Hexavalent chromium reduction in a photocatalytic membrane reactor in the presence of organic acids

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Abstract This study deals with the photocatalytic reduction of carcinogenic hexavalent chromium, encountered in industrial effluents and surface waters, to much less toxic and harmful trivalent form. Experiments were performed in a pilot scale Photocatalytic Membrane Reactor employing titanium dioxide suspension as a catalyst, UVC lamps as irradiation source and hollow fiber UF membranes as separation media. It is observed that the reduction of Cr(VI) is enhanced in the presence of carboxylic acids, which are used as sacrificial agents and act as electron donors, mainly due to formation of Cr(VI)/organic-acid complexes. The effect of all key operating parameters, including pH, catalyst loading, hydraulic retention time, UV dose, organic acid type and molar ratio over Cr(VI) ions, water matrix, on system performance is also examined. Encouraging results are obtained since complete reduction can be achieved in the presence of 300 mg/L citric acid or 180 mg/L oxalic acid under acidic conditions (pH 3), meeting the standards for safe disposal to natural water bodies. Complete reduction can be also obtained at higher pH values (~5.5) with simultaneous 'on-line' dosing of approx. 8 mg/L/min H_2O_2. Moreover, up to 62% photocatalytic oxidation of organics is attained, under the most favorable conditions.
Keywords: advanced oxidation processes, heterogeneous photocatalysis, ultrafiltration, titanium dioxide nanoparticles, wastewater treatment

1. Introduction

Hexavalent chromium Cr(VI) is considered as one of the most dangerous and toxic inorganic environmental contaminants. It is a well-documented carcinogen, also associated with other harmful effects on human health. Thus, 50 µg Cr/L is defined as the maximum allowable limit for total chromium concentration in the drinking water regulations of European Union. Cr(VI) is encountered in very high concentrations in many industrial effluents, from processes related to electroplating, metal finishing, mining, pigments production, wood processing and leather tanning. However, the reduction of hexavalent chromium ions to the (one hundred times) less toxic trivalent form still remains a major issue.

Typical methods for treating high Cr(VI) concentration wastewater and water streams, usually include chemical reduction (followed by coagulation-precipitation), adsorption (powdered activated carbon), ion exchange (resins, zeolites), RO membranes, electrocoagulation, electrodialysis and biological methods (bacteria and other microorganisms) (Barrera-Díaz et al., 2012, Owlad et al., 2019). However, there are drawbacks of these methods that include: the formation of sludge that needs further treatment before its final disposal, rather high installations and maintenance costs, inadequacy of methods at high concentrations, essentially transferring the problem to another medium for final solution.

A very promising process reported in literature for the reduction of Cr(VI) is heterogeneous photocatalysis, which is based on the •OH generation. Among many advantages, photocatalysis exhibits non-selectivity, low cost, operation at mild temperature and pressure, high efficiency and flexibility. Considering these attributes, several studies have already investigated the Cr(VI) reduction in presence of organic sacrificial compounds (Meichtry et al. 2007, Wang et al. 2010). A related interesting development involves implementation of the advanced technology of photocatalytic membrane reactor (PMR), employing UV irradiation and TiO_2 nanoparticles, coupled with ultrafiltration (UF) membranes. Although the excellent PMR performance regarding organics oxidation is proven, the combined/synergistic effects on Cr(VI) reduction remain a significant challenge, poorly treated in the literature.

Therefore, this study aims to evaluate the performance of a pilot scale PMR process, combining Cr(VI) reduction and total organic carbon removal. The focus is on identifying conditions maximizing process efficiency, while two mechanisms proceed simultaneously; i.e. the reduction of Cr(VI) to Cr(III) through electrons provided by a sacrificial agent and the oxidation of carboxyl acids through the hydroxyl radicals generated by UV light.

2. Materials and Methods

2.1. Materials and chemical reagents

Ultrafiltration hollow fibers (PURON®, Koch Membrane Systems, Inc,) made of PVDF, with nominal pore size 30 nm and OD 2.6 mm, were employed to construct a membrane module of total surface area 4.19 m^2. Four germicidal lamps (39W Puro s.r.l), emitting at 253.7 nm were used as a source of UVC irradiation. The titanium dioxide (TiO$_2$) used in form of suspension, as photo-catalyst was comprised of a mixture of 75% anatase and 25% rutile, with an average primary particle size of 21 nm and a BET surface area of 50 m^2/g (Aeroxide® P25, Evonik). Potassium dichromate (K$_2$Cr$_2$O$_7$, J.T. Baker), citric acid monohydrate (C$_6$H$_8$O$_7$·H$_2$O, Riedel de Haen), formic acid (CH$_2$O$_2$, Panreac) and oxalic acid dihydrate (C$_2$H$_2$O$_4$·2H$_2$O, Baker) were used for the preparation of feed stock solutions. Hydrogen peroxide (H$_2$O$_2$, Chem-Lab) solution 30% w/w was added to enhance process efficiency. Sulfuric acid (H$_2$SO$_4$, Fluka) solution 98% w/w and sodium hydroxide (NaOH, Merck) solution 5N, were employed for pH adjustment, while 1,5-diphenylcarbazide (C$_{13}$H$_{14}$N$_4$O, Panreac) and titanium (IV) oxysulfate (TiOSO$_4$, Sigma-Aldrich) were used for the determination of hexavalent chromium and hydrogen peroxide, respectively. All the above reagents were of analytical grade and used without any pretreatment. The water matrix in all experiments was tap water (TW), while all the solutions were prepared with deionized water (DW), produced from groundwater by a reverse osmosis system.
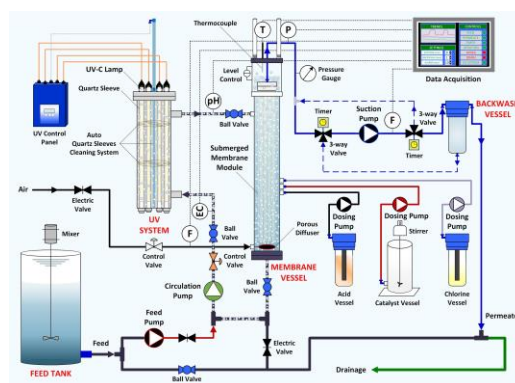
2.2 Analytical methods

Determination of Cr(VI) concentration was carried out by the diphenylcarbazide method (APHA 3500-CR). H$_2$O$_2$ concentration of permeate samples was also determinated colorimetrically. For selected samples, the total chromium concentration of was measured by Inductively Coupled Plasma Mass Spectrometry (ICP MS). The Total Organic Carbon (TOC) concentration of the samples was measured directly by employing a TOC analyzer, whereas the concentration of intermediate by-products was measured by High-performance Liquid Chromatography (HPLC). The pH was determined with a pHmeter and the electrical conductivity with a conductivity meter.

2.3 Experimental set-up and procedures

The PMR pilot unit (Fig. 1) consisted mainly of a commercial UV sterilization system and a membrane vessel. The UV system, eqquiped with a control panel, is a SS 316L closed cylindrical chamber, in which four quartz glass sleeves are vertically located and four UV-C lamps are encased within. The membrane vessel, made of Plexiglass®, has a cylidrical shape and a handmade membrane module is submerged therein. Moreover, a 200L feed tank and a backwash vessel, where the permeate is collected complement the basic parts of the

PMR pilot unit. The latter operates in continuous mode, has total effective volume 25L and treatment capacity 1.2 m^3/d. A centrifugal pump serves for recirculation of feed solution-catalyst mixture, between UV system and the membrane vessel, and gear pumps are used for permeate suction and for supplying feed solution into the system. A N$_2$ cylinder provides sufficient N$_2$ for system aeration. The 'on-line' addition of H$_2$O$_2$ is made with a dosing pump. A touch-screen/panel PC, an appropriate data logging system with a memory card serve for monitoring and recording data that include transmembrane pressure (TMP), permeate flux, air flow, pH, electrical conductivity and temperature of the system. A periodoc backwashing protocol; i.e. 1 min backwash with the permeate after 9 min suction, is implemented.

Figure 1. Schematic diagram of the PMR pilot unit

For preparation of feed solution, appropriate volumes of Cr(VI) and organic acid stock solutions were diluted with TW to achieve the desirable concentrations. Next, the pH of feed solution was adjusted (only when needed) with a small volume of H$_2$SO$_4$ or NaOH solution. In parallel, the photocatalyst suspension was prepared; i.e. a specific amount of TiO$_2$ powder was diluted with DI and magnetically stirred for about 3h, to achieve satisfactory dispersion. The experiment was seperated in two stages. In the first stage (adsorption, duration 2h), the system operated with permeate recirculation from membrane vessel back to the feed tank. This time period was adequate for the complete adsorption of species in the feed solution onto the system (membranes, tank, vessels etc.) and for reaching equilibrium concerning chromium concentration ([Cr(VI)$_{feed}$]=[Cr(VI)$_{perm}$]). In the second stage (photocatalysis, duration 3h), catalyst dispersion entered the system from the membrane vessel. The feed solution-catalyst mixture recirculated for about 15-20 min (in the dark) to achieve mixture homogeneity and uniformity of the catalyst concentration. Right after, UV-C lamps were switched-on denoting time zero (t=0). At the same time, H$_2$O$_2$ was dosed when required. Samples were collected at specific time intervals for Cr(VI) and TOC determination.
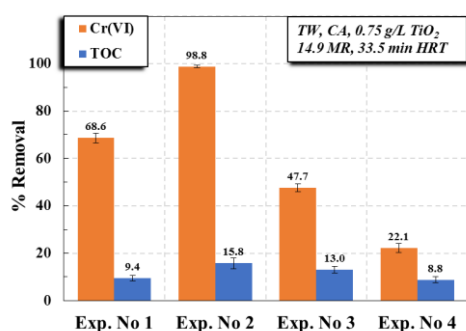
3. Experimental Results

3.1 Effect of operating parameters

The effect of all key operating parameters on system performance were investigated, including UV dose (P$_R$),

pH, molar ratio of citric acid over Cr(VI) ions (MR), Hydraulic Retention Time (HRT), Hole Scavengers type (HS), water matrix and TiO_2 loading. Rerformance was evaluated in terms of Cr(VI) and TOC percent removal. Moreover, the effect of H_2O_2 addition was assessed on PMR overall efficiency. Experimental results after 3h treatment with photocatalysis are presented in Figures 2-5. Initial concentration of Cr(VI) was 10 mg/L in all tests.

As shown in Fig. 2 (Exp. No 1, 2), P_R has a significant positive effect on Cr(VI) removal; i.e. 30 percentage units increase when 4 lamps were used instead of 2. Additionally, the application of UV dose 2.08 W/L increases the TOC removal approx. 68%.

Concerning feed solution pH, the comparison of three experiments (Exp. No 2, 3 and 4), denoted that acidic conditions strongly favor the PMR efficiency; i.e. increase from 22% to 99% and from 9% to 16% of Cr(VI) and TOC removal, respectively, after changing the pH from 8.2 to 2.8. This trend is attributed to the electrostatical attraction occuring between the positively charged catalyst ($pH<pH_{zpc}$) and the negatively charged forms of chromium (CrO_4^{2-} and $Cr_2O_7^{2-}$). As the pH value increases the above attraction decreases and when pH is greater than pH_{zpc} (pH>6.5) catalyst becomes negatively charged and thus the Cr(VI) reduction decreases.
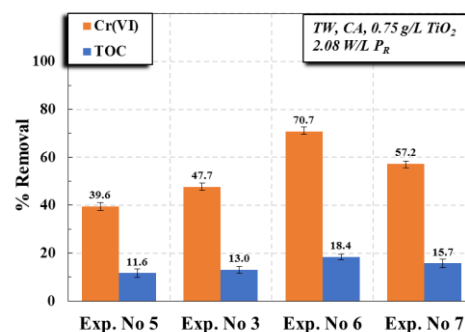

Figure 2. Effect of P_R (Exp. No 1, 2) and pH (Exp. No 2, 3, 4) on PMR system performance. *Experimental conditions: Exp. No 1: 2.9 pH, 1.04 W/L P_R, Exp. No 2: 2.8 pH, 2.08 W/L P_R, Exp. No 3: 6.1 pH, 2.08 P_R, Exp. No 4: 8.2 pH, 2.08 W/L P_R*

From Fig.3 is observed that the PMR efficiency clearly increases when MR and HRT values are increased. Specifically, the increase of MR from 10.8 to 23.3 lead to over 31 percentage units growth (Exp. No 5, 6). This may be expected due to the greater number of electrons provided by the degradation of the CA molecules for the photocatalytic reduction of Cr(VI). Additionally, higher acid concentration leads to lower feed solution pH, favoring red-ox reactions as mentioned above.
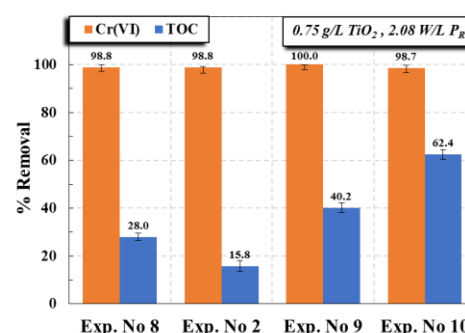
Further, when doubling the HRT from 33.5 to 67 min (Exp. No 3, 7), an increase of approx. 20% Cr(VI) as well as TOC removal is achieved. This improvement can be explained by the larger contact time between the Cr(VI) ions and TiO_2 nanoparticles and the larger irradiation time inside the photoreactor.

Among the three organic sacrificial agents tested under the same experimental conditions, FA presented the best

Figure 3. Effect of MR (Exp. No 5, 3, 6) and HRT (Exp. No 3, 7) on PMR system performance. *Experimental conditions: Exp. No 5: 6.1 pH, 10.8 MR, 33.5 min HRT, Exp. No 3: 6.1 pH, 14.9 MR, 33.5 min HRT, Exp. No 6: 4.7 pH, 23.3 MR, 33.5 min HRT, Exp. No 7: 6.4 pH, 14.9 MR, 67 min HRT*

performance regarding TOC percentage removal; i.e. 40%. OA and CA followed with 28% and 16% respectively (Fig. 4, Exp. No 8, 2, 9). This is attributed to the small molecular weight of FA and OA, comprising only 1 and 2 atoms of carbon, respectively. On the contrary, CA having six carbon atoms can be mineralized to a lesser extent due to the formation of low molecular weight oxidation by-products. Furthermore, CA leads to the formation of complexes [e.g. Cr(V)/CA] on catalyst surface, which inhibit further CA oxidation. However, it is noted that complete reduction of Cr(VI) was achieved after 3h treatment with all the three sacrificial agents.
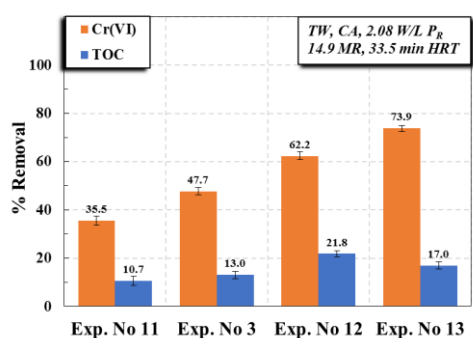

Figure 4. Effect of HS (Exp. No 8, 2, 9) and water matrix (Exp. No 9, 10) on PMR system performance. Experimental conditions: *Exp. No 8: TW, OA, 3.3 pH, 14.9 MR, 33.5 min HRT, Exp. No 2: TW, CA, 2.8 pH, 14.9 MR, 33.5 min HRT, Exp. No 9: TW, FA, 2.9 pH, 67.8 MR, 67 min HRT, Exp. No 10: DW, FA, 3.2 pH, 67.8 MR, 67 min HRT*

Two experiments with different water matrix, otherwise identical conditions, were carried out (Exp. 9, 10) and compared. Fig. 4 shows that complete Cr(VI) reduction, due to acidic pH and H_2O_2 addition, was achieved in both tests. However, FA mineralization was 55% higher (reaching 62%) when treated with DW, as probably expected. Obviously, the inorganic anions (Cl^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-) and cations (Ca^{2+}, Mg^{2+}) in TW compete with the Cr(VI) ions for active sites on the catalyst surface, thus inhibiting the photocatalysis mechanism.

As shown in Fig. 5 (Exp. No 11, 3) the increase in catalyst concentration from 0.4 to 0.75 g/L improves Cr(VI) reduction by approx. 35%. This is due to

availability of more active sites on catalyst surface for organic acids oxidation. Further increase of TiO_2 loading could probably lead to scattering phenomena and larger agglomerates hindering the photoreduction of Cr(VI).

Experiments with 'on-line' dosing of H_2O_2, in the photoreactor resulted in considerable enhancement of PMR efficiency; i.e. 30-67% and 31-55% Cr(VI) reduction and CA mineralization respectively (Fig. 5, Exp. 3, 12, 13). Moreover, TOC removal increased by 28% when H_2O_2 dosing was increased from approx. 5.5 to 8 mg/L (Exp. No 12, 13). H_2O_2 reacts with electrons which are emitted by TiO_2 to directly generate •OH and anions. At the same time it inhibits the electron/hole pairs recombination on the catalyst surface, thus promoting the photoxidation rates of the sacrificial agents. The H_2O_2 consumption in the system was fairly high in all cases (85%, data not shown).

Figure 5. Effect of TiO_2 loading (Exp. No 11, 3) and H_2O_2 dosing (Exp. No 3, 12, 13) on PMR system performance. *Experimental conditions: Exp. No 11: 6.8 pH, 0.40 g/L TiO₂, Exp. No 3: 6.1 pH, 0.75 g/L TiO₂, Exp. No 12: 6.2 pH, 0.75 g/L TiO₂, 8 mg/L/min H₂O₂, Exp. No 13: 6.0 pH, 0.75 g/L TiO₂, 5.5 mg/L/min H₂O₂*

3.2 Total Chromium, Intermediates and UF performance

Cr(III) can be estimated indirectly from measurements of total chromium concentration in selected samples from feed and permeate. In cases of complete reduction, results showed negligible concentration of total chromium in the permeate (data not shown) confirming that Cr(VI) removal can be exclusively attributed to photocatalytic reduction to Cr(III) and not to other processes (e.g. adsorption, photolysis). The rather low mineralization percentages and the deviation of TOC mass balances led to the hypothesis that during oxidation of sacrificials agents, other organic compounds could be formed. Indeed, HPLC measurements confirmed the existance of intermediate by-products such as acetic, oxalic, succinic, isocitric and malic acid. The estimated decomposition rates of acids were high (75-90%, data not shown). Membrane filtration performance was excellent and no fouling was detected as TMP remained stable after 3h treatment, regardless of experimental conditions, denoting the successful backwashing protocol applied.

4. Conclusions

Very promising experimental results regarding photoreduction of hexavalent chromium were obtained from this study employing a PMR pilot unit. The importance of the presence of organic carboxylic acids (hole scavengers) on process efficiency was confirmed and high level efficiencies were attained. Specifically, complete reduction of Cr(VI) to Cr(III) was achieved in the presence of 300 mg/L citric acid or 180 mg/L oxalic acid at pH 3. The reduction of chromium was favored under acidic conditions, when the catalyst was positively charged and attracted the negatively charged chromium ions. However, complete reduction was obtained at higher pH values (~5.5) in the presence of 300 mg/L formic acid and by a dosimetrical 'on-line' addition of approx. 8 mg/L/min H_2O_2. Under such conditions, production of •OH was enhanced offering faster and more effective reduction of chromium. In parallel with the Cr(VI) photoreduction, photocatalytic oxidation of organics occured; i.e. 22%, 28% and 62% for citric, oxalic and formic acid respectively, under the most favorable experimental conditions. Concerning the other operating parameters, UV dose and molar ratio had a significant positive effect (approx. 45-78% increase) on the PMR system efficiency. Smaller but still positive effect (approx. 20-35% increase) resulted by increasing the hydraulic retention time and the catalyst loading. Although the hexavalent chromium concentration of the permeate stream met the standards for safe disposal to natural water bodies (0.2-1 mg/L depending on the aquifer) in many of experiments, further research and optimization of PMR technology is needed, targeting to practical applications in drinking water and wastewater treatment.

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