PHOTOREDUCTION OF HEXAVALENT CHROMIUM USING TIO_2 AND *Scenedesmus obliquus* UNDER DIFFERENT AIR CONDITIONS

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ABSTRACT

The paint, chlorine, PVC plastics, and metallurgical industries produce effluents with heavy metals. Among them, chromium (Cr) stands out. In its 6^+ oxidation state, chromium is toxic and carcinogenic. Traditional chromium treatments demand a high chemical load. Therefore, it is relevant to propose alternative processes. Photocatalytic processes have been studied due to their more sustainable aspect, high yield, and wide application in effluent treatment. Inorganic, organic, and microorganisms are used as photocatalysts. The current study evaluated the influence of dissolved oxygen in the photo-reduction of hexavalent chromium using titanium dioxide and *Scenedesmus obliquus* as photocatalysts under natural sunlight illumination. For condition 1 g/L of catalyst, 10 mg/L Cr (VI), pH 3, and 3 h experimental time, dissolved oxygen did not significantly affect the photo-reduction of Cr (VI) in TiO_2. However, the depletion of O_2 increased the Cr (VI) photoreduction in the presence of *S. obliquus*.

Keywords: Heavy metal. Photocatalysis. Titanium dioxide. Algae. Dissolved oxygen.

1 INTRODUCTION

In general, heavy metals are pollutants since they are not biodegradable and tend to accumulate in living organisms, leading to diseases [1]. Among the heavy metals, the study of chromium is relevant due to its toxicity for biological systems and its industrial application. The chromium oxidation states vary between 2^+ to 6^+, being the trivalent and hexavalent the most stables[2]. Cr (VI) found mainly as chromate and dichromate, has carcinogenic properties in humans. Different technologies are used for chromium reduction and/or removal from industrial residues. The main techniques for hexavalent chromium removal from industrial wastewater are reduction, precipitation, ion exchange, and evaporative techniques [3]. However, these treatments produce sludge containing metals that must be sent to controlled landfills for hazardous industrial waste.

The Advanced Oxidative Processes (AOP) have been recently studied and gained prominence in research as this technology has a higher long-term sustainability. Also, due to the formation of hydroxyl radicals, highly oxidizing agents, the AOPs can be used for a variety of compounds, generating less toxic substances like CO_2 and water. Among the AOPs, heterogeneous photocatalysis has been studied for wastewater treatment. The main photocatalysts used in heterogeneous photocatalysis are transition metal oxides, such as Fe_2O_3, ZnO, ZnS, CdS, and TiO_2. In addition, titanium dioxide is mostly used due to its high photo sensibility, non-toxic nature, ideal band-gap value for UV radiation and sometimes for natural sunlight, high chemical stability, employability at ambient temperature and pressure, relatively low cost, obtainment easiness and does not require the use of supporting reagents[4].

From an economic point of view, the use of algae as photocatalysts is a very advantageous alternative, since these materials are available in large quantities in nature and are relatively easily obtained. In addition, algae have a high efficiency in removing metal ions from very dilute effluents. It is observed that the algae use the protons existing in the aqueous medium in the reduction process. The electrons necessary for the reduction of chromium (VI) are provided by the biomass itself, resulting in the oxidation of organic compounds, which are partially released into the solution[5]. Regarding the algae, there is still no established mechanism for its activity, and photocatalysis phenomena are still being studied.

2 MATERIAL & METHODS

For the photocatalysis, titanium dioxide (99% purity, Reagent) was used as an inorganic photocatalyst, and potassium dichromate ($K_2Cr_2O_7$, 99%, Vetec, Brazil) was used to prepare chromium solutions. The green algae *S. obliquus* (Hungary) cultures were inoculated and grown in a sterile modified Arnon medium with the addition of $NaNO_3$ as a nitrogen source. The algae were kept in a 5 L batch mode, at 23 ± 2 °C, pH 8.0 ± 0.1, and 150 µmol/m^2·s until the algae concentration reached 1 g/L. Then they were inoculated and grown in 85 L bubble columns in a media composed of fertilizers suggested by Morillas-España et al. (2022)[6] (Table 1) at controlled pH 8 and natural sunlight illumination.

Table 1 – Composition of bubble column medium

Compound	Solid mass (g) per liter
$NaNO_3$	0.90
$MgSO_4$	0.18
$HK2PO_4$	0.14
Karentol®	0.03

The Karentol® fertilizer (Konegard, Barcelona, Spain) composition is shown in Table 2. The columns were refreshed every 7 days or when 40 L were used in the same period. The system to evaluate the dissolved O_2 effect and compare the algae and TiO_2 application as photocatalysts consisted of a cylindrical reactor 6 cm in height and 24 cm in diameter under magnetic stirring with inner gas dispersion (Figure 1). 1,400L of 1 g/L algal culture or TiO_2 dispersions were added to the reactor (3 cm suspension height). The dissolved O_2 concentration was adjusted to saturation and depletion using O_2 and N_2 gas cylinders. The pH was adjusted to 3 using 10 %v/v H_2SO_4 and 1 M NaOH solution. The $K_2Cr_2O_7$ was added to obtain a concentration of 10 mg/L Cr (VI). Samples were collected in the beginning and after 3 h of process for analyses of hexavalent chromium concentration according to the diphenylcarbazide method[7]. Before Cr (VI) concentration analyses, samples were filtered through a 0.22 µm PTFE syringe filter.

Table 2 – Karentol® composition

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

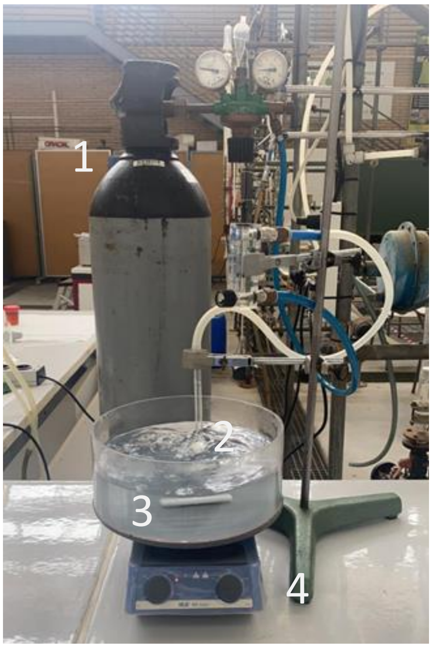

Figure 1 System for dissolved O_2 experiments composed by a gas cylinder (1), a diffusion rock (2), a cylindrical reactor (3) and a magnetic stirrer (4)

3 RESULTS & DISCUSSION

Figure 2 shows the photoreduction of Cr (VI) in the presence of TiO_2 and *S. obliquus* under different dissolved O_2 conditions after a 3 h process using 1 g/L catalyst, pH 3, and an initial 10 mg/L Cr (VI). The dissolved O_2 did not significantly affect the photoreduction of Cr (VI) in the presence of TiO_2. As discussed by Chen and Ray (2001)[8], Cr (VI) and O_2 have similar reduction potential at 3 and, therefore, they will not compete for the reduction sites of the TiO_2. However, the influence of dissolved oxygen in the photoreduction of Cr (VI) using TiO_2 is still not clear as positive[9], negative[10], and no effects[11] were reported. The difference in the results is related to the experimental conditions performed by the researchers. However, in the presence of algae, the depletion of O_2 increased the Cr (VI) photo-reduction. As algae require nutrients such as nitrates, phosphates, and sulfur to produce and convert them into proteins, fats, and carbohydrates, the increase of N_2 will induce the growth of the algae and the production of these metabolites which have a positive effect on the Cr (VI) photoreduction[12].

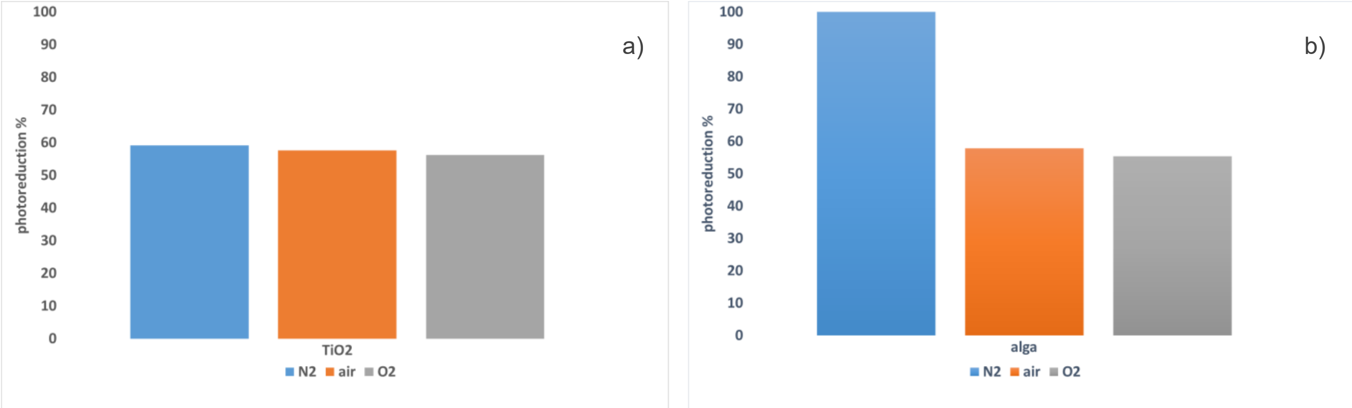

Figure 2 Influence of dissolved O_2 using 10 mg/L Cr(VI) pH of 3 in the presence of 1g/L a) TiO_2 and b) *S. obliquus.*

4 CONCLUSION

For the photocatalysis of 10 mg/L Cr (VI) using 1 g/L catalyst under pH 3 and natural sunlight, the Cr (VI) photo-reduction did not change using TiO_2 and there is not an expected result since different studies showed different influences. However, the Cr (VI) photo-reduction increased under depletion of O_2 using the algae since the induced production of organic matter affects positively the process.

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