Journal of Environmental Management 217 (2018) 555–564

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

# Strategies to reduce mass and photons transfer limitations in heterogeneous photocatalytic processes: Hexavalent chromium reduction studies

Belisa A. Marinho [a, b], Raquel O. Cristóvão [a, *], Ridha Djellabi [a], Ana Caseiro [a], Sandra M. Miranda [a], José M. Loureiro [a], Rui A.R. Boaventura [a], Madalena M. Dias [a], José Carlos B. Lopes [a], Vítor J.P. Vilar [a, **]

[a] Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua do Dr. Roberto Frias, 4200-465, Porto, Portugal
[b] CAPES Foundation, Ministry of Education of Brazil, Brasília, DF 70040-020, Brazil

ARTICLE INFO

*Article history:*
Received 11 December 2017
Received in revised form
28 March 2018
Accepted 1 April 2018

*Keywords:*
Heterogeneous photocatalysis
Process intensification
Hexavalent chromium reduction
NETmix photoreactor
Microscale illumination

ABSTRACT

The current work presents different approaches to overcome mass and photon transfer limitations in heterogeneous photocatalytic processes applied to the reduction of hexavalent chromium to its trivalent form in the presence of a sacrificial agent. Two reactor designs were tested, a monolithic tubular photoreactor (MTP) and a micro-meso-structured photoreactor (NETmix), both presenting a high catalyst surface area per reaction liquid volume. In order to reduce photon transfer limitations, the tubular photoreactor was packed with transparent cellulose acetate monolithic structures (CAM) coated with the catalyst by a dip-coating method. For the NETmix reactor, a thin film of photocatalyst was uniformly deposited on the front glass slab (GS) or on the network of channels and chambers imprinted in the back stainless steel slab (SSS) using a spray system. The reaction rate for the NETmix photoreactor was evaluated for two illumination sources, solar light or UVA-LEDs, using the NETmix with the front glass slab or/and back stainless steel slab coated with $TiO_2$-P25. The reusability of the photocatalytic films on the NETmix walls was also evaluated for three consecutive cycles using fresh Cr(VI) solutions. The catalyst reactivity in combination with the NETmix-SSS photoreactor is almost 70 times superior to one obtained with the MTP.



## 1. Introduction

Hexavalent chromium (Cr(VI)) is a priority contaminant in wastewater discharged from chromate, mining, tanning, manufacturing and electroplating industries (Yu et al., 2015). On the other hand, trivalent chromium (Cr(III)) is less toxic and, at low concentrations, serves as a nutrient for humans (Meng et al., 2017). Photocatalytic technologies for Cr(VI) reduction to Cr(III) have received considerable attention due to their mild reaction conditions, use of solar energy and apparent purification effects (Mohamed et al., 2016; Zhang et al., 2011, 2012). Catalysts have been used in both slurry and immobilized forms. However, for any real-world device in large applications, catalysts immobilized onto rigid inert supports are ideal in order to avoid a post-treatment step for its recovery, which can become costly. Nevertheless, these configurations also have their own problems: the catalyst surface accessibility to the reactants, pollutants and photons, due to the high diffusional length. Process intensification of heterogeneous photocatalysis through the use of innovative reactor configurations can be a good approach to enhance mass and photons transfer (Li et al., 2011). The monolithic photoreactor is known to provide a high catalyst surface-to-volume ratio, improving the contact between the photocatalyst and the contaminant(s)/reactant(s) (da Costa Filho et al., 2017), as well as a more efficient exposure of the photocatalyst to the radiation (Marinho et al., 2017a). In addition to the large number of walls used for photocatalyst deposition, thin walled monolithic structures made of cellulose acetate are

* Corresponding author.
** Corresponding author.
*E-mail addresses:* raquel.cristovao@fe.up.pt (R.O. Cristóvão), vilar@fe.up.pt (V.J.P. Vilar).

https://doi.org/10.1016/j.jenvman.2018.04.003
0301-4797/

**Nomenclature**

| | |
|---|---|
| λ | Wavelength (nm) |
| $E_{CB}$ | Energy level of conduction band edge (V) |
| $E_g$ | Energy of band gap (V) |
| $E_{VB}$ | Energy level of valence band edge (V) |
| $k$ | Kinetic constant ($min^{-1}$, L $kJ^{-1}$) |
| $Q_{UV,n}$ | Accumulated UV energy per liquid volume (kJ $L^{-1}$) |
| $\phi$ | Quantum yield |
| BSI | Back-side illumination |
| CA | Cellulose acetate |
| CAM | Cellulose acetate monolithic structures |
| CPC | Compound parabolic collector |
| FSI | Front-side illumination |
| GS | Glass slab |
| LEDs | Light-emitting diode |
| MTP | Monolithic tubular photoreactor |
| PEG | Polyethyleneglycol 20000 |
| $pH_{ZPC}$ | pH of zero point of charge |
| SSS | Stainless steel slab |
| SUNTEST | Solar radiation simulator |
| TNBT | Tetra-n-butyl orthotitanate |
| UV | Ultraviolet |
| UVA | Ultraviolet A |
| Vis | Visible |

potential supports, due to their UV-transparency, lightweight and low cost (Portela et al., 2007). However, the quantity of light flux that goes through the monolithic structure walls depends on the thickness of the photocatalyst coating (Van Gerven et al., 2007) and on the monolithic structure geometry (Marinho et al., 2017a). In systems with photocatalysts films, two irradiation mechanisms can be encountered: back-side illumination (BSI) and front-side illumination (FSI). In the BSI, the incident irradiation and the catalyst film are on opposite sides of the support structure. On the other hand, in the FSI mechanism both incident irradiation and catalyst film are at the same side of the support structure (Marinho et al., 2017a). Microstructured reactors are known for their unique features such as fast mixing and short molecular diffusion distance, laminar flow and large surface-to-volume ratio, allowing high mass transfer and reduced photon transport limitations. Therefore, microreactors are expected to exhibit some characteristics that favor photoreactions, namely their higher spatial homogeneity of irradiance and better light dissemination through the entire reactor depth, leading to high reaction rates (Padoin and Soares, 2017; Gorges et al., 2004). Our research group has been successfully using an innovative micro-meso-structured photoreactor (NETmix) developed by Lopes et al. (2013), for environmental remediation (da Costa Filho et al., 2017; Marinho et al., 2017a). However, a deeper study to evaluate the influence of the irradiation source and the illumination mechanism is still necessary, as well as the comparison with the classical tubular reactor.

Therefore, the main goal of this work is the process intensification of heterogeneous photocatalysis using a micro-meso-structured photoreactor (NETmix), towards Cr(VI) reduction, in order to reduce mass and photon transfer limitations. The comparison with a monolithic tubular photoreactor (MTP) packed with cellulose acetate monoliths (CAM) as catalyst support was also performed. Regarding the NETmix reactor, several parameters were also optimized, namely the photocatalyst type and dosage, the irradiation source (sunlight or UVA-LEDs light), as well as two different catalyst supports: the front glass slab (BSI mechanism) or the back stainless steel slab where the network of channels and chambers are imprinted (FSI mechanism). Finally, the reuse of the photocatalytic films was evaluated for the different support configurations.

## 2. Materials and methods

### 2.1. Chemicals

Cr(VI) solutions were prepared from potassium dichromate (Merck, purity 99.9%). 1,5-diphenylcarbazide (Merck, purity 98%) was used as colorimetric reagent to determine Cr(VI) concentration. $TiO_2$ Degussa P25 (Evonik), $TiO_2$ PC105 (Cristal ACTiV), $TiO_2$ PC500 (Cristal ACTiV), CdS (Sigma-Aldrich), $WO_3$ (Sigma-Aldrich), ZnO (Sigma-Aldrich) and $Fe_2O_3$ (Sigma-Aldrich) powders were used as delivered, without further modification or purification. Tetra-n-butyl orthotitanate (Merck, purity 98%) and polyethylene glycol 20000 (Merck) were used to prepare CdS and $WO_3$ suspensions. For the others catalysts suspensions preparation it was used TritonTM X-100 (t-Oct-$C_6H_4$-$(OCH_2CH_2)_n$OH, $n = 9–10$, Sigma–Aldrich). Cellulose acetate monolithic (CAM) structures (Wacotech GmbH & Co. KG.) were used as catalyst support. An alkaline detergent solution (Derquim LM 01, Panreac Química, S.A.U.) was used for cleaning the inert surfaces used for catalyst deposition. 0.1 M hydrofluoric acid solution (Merck, 38–40% purity) was employed in the pre-treatment of the NETmix glass slab. Tartaric acid (Fisher, purity 100%) was used as scavenger. $FeCl_3.6H_2O$ (Chem-Lab, purity 99%) was used as iron source. 1,10-Phenanthroline 1-hydrate (Panreac, PA-ACS), glacial acetic acid (Fischer), ammonium acetate (Fischer, purity 99.6%) and ascorbic acid (Fischer, purity 99%) were used as colorimetric reagents to determine dissolved iron concentration. Sulfuric acid (Pronalab, purity 96%, 1.84 g $cm^{-3}$) and sodium hydroxide (Merck) were used for pH adjustment. All samples were filtered through 0.45 μm cellulose acetate membranes (Sartorius) before analysis.

### 2.2. Analytical determinations

Total chromium, hexavalent chromium, total dissolved organic carbon (DOC) and tartaric acid concentrations were determined according to the procedures already reported by Marinho et al. (2017a).

### 2.3. Catalyst preparation

CAM structures, whose characteristics are described in Table S1, were uniformly coated with several photocatalyst amounts according to the dip-coating method described by Marinho et al. (2017a). These structures were assembled into the MTP reactor for the Cr(VI) reduction studies.

Before use, the glass slab (GS) of the NETmix was soaked in hydrofluoric acid solution (0.1 M) for 1 h, then the GS was washed with distilled water and alkaline detergent, subsequently washed with ultrapure water, and dried at 50 °C for 30 min. After that, the GS was uniformly coated with a catalyst thin film using a spray system. The photocatalyst suspension (2 wt%) was sprayed over one side of the GS that was laid on an electric heating plate at 150 °C. After each application, the slab was dried on the heating plate for 20 min and then cooled at room temperature before being weighed. This procedure was repeated until the required amount of