PHOTOCATALYTIC REDUCTION OF Cr(VI) USING DIFFERENT HYBRID MATERIALS: TITANIUM NANOSHEETS/POZZOLAN AND KAOLIN/POLYSILOXANES

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ABSTRACT – This work evaluates the photocatalytic reduction of Cr(VI) to Cr(III) using different catalysts: titanium-based and kaolin-based materials. The assays were conducted in the presence of citric acid/tartaric acid as hole/HO• scavenger, using a tubular photoreactor irradiated by UVA light. The Cr(VI) reduction reaction rate in the presence of titanium nanosheets with pozzolan (TNS-PZ) showed a ten-fold increase when compared with commercial TiO₂-P25 nanoparticles. The effect of the catalyst loading on Cr(VI) reduction was evaluated using TNT-PZ. Then, at the optimum catalyst loading (100 mg L⁻¹), hybrid kaolin materials with polysiloxanes were also tested. The best results were obtained using kaolin+methyl polysiloxane as catalyst, resulting in a catalyst reactivity in combination with the photoreactor of 0.12 mmol Cr(VI) m⁻³ reactor s⁻¹ ([Cr(VI)]₀=0.20 mM; 100 mg catalyst L⁻¹; [tartaric acid]₀:[Cr(VI)]₀ molar ratio of 6:1, pH 3.0 and 25 °C).

INTRODUCTION

Cr(VI) is a common toxic pollutant present in wastewaters originated from various industrial processes as electroplating, pigment production, and leather tanning. Heterogeneous photocatalytic processes are envisaged as a convenient technology for the conversion of toxic metals present in water matrices into less toxic species (Litter, 2017). TiO₂ is an extensively investigated photocatalyst due to its properties such as high refractive index and ultraviolet (UV) absorption, good photocatalytic activity, photostability, chemical stability, and nontoxicity. However, one of the main drawbacks of heterogeneous TiO₂ photocatalysis is that the generated electron-hole pairs can easily recombine (Jaiswal et al., 2012).

To overcome the abovementioned problem, in the presence work, different hybrid materials were synthesized and tested as photocatalysts for the reduction of Cr(VI) in aqueous solution. The tested catalysts were divided into two categories: i) titanium nanosheets (TNS) doped with pozzolan (TNS-PZ), and ii) kaolin incorporated with different polysiloxanes (methyl polysiloxane (MK), methyl-phenyl polysiloxane (H44), tetraethyl ortho silicate (TEOS) and 3-amino-propyltriethoxysilane (APTES).
1. MATERIAL AND METHODS

2.1 Chemicals
Cr(VI) solutions were prepared from K₂Cr₂O₇ salt (Merck, purity 99.9%). The colorimetric reagent 1,5-diphenylcarbazide (Merck, purity 98%) was used in the analytical method for the determination of Cr(VI) concentration. TiO₂ (Degussa P25 powder), citric acid (Nuclear, purity 99.5%) and tartaric acid (Neon, purity 99.5%) were used in the photocatalytic experiments. Sulfuric acid (Lafan, 98%) and sodium hydroxide (Lafan 97%) were used for pH adjustment.

Natural pozzolan, ethanol, titanium (IV) isopropoxide and nitric acid were used in the preparation of the TNS-PZ catalyst. Kaolin was obtained from a mining industry. The polysiloxanes MK, H44, TEOS and APTES were purchased from Silres® Wacker Chemie AG and Sigma Aldrich. Nitric acid and ethyl alcohol were used for the synthesis of these materials.

2.2 Preparation of titanium nanosheets and titanium nanosheets/pozzolan
TNS was synthesized from titanium (IV) isopropoxide and ethanol. Natural pozzolan was collected from the region of Cameroon. TNS-PZ was prepared by mixing natural pozzolan in solutions of ethanol and titanium (IV) isopropoxide. The suspension was agitated, and ethanol was added. Then, the suspension was centrifuged and dried. The obtained material was calcinated at 600 °C and subsequently was hydrothermally treated in a Teflon reactor at 140 °C for 36 h. The resulting material was firstly neutralized with a nitric acid solution until achieving a final pH close to 0. Posteriorly, it was washed with distilled water until neutral pH. Finally, the material was dried at 100 °C for 24 h.

2.3 Preparation of kaolin/polysiloxane
The kaolin was dispersed with each polysiloxane in a 1:1 ratio (w/w). An aliquot of 10 mL of ethanol per gram of precursor was used, and the solution was refluxed for 48 h. Hydrolysis and polycondensation of the reactants were catalyzed under acidic conditions by adding 0.2 mL of nitric acid per 100 mL of solution. Then, ethanol was removed and samples were pyrolyzed at 500 °C under an inert atmosphere for 1 h. Finally, the samples were ground and sieved with aperture sieves smaller than 250 μm.

2.4 Experimental procedure
The Cr(VI) reduction reactions were performed in a lab-scale tubular photoreactor, with a total volume of 1.5 L and an illuminated volume of 0.59 L. The detailed description of the photoreactor and experimental procedure are presented elsewhere (SALIM et al., 2016; MARINHO et al., 2017). The UV photonic flux reaching the reaction medium of 1.67×10⁶ einstein s⁻¹ was determined by ferrioxalate actinometry. Total chromium concentration was determined by atomic absorption spectrometry (AAS, Shimadzu model AA 6300) using an Air-Acetylene flame. Hexavalent chromium concentration was measured by molecular absorption spectrophotometry. The procedure followed is based on the formation of a pink complex of Cr(VI) with 1,5-diphenylcarbazide in acid solution, which absorbs at 540 nm.

3. RESULTS AND DISCUSSION
Different Ti-based materials were tested on the reduction of 0.2 mM Cr(VI), in the presence of citric acid as a scavenger (Fig. 1): TiO$_2$-P25, TNS and TNS-PZ. A ten-fold increase on the photocatalytic reduction rate (pseudo-first order kinetic) was observed using TNS-PZ as photocatalyst when compared to TiO$_2$-P25 (Table 1). Besides, the TNS-PZ/UV/citric acid system showed a photocatalytic Cr(VI) reduction rate five times superior to that obtained with the TNS/UV/citric acid (Table 1). This increase is mainly attributed to the metallic species present in pozzolan, facilitating charge separation and electron-holes trapping.

The photocatalytic reduction of Cr(VI) was evaluated at different catalyst loading (S/L) values. Taking into account the photoreactor pathlength, the optimal S/L value was 100 mg L$^{-1}$. A further increase on S/L ratio showed a negligible influence on reduction rate. Increasing the catalyst concentration, the quantity of photons absorbed, and consequently the reduction rate, increases, because at this level the catalyst surface and absorption of light by the catalyst are the limiting reaction step. As the number of catalyst particles increases above an optimum dose, the particle–particle interaction becomes significant, reducing the light penetration and consequently the site density for surface holes and electrons. Tartaric acid was used as a sacrificial agent since it presented better performance in the photoreduction of Cr(VI) when compared with citric acid (data not shown).

In this work, different kaolin-based catalysts were also prepared and tested in the photocatalytic reduction of Cr(VI) in aqueous solutions. Pure kaolin catalyst presents a lower efficiency for Cr(VI) reduction than TNS-PZ (Fig. 2). However, all kaolin/polysiloxane based catalysts enhanced substantially the Cr(VI) reduction when compared to TNS-PZ (Fig. 2).

For all experiments, total chromium concentration remained constant through the reaction, which indicates no adsorption of Cr(VI) and Cr(III) species on the surface of the

![Figure 1](image1.jpg) ![Figure 2](image2.jpg)
catalysts.

Table 1 – Pseudo-first and pseudo-zero orders kinetic constants and the corresponding coefficient of determination ($R^2$).

| Experiment | Catalyst loading (mg L$^{-1}$) | [Scavenger]/[Cr(VI)]$_0$ molar ratio | $k \times 10^{-3}$ (min$^{-1}$) | $r_0 \times 10^{-3}$ (mmol L$^{-1}$ min$^{-1}$) | $R^2$ |
|------------|-------------------------------|---------------------------------|-----------------|------------------|------|
| Influence of the catalyst type in the system TiO$_2$-based materials/citric acid/UVA | | | | | |
| TiO$_2$ | 15 | 3:1 | 1.1 ± 0.1 | 0.21 ± 0.02 | 0.987 |
| TNS | 15 | 3:1 | 2.0 ± 0.2 | 0.36 ± 0.03 | 0.983 |
| TNS-PZ | 15 | 3:1 | 10 ± 3 | 2.0 ± 0.7 | 0.931 |
| Influence of the catalyst type in the system kaolin-based materials/tartaric acid/UVA | | | | | |
| Kaolin | 100 | 6:1 | 0.43 ± 0.04* | - | 0.960 |
| Kaolin+APTES | 100 | 6:1 | 2.1 ± 0.2* | - | 0.975 |
| Kaolin+TEOS | 100 | 6:1 | 2.4 ± 0.3* | - | 0.962 |
| Kaolin+H44 | 100 | 6:1 | 1.9 ± 0.2* | - | 0.974 |
| Kaolin+MK | 100 | 6:1 | 2.9 ± 0.2* | - | 0.991 |

* (mM min$^{-1}$)

4. CONCLUSIONS

Comparing the titanium-based materials, TNT-PZ showed better results than TiO$_2$-P25 commercial nanoparticles. However, kaolin-based catalysts, in special the kaolin+MK, showed a much better performance over the Cr(VI) reduction, resulting in a catalyst reactivity in combination with the photoreactor of 0.12 mmol Cr(VI) m$^{-3}$ reactor s$^{-1}$. Thus, these hybrid materials may reduce the electron-hole recombination, improving its photocatalytic activity.

5. REFERENCES

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