Reduction of Cr(VI) to Cr(III) from Photovoltaic Waste-Water

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***Abstract*—** The objective of this study is the use of two photocatalysts based on metal oxides which are titanium dioxide (TiO_2) and zinc oxide (ZnO) to reduce hexavalent chromium Cr(VI) which is a photovoltaic industry pollutant to trivalent chromium Cr(III) in the UV field. The effects of various parameters such as pH, the amount of the catalyst, the concentration of the pollutant and the volume of hydrogen peroxide (H_2O_2) are discussed. As a final test, we used sunlight instead of the UV lamp. It was found that the catalytic process exhibited the highest photocatalytic activity using TiO_2 anatase than ZnO under the same operating conditions, so the reduction rates are higher with titanium oxide than with zinc oxide. For TiO_2 the optimum dose of the photocatalyst is 0.5 $g.L^{-1}$ at pH 1, the concentration of Cr(VI) is 1.0 $mg.L^{-1}$ and the rate of the H_2O_2 is 0.15% (v/v). For ZnO the optimum dose of the photocatalyst is 0.8 $g.L^{-1}$ at pH 4, the concentration of Cr(VI) is 1.0 $mg.L^{-1}$ and the rate of the H_2O_2 is also 0.15%. The comparison of the process under the optimal conditions of UV light and sunlight, the removal rates in case of titanium oxide are 52.51% and 9.63% respectively, in case of zinc oxide are 26.51% and 2.10%.

Key-Words— *waste-water, photocatalysis, TiO_2, ZnO, hexavalent chromium.*

I. INTRODUCTION

In photovoltaic industry, a wide variety of chemicals are involved in wafers manufacturing by using a large number of complex and sensitive processes, which include silicon crystal growth, cutting, metallization, photolithography, washing and cleaning. As a result, huge quantities of waste-water are generated with higher concentrations of heavy metals, such as hexavalent chromium Cr(VI), which is derived from the use of chromic acid (H_2CrO_4) in combination with hydrofluoric acid (HF) in etching operations [1].

In order to reduce the negative effect of the heavy metals, including hexavalent chromium, several purification processes have been studied, such as photocatalysis, adsorption, anion exchange, membrane filtration. Many works have been dedicated to the study of photocatalysis as an alternative to conventional semiconductor effluent treatments [2], [3].

II. EXPERIMENTAL

A. Experimental procedure

All tests were carried out in batch mode and at ambient temperature. The mixing at 200 rpm of 1 min maintained constant for all tests. The synthetic solution to be treated with a volume of 200 mL was introduced into a glass reactor and kept in dark for 30 minutes in order to reach the adsorption equilibrium between the pollutant and the photocatalyst.

B. Analytical method

The concentration of Cr(VI) was measured using the 1,5-diphenylcarbazide method [4]. The measuring equipment used is an HACH® DR 2500 spectrophotometer. The pH values were determined by using pH meter HANNA® HI 8424.

III. Results and Discussion

A. Effect of pH

In order to follow the evolution of the hexavalent chromium reduction under the effect of the variation of the parameters, graphs were plotted by the ratio of the final concentration to the initial concentration (C/C_0).

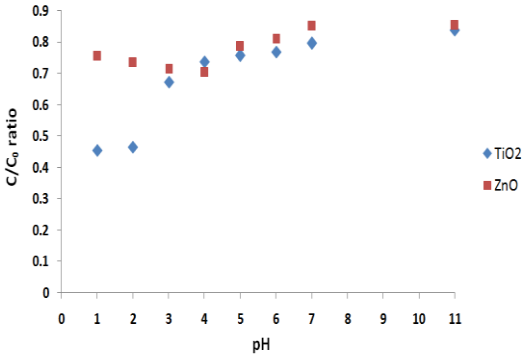

Figure 1. Effect of pH on Cr(VI) reduction by TiO_2 and ZnO.

From Figure 1, it is clear that in photocatalytic process the pH of the solution is an important parameter in the Cr(VI) reduction for both TiO_2 and ZnO. In the case of the photocatalyst TiO_2, it was noted that the concentration of chromium increases with the pH, in fast way at the pH range 1-3 then in slow way. In the case of the photocatalyst ZnO, it was noted that the concentration of chromium decreases between pH 1 and pH 4 then it increases. It can be conclude that the acid pH is favorable for both TiO_2 and ZnO photocatalysis.

B. Effect of photocatalyst concentration

The effect of the photocatalyst concentration on the photoreduction of Cr(VI) was studied in range of 0.1 $g.L^{-1}$ to 1.0 $g.L^{-1}$. The best results were obtained for TiO_2 at 0.5 $g.L^{-1}$ and for ZnO at 0.8 $g.L^{-1}$ as shown in Figure 2.

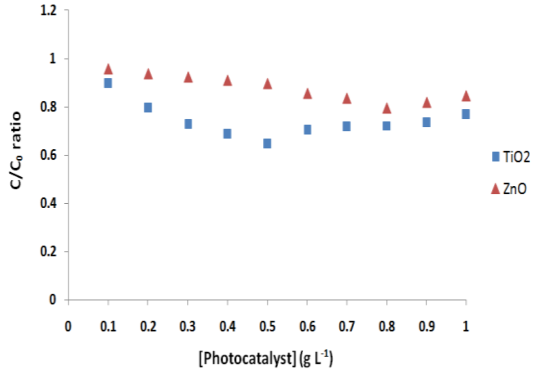

Figure 2. Effect of photocatalyst concentration on Cr(VI) reduction.

C. Effect of initial pollutant concentration

From Figure 3, it can be noted that the increase of the pollutant initial concentration is unfavorable parameter to TiO_2 and ZnO photocatalysis. The best results were obtained for both TiO_2 and ZnO at 1 $mg.L^{-1}$ which is the lowest initial concentration of chromium(VI).

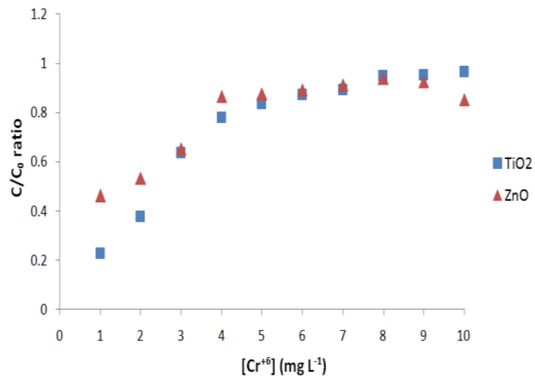

Figure 3. Effect of initial pollutant concentration on Cr(VI) reduction.

D. Effect of hydrogen peroxide

The results obtained in Figure 4, showed that the addition of the hydrogen peroxide (H_2O_2) makes it possible to obtain a better reduction of hexavalent chromium; with a volume of 400 µL of H_2O_2, it can be noted that we have a total reduction of Cr(VI) to Cr(III) for both TiO_2 and ZnO.

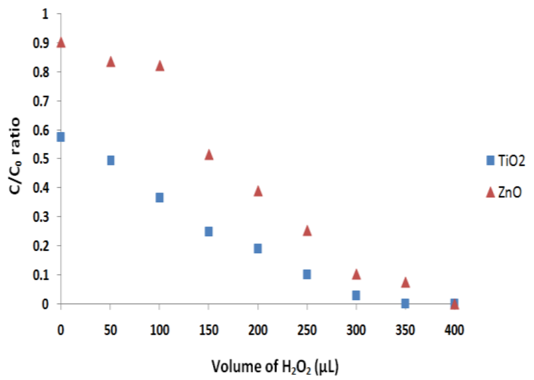

Figure 4. Effect of H_2O_2 volume on Cr(VI) reduction by TiO_2 and ZnO.

E. Sunlight tests

The tests under the sunlight showed that the reduction of Cr(VI) was more efficient by the TiO_2 than by ZnO. On the other hand, the elimination percentages were lower than those of the UV light tests. TiO_2 is a very good catalyst for application in photocatalysis, however the width of its band gap for anatase (3.2 eV) requires excitation by a wavelength of less than 380 nm. This domain represents only a small part of about 5% of the solar spectrum.

Table. Reduction percentage of chromium(VI) by TiO_2 and ZnO under the sunlight and the UV light at the same operating conditions.

	TiO_2	ZnO
Tests under the sunlight (%)	**9.63**	**2.10**
Tests under the UV light (%)	**52.51**	**26.51**

IV. CONCLUSION

Based on the results of this study, it can be conclude that the acid pH, the low pollutant concentration, the appropriate amount of photocatalyst and the adding of H_2O_2 are favorable parameters for both TiO_2 and ZnO photocatalysis. It was found that the catalytic process exhibited the highest photocatalytic activity using TiO_2 anatase than ZnO under the same operating conditions. Overall, the application of the TiO_2 and ZnO photocatalysis is an efficient process to eliminate hexavalent chromium Cr(VI) from photovoltaic waste-water using UV light or under sunlight.

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