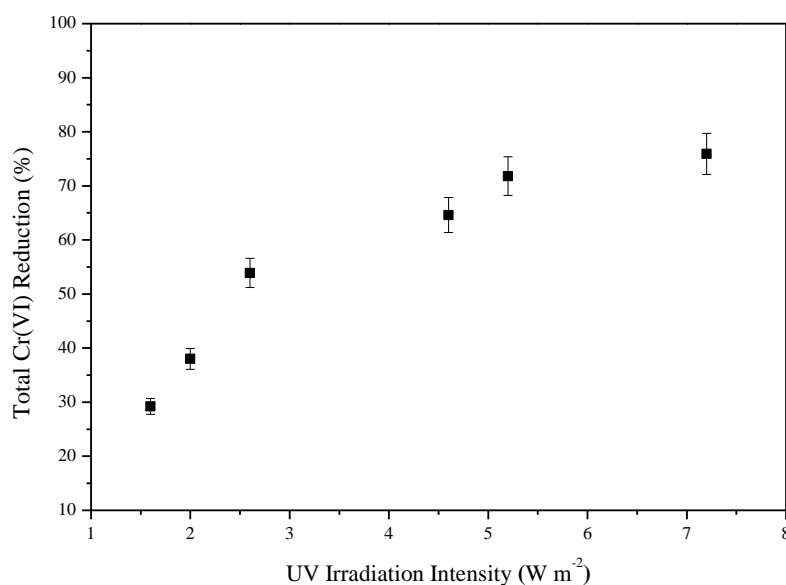
Figure 5. 3: Effect of UV irradiation intensity on total Cr(VI) reduction. ($C_{C_{r(VI)}}$ = 20 mg L^{-1}, pH = 2.0, V$_{ethanol}$ = 5.0% (v/v), T = 30 °C e υο = 6.7 L min^{-1})

As can be seen, the greater the photon amount supplied to the system, the higher the total Cr(VI) reduction with a tendency to form a plateau. Similar behaviors have been reported in the literature (KU and JUNG, 2001; CHAKRABARTI *et al.*, 2009). That is, there is an irradiation intensity (I_{lim}) for which the increased photon amount supplied to the system will not be accompanied by an increase in Cr(VI) reduction. In the tubular reactor, I_{lim} was not achieved due to limitations of the experimental apparatus.

However, tests carried out in a batch reactor showed that I_{lim} is achieved when the ratio of molar concentration of photons and the initial molar concentration of Cr(VI) ($\frac{C_p}{C_{Cr_0}}$) is equal to or greater than 36. For a UV irradiation intensity equal to 7.2 W m^{-2} (16 lamps), a total Cr(VI) reduction of 75.9% and ($\frac{C_p}{C_{Cr_0}}$) = 13, which is less than I_{lim}, was observed.

3.3 Tests with synthetic solution under sunlight

Experiments under sunlight were performed using the synthetic solution. These reactions occurred in 4 hours under the following experimental conditions: initial Cr(VI) concentration of 20 mg L^{-1}, initial pH of the solution equal to 2.0, ethanol volume equal to 5.0% (v/v), room temperature, volumetric flow rate equal to 6.7 L min^{-1}. The irradiation intensity of sunlight was determined using a digital radiometer and it was measured hourly during the experiment, at

different points of the reactor. UV radiation was considered the average of the measured values. Results are presented in Table 5.2.

Table 5. 2: Tests under sunlight: UV irradiation intensity and total Cr(VI) reduction.

Elapsed time (min)	Time	UV Irradiation Intensity (W m^{-2})	Total Cr(VI) Reduction (%)
0	10:00h	6.8	0.0
60	11:00h	10.4	87.3
120	12:00h	10.8	96.0
180	13:00h	7.9	96.5
240	14:00h	7.5	96.5

It is observed in Table 5.2 that at 1 hour of reaction there is a total Cr(VI) reduction of 87.3%. This was greater than the reduction obtained from the tests with artificial radiation (75.9%). The reason is the higher UV irradiation intensity from sunlight. Furthermore, it is observed that the total Cr(VI) reduction becomes practically constant after 2 hours of reaction, reaching a maximum of 96.5% reduction after 4 hours of reaction.

3.4 Tests with real wastewater

Tests were performed using real wastewater from the electroplating industry containing hexavalent chromium. These reactions occurred in 6 hours under the following experimental conditions: initial Cr(VI) concentration of 1100 mg L^{-1}, initial pH of the solution equal to 2.2, ethanol volume equal to 40% (v/v), room temperature, volumetric flow rate equal to 6.7 L min^{-1}. These experiments were carried out under artificial radiation and under sunlight. Results are presented in Figure 5.4.

Figure 5.4 indicates a total Cr(VI) reduction of 56.1% and 86.7% for reactions under artificial radiation and sunlight, respectively. The total Cr(VI) reduction was higher for the tests conducted under sunlight, which is compatible with the results obtained with the synthetic Cr(VI) solution (20 mg L^{-1}). Thus, the solar tubular reactor, which was designed and built, was effective when applied to real wastewater from the electroplating industry.
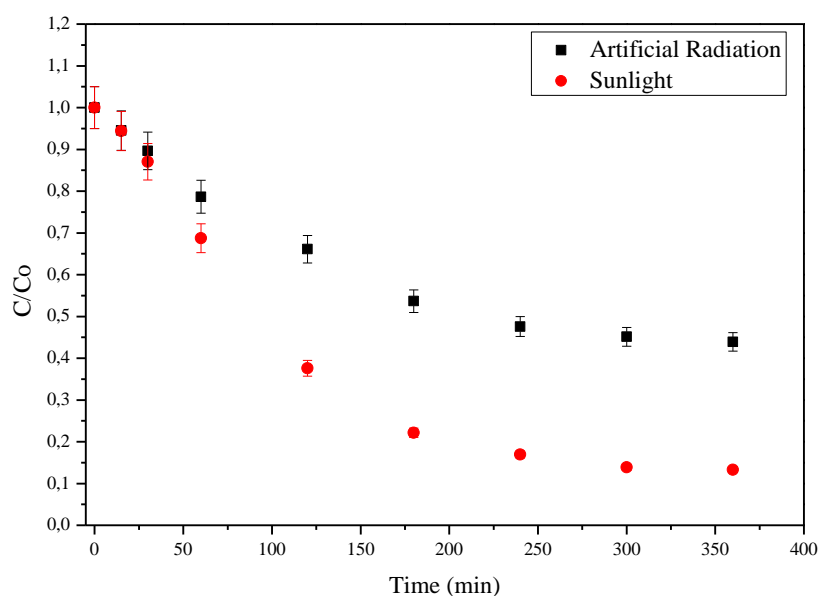
Figure 5. 4: Tests of photochemical reduction of Cr(VI) with real wastewater. ($C_{Cr(VI)}$ = 1100 mg L^{-1}, pH = 2.2, $V_{ethanol}$ = 40% (v/v), T = 30 ºC e υo = 6,7 L min^{-1})

3.5 Comparison between the studied reactors

The photonic efficiency, ξ, defined as the ratio of the reaction rate and the incident photon flux (MILLS and LEHUNTE, 1997; SERPONE and EMELINE, 2002; OHTANI, 2010; TOKODE *et al.*, 2012; BOUZID *et al.*, 2014) was calculated according to Bouzid et al. (2014) in order to compare the tubular reactor used in this work with other reactors studied by this research group: batch reactor (MACHADO *et al.*, 2014) and spiral shaped reactor (MACHADO *et al.*, 2015). The reactors are compared in Table 5.3.

Table 5. 3: Comparison between the batch, spiral shape (SSR) and tubular (TR) reactors.*

Specifications	Batch	SSR	TR (artificial radiation)	TR (sunlight)
Total Cr(VI) reduction (1h)	96.1%	46.0%	75.9%	87.3%
Reaction volume	0.15 L	2.8 L	21 L	21 L
Irradiated surface area	0.006 m^2	0.080 m^2	1.414 m^2	1.414 m^2
UV irradiation	58 W m^{-2}	25 W m^{-2}	7.2 W m^{-2}	8.6 W m^{-2} **
Photonic efficiency	**1.4%**	**2.5%**	**5.6%**	**5.5%**

* Experimental conditions: initial Cr(VI) concentration of 20 mg L^{-1}, initial pH of the solution equal to 2.0, ethanol volume equal to 5.0% (v/v) and room temperature (approximately 30 °C).
** Average radiation measured in the reaction time interval (1 hour).

Table 5.3 shows that the TR is more efficient than the SSR, which is more efficient than the batch reactor, supporting the industrial application of the TR. Additionally, the tubular reactor presented similar efficiency when used with either lamps or sunlight, enabling its use in both forms. However, the use of a solar tubular reactor minimizes the amount of electricity

required for the reaction, which not only reduces process costs, but also makes the technology more environmentally sustainable.

4 Conclusion

A tubular reactor (artificial radiation and sunlight) was designed and built in semi-pilot scale, and its application in treating wastewater from electroplating industries containing Cr(VI) was studied. The results obtained showed that the tubular reactor presented similar behavior to a PFR. In addition, tests conducted under sunlight showed a higher total Cr(VI) reduction than the tests with artificial radiation, using both synthetic Cr(VI) solution and real wastewater. The remediation of Cr(VI) present in the wastewater of electroplating industries was 86.7% at 6 hours of reaction under sunlight. The calculation of the photon efficiency showed that the TR is more efficient than the SSR, which is more efficient than the batch reactor. Thus, the tubular reactor, which was designed and built, was effective when applied to the treatment of real wastewater containing Cr(VI), using a photochemical reduction process. Furthermore, the use of a solar tubular reactor minimizes the electricity requirements, making it an environmentally sustainable technology.

5 Acknowledgements

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CAPÍTULO VI – CONSIDERAÇÕES FINAIS

Neste projeto de doutorado foi desenvolvida uma tecnologia mais sustentável para o tratamento de efluentes contendo cromo hexavalente, provenientes de uma indústria galvânica. Para isto, o trabalho foi dividido em três etapas, que serão descritas a seguir, juntamente com as conclusões obtidas a partir da análise dos resultados.

Na primeira etapa, foram investigadas as reações de fotocatálise heterogênea e fotoquímica com álcoois para redução de cromo hexavalente, usando um reator batelada. Nesta etapa pode-se concluir o que segue.

i) A redução fotocatalítica de Cr(VI) com TiO_2 e ZnO, sob radiação UV, é dependente da concentração de catalisador, do pH inicial da solução e da concentração inicial do substrato, para ambos catalisadores estudados. Ainda, a redução total de Cr(VI) aumenta com acréscimo da quantidade de catalisador e diminui com aumento do pH inicial da solução e da concentração inicial de Cr(VI). Além disso, foram alcançadas reduções totais de Cr(VI) de 66,5% e 56,7% para os catalisadores TiO_2 e ZnO, respectivamente, indicando que o catalisador TiO_2 é mais indicado para esta reação que o catalisador ZnO.

ii) As reduções fotoquímicas de Cr(VI) com etanol, sob radiação UV e visível, são dependentes do pH inicial da solução da concentração inicial de Cr(VI) e do volume de etanol. Para estas reações, a redução total de Cr(VI) diminui com o aumento do pH inicial da solução e da concentração inicial de Cr(VI) e aumenta com aumento do volume de etanol. Além disso, a fotoquímica com etanol no UV (96,10%) mostrou-se mais eficiente do que a fotoquímica com etanol no visível (48,07%).

iii) A redução fotocatalítica de Cr(VI) com TiO_2, na presença de etanol, sob radiação UV, é dependente da concentração de catalisador, do pH inicial da solução, da concentração inicial do

substrato e do volume de etanol. Neste caso, a redução total de Cr(VI) aumenta com acréscimo da quantidade de catalisador e do volume de etanol e diminui com aumento do pH inicial da solução e da concentração inicial de Cr(VI). Ainda, nestas reações observou-se uma redução de Cr(VI) de 92,97% maior do que a redução obtida nas reações fotocatalíticas com TiO_2 sob radiação UV (66,5%), evidenciando o efeito sinérgico entre a oxidação do etanol e a redução do Cr(VI).

Na segunda etapa, foram realizados experimentos com efluente industrial proveniente de uma indústria galvânica. Nesta etapa pode-se observar que os processos usados para remediação de cromo hexavalente apresentam altos valores de redução total de Cr(VI), possibilitando o seu uso para o tratamento de efluentes de indústrias galvânicas. Nestes experimentos, obteve-se uma redução total de Cr(VI) de 99,21% para a reação de redução fotocatalítica de Cr(VI) com TiO_2, na presença de etanol, sob radiação UV, enquanto que para as reações de redução fotoquímica de Cr(VI) com etanol sob radiação UV e visível, as reduções totais de Cr(VI) obtidas foram de 98,48% e 89,74%, respectivamente. Assim, dentre estes processos o mais indicado para aplicação industrial é a fotoquímica com etanol sob radiação UV, pois, apesar de não apresentar a maior redução total de Cr(VI), dispensa o uso de processos de separação do catalisador e apresenta menores custos com reagentes, sendo o etanol de baixo custo, não tóxico e de fácil aquisição.

Na terceira etapa, foram projetados e construídos reatores, em maior escala, para viabilizar a aplicação industrial do melhor processo de redução de Cr(VI), a fotoquímica com etanol. As principais realizações e conclusões desta fase passam a ser descritas.

i) Primeiramente, foi projetado e construído um reator contínuo em forma de espiral. Este reator apresentou um comportamento semelhante à de um reator tubular com escoamento em *plug flow* (PFR). As reações de redução fotoquímica com etanol, sob radiação UV, realizadas neste reator apresentaram comportamentos semelhantes as reações realizadas no reator batelada. Porém, comparando os ensaios realizados nestes reatores, nas melhores condições experimentais, o reator batelada apresentou maior redução total de Cr(VI) (96,1%) do que o reator contínuo espiral (46,0%). No entanto, o reator contínuo espiral mostrou-se mais eficiente do que o reator batelada, apresentando uma eficiência fotônica de 2,52% comparada a 1,43% para o reator batelada. Ainda, o reator projetado foi efetivo quando usado com efluente industrial, apresentado uma redução total de Cr(VI) de 51,8%, em 6 horas de reação, e sua configuração foi considerada suscetível para um *scale-up*.

ii) Na sequência, foi projetado e construído um reator contínuo tubular (radiação artificial e luz solar) em escala semi-piloto. Este reator apresentou um comportamento semelhante à de um reator tubular com escoamento em *plug flow* (PFR). Os ensaios realizados sob luz solar apresentaram uma redução total de Cr(VI) (87,3% e 86,7%) maior do que os ensaios realizados com radiação artificial (75,9% e 56,1%), tanto para a solução sintética de Cr(VI) como para o efluente industrial, respectivamente. A remediação de Cr(VI), presente em um efluente oriundo de uma indústria galvânica, foi de 86,7% em 6 horas de reação sob luz solar. O cálculo da eficiência fotônica mostrou que o reator tubular é mais eficiente (5,5%) que o reator contínuo espiral (2,5%), sendo este mais eficiente que o reator batelada (1,4%). Ainda, o reator tubular apresentou eficiência fotônica similar quando usado com lâmpadas (5,6%) ou luz solar (5,5%), podendo ser usado em ambas às formas. Assim, o reator tubular, projetado e construído, mostrou-se eficiente quando aplicado para o tratamento de efluente industrial contendo Cr(VI), pelo processo de redução fotoquímica. Além disso, o uso do reator tubular solar minimiza a quantidade de energia elétrica necessária para a reação, reduzindo não somente os custos do processo, como também se tornando uma tecnologia ambientalmente sustentável.

Em conclusão, os estudos realizados neste trabalho demostraram que a redução fotoquímica de Cr(VI) com etanol sob radiação UV foi o processo mais indicado para remediação do cromo hexavalente presente em efluentes de indústria galvânica, apresentando altas reduções de Cr(VI) e menores custos com o processo. Além disso, os reatores projetados e construídos foram mais eficientes que o reator batelada (reator tubular > reator espiral > reator batelada) e obtiveram resultados satisfatórios quando aplicados ao efluente industrial. Ainda, o uso do reator tubular solar apresentou alta redução de Cr(VI) presente no efluente industrial e mostrou-se mais eficiente que os demais reatores estudados, sendo esta configuração de reator mais suscetível para aplicação na indústria, devido ao seu menor consumo com energia elétrica, o que significa menos custos para empresa, e tornando-o mais sustentável ambientalmente. Enfim, este projeto de doutorado conseguiu alcançar seu objetivo principal: foi definida uma tecnologia mais sustentável para o tratamento de efluentes contendo cromo hexavalente, a redução fotoquímica com etanol; e o reator tubular, que foi projetado e construído em escala semi-piloto, usado sob luz solar viabilizou a aplicação deste processo para a remediação de cromo hexavalente presente nos efluentes provenientes de uma indústria galvânica.

CAPÍTULO VII – PERSPECTIVAS

O trabalho realizado permitiu o estudo da aplicação da redução fotoquímica de Cr(VI) com etanol, usando um reator tubular solar, para o tratamento de efluentes provenientes de uma indústria galvânica. Os resultados obtidos demonstraram que outros estudos podem ser realizados para otimizar o uso deste reator tubular solar, para o tratamento de efluentes, na indústria galvânica, entre eles destacam-se:

Projeto e utilização de concentradores solares, ou seja, superfícies refletoras moldadas no formato de involutas e posicionadas ao redor dos tubos cilíndricos de vidro borossilicato, visando um maior aproveitamento da luz solar.

Uso de um filtro prensa na saída do reator tubular solar, pois o cromo hevaxalente presente em altas concentrações no efluente é reduzido a cromo trivalente, sendo este precipitado durante o processo de tratamento. Além disso, deve-se verificar a pureza deste cromo trivalente, a fim de avaliar o destino do mesmo, aterro sanitário ou venda como matéria prima.

Avaliação ecotoxicológica do efluente tratado por este processo e destino do mesmo na indústria galvânica, como, por exemplo, retorno ao processo, onde o efluente tratado seria utilizado nas etapas de lavagem das peças.

Após feitas estas melhorias no processo, realizar uma análise econômica da aplicação deste tratamento de efluentes e compará-lo com o tratamento convencional usado atualmente pela empresa.

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APÊNDICE A – RESULTADOS NÃO APRESENTADOS NOS ARTIGOS

REDUÇÃO FOTOQUÍMICA DE CROMO HEXAVALENTE POR ÁLCOOIS SOB RADIAÇÃO UV

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RESUMO – No presente trabalho se estuda a redução fotoquímica de Cr(VI) por álcoois, metanol, etanol e propan-2-ol, sob radiação UV. Os experimentos foram realizados em um reator batelada de vidro com controle de temperatura e agitação, sob radiação UV. Primeiramente, avaliou-se a influência do pH inicial da solução, do volume de álcool e da concentração inicial de cromo hexavalente na redução total de Cr(VI). Os resultados obtidos permitiram concluir que a redução total de Cr(VI) é dependente da natureza do álcool, diminuindo na seguinte ordem: propan-2-ol > etanol >> metanol. Por fim, realizaram-se experimentos com um efluente industrial, originado em uma indústria de galvanoplastia, tendo sido observados altos valores de redução total de Cr(VI).

1 Introdução

O cromo hexavalente é tóxico para a maioria dos organismos, sendo carcinogênico e mutagênico para os animais, podendo causar irritação e corrosão na pele humana. Os metais pesados encontrados no ambiente originam-se, principalmente, da descarga inadequada de efluentes industriais (KU e JUNG, 2001), estando as empresas de curtimento de couro, tintas, corantes, materiais fotográficos, galvanoplastia, mineração, metalúrgicas e de eletrônicos, entre as possíveis fontes de cromo (SCHRANK *et al.*, 2002; MOHAPATRA *et al.*, 2005; CHAKRABARTI *et al.*, 2009). Dentre estas, a indústria de galvanização é caracterizada pelo excessivo consumo de água e energia e pela grande geração de efluentes líquidos contendo metais pesados, tais como, cobre, níquel e cromo. Estes efluentes provêm, principalmente, do descarte das águas de enxágue das peças retiradas dos banhos eletroquímicos.

O cromo ocorre na natureza em dois estados de oxidação, Cr^{+3} e Cr^{+6} ou Cr(III) e Cr(VI). O Cr(VI) é altamente solúvel, o que possibilita a contaminação de lençóis freáticos e outras fontes de água potável, sendo mais estável que o trivalente. A forma hexavalente do cromo é 100 vezes mais tóxica que a trivalente (MOHAPATRA *et al.*, 2005; DAS *et al.*, 2006; XU *et al.*, 2006; YANG e CHAN, 2009; CHAKRABARTI *et al.*, 2009). Por outro lado, o cromo trivalente é facilmente precipitado e não apresenta toxicidade, sendo considerado um elemento essencial para o metabolismo humano, em níveis controlados (KIM *et al.*, 2002; MOHAPATRA *et al.*, 2005).

O tratamento convencional para águas residuais contendo Cr(VI) é a redução com sulfito de sódio ou metabissulfito. Este método, no entanto, apresenta alguns problemas: exige um excesso de produtos químicos para garantir a conversão completa do Cr(VI) e ocorre a formação de lama ou a liberação de dióxido de enxofre. Desta maneira, estudos vêm sendo direcionados ao desenvolvimento de tecnologias mais limpas para remediação de efluentes contendo cromo, entre eles, a fotoquímica com álcoois.

A absorção da luz ultravioleta ou visível pela matéria pode promover elétrons para níveis de energia mais altos, gerando espécies eletronicamente excitadas. Esta excitação eletrônica pode ocasionar mudanças químicas, como o desaparecimento de corantes, a fotossíntese em plantas, a degradação/redução de moléculas (WARDLE, 2009). A redução fotoquímica de Cr(VI), na presença de compostos orgânicos e sob radiação UV ou visível, tem sido estudada. Na literatura são encontrados alguns trabalhos sobre a redução fotoquímica de Cr(VI) por álcoois (MYTYCH

et al., 2003), fenol e seus derivados halogenados (MYTYCH e STASICKA, 2004) e glicerol (YURKOW *et al.*, 2002). Nestes trabalhos, não há um estudo sistemático e comparativo, que analise o efeito de cada parâmetro da reação, bem como a interação entre eles. Além disso, não foi encontrado nenhum estudo sobre a aplicação de processos fotoquímicos para remediação de Cr(VI) presente em um efluente de uma indústria Galvânica.

Assim, no presente trabalho foi investigada a redução fotoquímica de cromo hexavalente por álcoois, sob radiação UV. Para avaliar a redução de Cr(VI) por fotoquímica com metanol, etanol e propan-2-ol, foram utilizados planejamentos experimentais que investigaram a influência do pH inicial da solução, do volume de álcool e da concentração inicial de cromo hexavalente na redução total de Cr(VI). Além disso, realizaram-se experimentos com um efluente industrial, originado em uma indústria Galvânica.

2 Materiais e Métodos

Materiais: Dicromato de potássio (Fmaia) foi usado como recebido e água destilada e deionizada foi utilizada para preparar as soluções. Os álcoois etílico absoluto P.A. (Nuclear), metílico P.A. (Química Moderna) e isopropílico P.A. (Dinâmica) foram utilizados nas reações de redução fotoquímica de Cr(VI).

2.1 Experimentos de Redução Fotoquímica

Os ensaios foram realizados em um reator batelada encamisado, irradiado com uma lâmpada de vapor de mercúrio (Philips HPL-N 125 Watt) modificada para emitir na região do UV, pela remoção da camada interna de fósforo do bulbo. A agitação do meio reacional foi mantida por um agitador magnético e a temperatura foi monitorada por um termopar do tipo K acoplado a um mostrador digital. A câmara de irradiação é constituída por uma caixa de madeira revestida internamente com papel alumínio e um sistema seringa-cateter foi utilizado para coleta de amostras líquidas em tempos determinados. A radiação da lâmpada foi ajustada e medida no início de cada ensaio através de um radiômetro (Cole-Parmer Instrument, Radiometer Series 9811). Uma representação esquemática do reator utilizado é apresentada na Figura A.1.
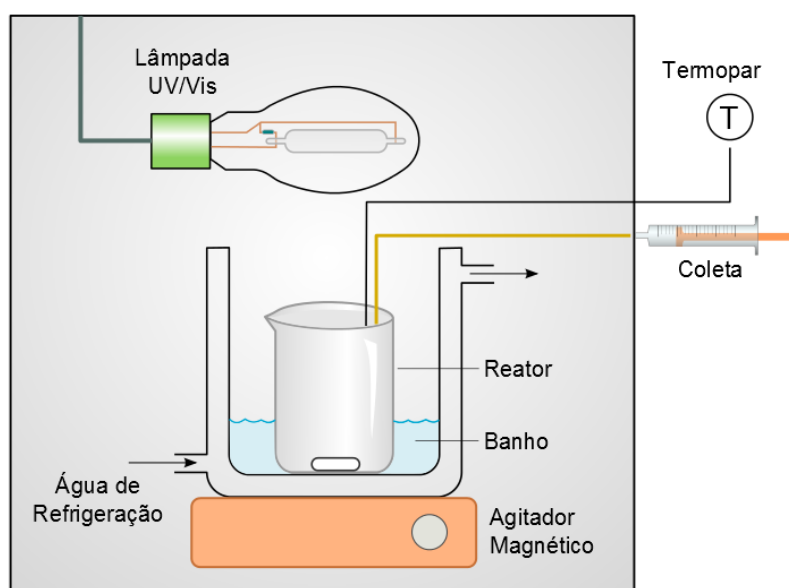
Figura A. 1: Figura esquemática do reator usado nos experimentos de fotoquímica.

A solução sintética de cromo hexavalente foi preparada a partir do dicromato de potássio ($K_2Cr_2O_7$), sendo mantida sob agitação magnética vigorosa por, aproximadamente, 1 h. Para as reações de redução fotoquímica com álcoois, um volume conhecido de álcool foi adicionado a 150 mL de solução aquosa de Cr(VI) e o pH inicial da solução foi ajustado. Estas reações ocorreram em 1 h, sendo o progresso da reação de redução fotoquímica de Cr(VI) acompanhado através de coletas de amostras em tempo determinados (0, 15, 30, 45 e 60 minuntos). Após as amostras foram analisadas no espectrofotômetro (Varian, Cary 100) através de medidas de absorbância, no comprimento de onda de 348 nm (MOHAPATRA *et al.*, 2005; DAS *et al.*, 2006; NASRALLAH *et al.*, 2011). As absorbâncias foram relacionadas com a concentração de Cr(VI) por uma curva de calibração, de acordo com a Lei de Lambert-Beer.

Nos ensaios realizados com efluente industrial diluído foi utilizada uma solução de cromo hexavalente, originada em uma indústria Galvânica, a qual foi diluída em água destilada e deionizada, a fim de obter a mesma concentração de cromo da melhor condição dos planejamentos de experimentos. Também foram realizados experimentos com efluente industrial na sua concentração original (1100 mg L^{-1}). Estes testes seguiram a mesma metodologia utilizada nas reações com solução sintética de Cr(VI).

2.2 Metodologia da Superfície de Resposta

O modelo estatístico de um planejamento composto central circunscrito (CCC) foi utilizado com o objetivo de otimizar o volume de álcool, o pH inicial da solução e a concentração

inicial de Cr(VI), para as reações de redução fotoquímica de Cr(VI) sob radiação UV com metanol, etanol e propan-2-ol. Este modelo consiste em um planejamento fatorial completo com 2^n (n = 3) experimentos, 6 pontos estrelas e 3 pontos centrais, dando um total de 17 experimentos. A quantidade de álcool foi variada entre 0,3% e 6,2%, o pH inicial da solução entre 1,5 e 4,0 e a concentração inicial de Cr(VI) entre 13 mg L^{-1} e 47 mg L^{-1}.

O fator de resposta, para todos os planejamentos de experimentos, foi definido como sendo a redução total de Cr(VI), após 1 h de reação. Os dados foram analisados usando o software Statistica 10, onde foi obtido o polinômio associado ao sistema de reações de redução total de Cr(VI) e as superfícies de resposta, para cada planejamento experimental. O modelo foi validado estatisticamente com o mesmo software usando ANOVA (nível de confiança de 95%).

3 Resultados e Discussão

3.1 Reações de Redução Fotoquímica de Cr(VI) com Álcoois

Com o objetivo de avaliar a influência da natureza do álcool sobre a redução fotoquímica de cromo hexavalente, bem como comparar as reações de redução fotoquímica de Cr(VI) com diferentes álcoois, foram realizados experimentos de redução fotoquímica de Cr(VI) com metanol, etanol e propan-2-ol, sob radiação UV. Nestas reações as variáveis estudadas foram o pH inicial da solução, a concentração inicial de Cr(VI) e o volume de álcool. Na Tabela A.1 são apresentados os experimentos de redução fotoquímica de Cr(VI) com metanol, etanol e propano-2-ol, sob radiação UV. Os números entre parênteses representam as variáveis codificadas e o fator de resposta (Y) foi definido como a percentagem de redução total de Cr(VI) após 1 h de reação.

Os polinômios (Equação (1)-(3)) obtidos a partir da análise multivariada apresentaram um coeficiente de correlação (R^2) de 0,9913, 0,9431 e 0,9413 para as reações com metanol, etanol e propan-2-ol, respectivamente, indicando um bom ajuste dos dados experimentais aos modelos estatísticos. O pH inicial da solução e o volume de álcool são as principais variáveis que afetam as reações com etanol e propan-2-ol, com interações quadráticas e lineares, enquanto que, para as reações com metanol, o volume de álcool é a principal variável que afeta estas reações. Nas equações polinomiais, os valores entre parênteses representam o desvio padrão para cada

coeficiente e x, y e z representam os valores codificados de pH inicial da solução, concentração inicial de Cr(VI) e volume de álcool, respectivamente:

$$Y_{Metanol}\ (\%) = 40,1(\pm0,7) - 13,9x\ (\pm0,6) - 4,3y\ (\pm0,6) + 17,2z\ (\pm0,6) - 2,9z^2\ (\pm0,6) - 6,2x.z\ (\pm0,8) \tag{1}$$

$$Y_{Etanol}\ (\%) = 72,3(\pm3,8) - 25,3x\ (\pm2,6) - 11,5x^2\ (\pm2,6) - 5,8y\ (\pm2,6) + 17,1z\ (\pm2,6) - 9,0z^2\ (\pm2,6) - 11,5x.z\ (\pm3,4) \tag{2}$$

$$Y_{Propan-2-ol}\ (\%) = 72,7(\pm4,5) - 23,7x\ (\pm2,8) - 9,4x^2\ (\pm2,9) - 9,6y\ (\pm2,8) + 20,5z\ (\pm2,8) - 9,1z^2\ (\pm2,9) - 9,3x.z\ (\pm3,6) \tag{3}$$

Tabela A. 1: Resultados dos planejamentos experimentais para reação de redução fotoquímica de Cr(VI) com álcoois sob radiação UV.

Ensaios	pH inicial da solução	Concentração inicial de Cr(VI) (mg L^{-1})	Volume de álcool (%) (v/v)	Redução Total de Cr(VI) (%) ($Y_{exp.}$) Metanol / Etanol / Propan-2-ol		
1	2(-1)	20(-1)	1,5(-1)	31,5	55,5	57,3
2	3,5(1)	20(-1)	1,5(-1)	13,5	28,9	29,9
3	2(-1)	40(1)	1,5(-1)	21,5	44,2	40,3
4	3,5(1)	40(1)	1,5(-1)	10,2	19,3	16,8
5	2(-1)	20(-1)	5(1)	79,4	96,1	98,6
6	3,5(1)	20(-1)	5(1)	41,0	34,8	55,1
7	2(-1)	40(1)	5(1)	67,6	94,9	98,2
8	3,5(1)	40(1)	5(1)	27,3	12,7	16,7
9	1,5(-1,68)	30(0)	3,25(0)	63,8	89,5	93,9
10	4(1,68)	30(0)	3,25(0)	15,5	0,0	5,7
11	2,75(0)	13(-1,68)	3,25(0)	46,3	86,0	89,9
12	2,75(0)	47(1,68)	3,25(0)	34,1	65,0	53,2
13	2,75(0)	30(0)	0,31(-1,68)	4,5	9,3	4,2
14	2,75(0)	30(0)	6,2(1,68)	61,8	94,5	96,8
15	2,75(0)	30(0)	3,25(0)	43,0	71,4	73,7
16	2,75(0)	30(0)	3,25(0)	39,1	74,0	76,2
17	2,75(0)	30(0)	3,25(0)	43,1	71,6	76,8

Nas Equações (1)-(3), pode-se observar, para todas as reações fotoquímicas (metanol, etanol e propan-2-ol), que os coeficientes referentes aos efeitos lineares do pH e da concentração de Cr(VI) apresentaram valores negativos, indicando que quanto menor for o pH inicial da solução e a concentração inicial de Cr(VI), maior será a redução total de Cr(VI), enquanto que o valor do coeficiente referente ao efeito linear do volume de álcool foi positivo, logo quanto maior for o volume de álcool, maior será a redução total de Cr(VI). Este comportamento pode ser

observado na Tabela A.1, onde os ensaios 5, para as reações com metanol, etanol e propan-2-ol, com menores valores de pH inicial da solução e concentração inicial de Cr(VI) e maior valor de volume de álcool, apresentaram as maiores reduções totais de Cr(VI) de 79,4%, 96,1% e 98,6%, respectivamente. Maiores informações a respeito das reações de redução fotoquímica de Cr(VI) com etanol sob radiação UV podem ser encontradas no trabalho de Machado et al. (2014).

Mytych et al. (2003) estudaram a redução fotoquímica de Cr(VI) mediada por álcoois alifáticos e observaram que a taxa da reação é dependente da natureza do álcool diminuindo na seguinte ordem: butan-1-ol > butan-2-ol >> propan-2-ol > etanol >> metanol > 2-metil-propan-2-ol. Comportamento semelhante foi verificado neste trabalho, onde os resultados das reações de redução fotoquímica de Cr(VI) com metanol, etanol e propan-2-ol, sob radiação UV, nas condições ótimas dos planejamentos experimentais, estão apresentados na Figura A.2. Como pode ser observado nesta Figura, o álcool isopropílico apresentou uma redução total de Cr(VI) de 98,6%, enquanto que o álcool etílico apresentou uma redução de 96,1%. No entanto, considerando o erro absoluto dos experimentos, os valores de redução total para o etanol e o propan-2-ol são iguais.
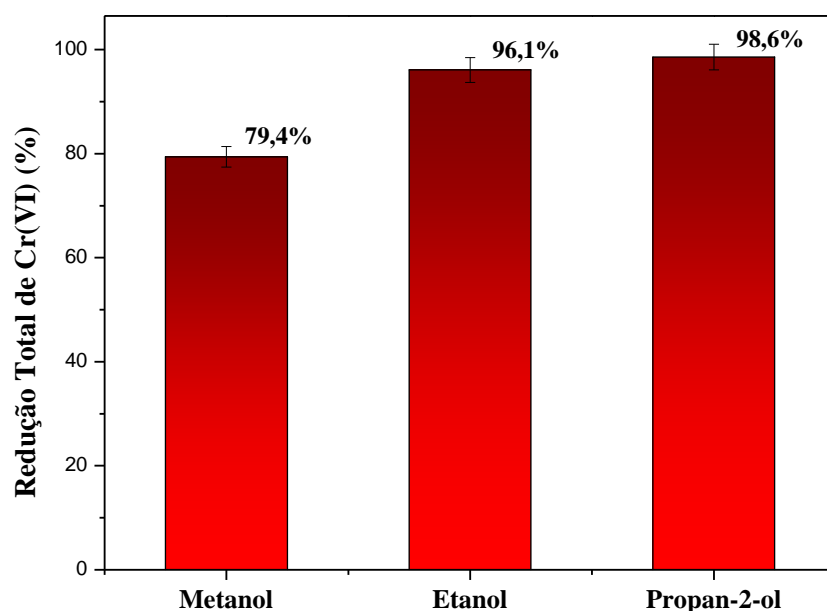

Figura A. 2: Comparação das reações de redução fotoquímica de Cr(VI) com diferentes álcoois, sob radiação UV ($C_{Cr(VI)}$ = 20 mg L^{-1}, $V_{álcool}$ = 5,0% (v/v), T = 30 °C, pH = 2,0 e 5,8 mW cm^{-2}).

3.2 Ensaios com Efluente Industrial

Com intuito de verificar a aplicação da fotoquímica com álcoois para remediação do cromo hexavalente presente no efluente de uma indústria Galvânica foram realizados ensaios de redução total de Cr(VI) com o efluente na sua concentração original (1100 mg L^{-1}). Para isto, utilizou-se um volume de álcool de 40% (v/v) e um tempo de reação de 6 horas. Os resultados são apresentados na Tabela A.2.

Tabela A. 2: Ensaios de redução total de Cr(VI) com efluente industrial na sua concentração original.

Reações	Condições Experimentais	Redução Total de Cr(VI) (%)
Fotoquímica Etanol	$C_{Cr(VI)} = 1100$ mg L^{-1}, pH = 2,0, $V_{etanol} = 40\%$ e 5,8 mW cm^{-2} 6 horas de reação	98,48
Fotoquímica Metanol	$C_{Cr(VI)} = 1100$ mg L^{-1}, pH = 2,0, $V_{metanol} = 40\%$ e 5,8 mW cm^{-2} 6 horas de reação	68,88
Fotoquímica Propan-2-ol	$C_{Cr(VI)} = 1100$ mg L^{-1}, pH = 2,0, $V_{propan-2-ol} = 40\%$ e 5,8 mW cm^{-2} 6 horas de reação	98,97

Pode-se observar, na Tabela A.2, que o processo de redução fotoquímica de Cr(VI) com isopropanol obteve uma redução total de Cr(VI) igual à obtida para fotoquímica com etanol, possibilitando o uso destes processos para o tratamento de efluentes de indústrias Galvânicas. No entanto, dentre os álcoois estudados, o etanol foi considerado o mais suscetível para aplicação industrial, devido ao seu baixo custo, não toxicidade e facilidade de aquisição (MACHADO *et al.*, 2014).

4 Conclusões

Os resultados obtidos permitiram concluir que as reações de redução fotoquímica de Cr(VI) com álcoois, sob radiação UV, são dependentes do pH inicial da solução, da concentração inicial de Cr(VI) e do volume de álcool. Para estas reações, a redução total de Cr(VI) diminui com o aumento do pH inicial da solução e da concentração inicial de Cr(VI) e aumenta com aumento do volume de álcool. Além disso, a redução total de Cr(VI) mostrou-se dependente da natureza do álcool, diminuindo na seguinte ordem: propan-2-ol > etanol >> metanol. Ainda, os resultados obtidos para os experimentos realizados com efluente industrial, originado em uma indústria

Galvânica, mostraram que, dentre os álcoois estudados, o etanol é o mais suscetível para aplicação industrial, devido ao seu baixo custo, não toxicidade e facilidade de aquisição.

5 Agradecimentos

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APÊNDICE B – PRODUTOS GERADOS DA TESE DE DOUTORADO

Os produtos associados a esta tese de doutorado foram:

- Apresentação de trabalho intitulado "Redução fotocatalítica de cromo hexavalente em solução aquosa sob radiação visível" no XIX COBEQ, Congresso Brasileiro de Engenharia Química, 2012, Búzio-RJ, Brasil;

- Apresentação de trabalho intitulado "Aplicação em um efluente industrial da redução de cromo hexavalente: fotoquímica com etanol e fotocatálise com TiO_2" no 7º EPOA e 1º CIPOA, Encontro sobre Aplicações Ambientais de Processos Oxidativos Avançados e Congresso Iberoamericano de Processos Oxidativos Avançados, 2013, Recife-PE, Brasil;

- Apresentação de trabalho intitulado "Aplicação em um efluente industrial da redução fotocatalítica de cromo hexavalente usando TiO_2 e ZnO" no 7º EPOA e 1º CIPOA, Encontro sobre Aplicações Ambientais de Processos Oxidativos Avançados e Congresso Iberoamericano de Processos Oxidativos Avançados, 2013, Recife-PE, Brasil;

- Apresentação de trabalho intitulado "Application in wastewater remediation of reduction of hexavalent chromium using photocatalysis and photochemistry" no SPEA8, 8th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications, 2014, Thessaloniki, Grécia;

- Apresentação de trabalho intitulado "Redução fotoquímica de cromo hexavalente por álcoois sob radiação UV" no XX COBEQ, Congresso Brasileiro de Engenharia Química, 2014, Florianópolis-SC, Brasil;

- Co-orientações de Iniciação Científica de alunos de graduação em Engenharia Química da Universidade Federal do Rio Grande do Sul (Simone Olszevski, Natália Matte, Jéssica Theisen e Pedro Gama);

- Co-orientação de um Trabalho de Conclusão de Curso (Graduação em Engenharia Química) realizado por Camila Silva Ribeiro e intitulado "Projeto e construção de um reator

fotoquímico e sua aplicação na redução de cromo hexavalente" na Universidade Federal do Rio Grande do Sul, 2013;

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- Artigo Submetido em Journal A1: Machado, Tiele Caprioli; Lansarin, Marla Azário. Proposal for Environmentally Sustainable Technology for the Treatment of Wastewater Containing Cr(VI): Design and Construction of a Solar Tubular Reactor. Chemical Engineering Research and Design.