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Cr^{+6} and Zn^{+2} Removal for Heterogeneous Photocatalysis with TiO_2 in Synthetic Wastewater

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Abstract : Water sources pollution caused by the presence of metals, it`s actually one of the environmental major concerns. In the present study, the hexavalent Chromium (Cr^{+6}) and divalent Zinc (Zn^{+2}) removal efficiency was evaluated using heterogeneous photocatalysis with titanium dioxide (Degussa P25) in a batch reactor. Both metal presents have harmful effects on public health and environment. The photocatalytic reduction process from Cr^{+6} to Cr^{+3} and Zn^{+2} to Zn^{0} in aqueous solutions with hexavalent Chromium or divalent Zinc initial concentrations of 5, 15 and 25 mg/L. It was performed in a batch reactor with a stipulated reaction volume of 250 mL, for the purpose it was provided a wooden box, which have a 20 W ultraviolet light lamp, installed in the chamber superior part. The tests were performed with pH initial conditions (2, 6 and 10 pH units) and photocatalyst doses (2.0, 2.5 y 3.0 g/L de TiO_2), from a multifactorial experimental design of three factor and three levels. From the obtained results it is noticed that the heterogeneous photocatalysis is an excellent instrument for the removal Cr^{+6} in aqueous solutions, when their concentrations are relatively low, because for the initial concentration of 5 mg/L from Cr^{+6} is possible its total removal. Furthermore, it was found that this technology is less effective for Cr^{+6} removal in high concentrations (15, 25 ppm), because this one presents slow reaction kinetics, which were studied in this investigation. For other hand, it was found that this technology is not effective for Zn^{+2}, because only 3% of removal was achieved.
Keywords : hexavalent Chromium, divalent Zinc, titanium dioxide, photocatalysis.

Introduction

Metallic species such as chromium, mercury, zinc and many others are among the priority pollutants of the US Environmental Protection Agency. (US EPA)[1]. In addition to the natural presence of chemical species in the environment, anthropogenic activities introduce several hundred billion tons of heavy metals per year into the terrestrial environment. At the same time as the environmental concern increases, the accumulation of metals in effluents represents significant economic losses in raw materials[2].

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Chromium is one of the heavy metals that have received most attention from the scientific community. This element is not easily degraded, neither by chemical or biological mechanisms. Hexavalent chromium is considered a highly toxic substance, capable of being absorbed through the skin and causing different conditions on human health because of its strong oxidant activity [3, 4, 5, 6].

Different methods for the treatment of industrial wastewater have been implemented over the past years. Some of them include precipitation, oxidation-reduction, ionic exchange, and evaporation recovery. However, these methods demand high costs and achieve low efficiencies[7, 8, 9, 10].

Since the beginning of heterogeneous photocatalysis, phototransformation, and photodeposition of metals, mainly the noblest, expensive and toxic, have been visualized as one of the most useful potential applications of the technology. Photocatalytic treatments can convert the ionic species to their metallic solid form and deposit them on the surface of the semiconductor, or transform them into other less toxic soluble species. At the end of the process, the metal species can be extracted from the suspension by mechanical or chemical means[11].

This project aims to evaluate the removal efficiency of the hexavalent chromium and divalent zinc metals present in synthetic wastewater, using the Advanced Oxidation Technique: Heterogeneous Photocatalysis with TiO_2. To evaluate the removal efficiency of the metals mentioned above, the influence of two parameters: pH and catalyst dose, on the reduction process.

Experimental

Materials

All chemical reagents were used as supplied. TiO_2 was Degussa P25, consisting of 80% anatase and 20% rutile, Glucose ($C_6H_{12}O_6$) 99%, Sodium formate (HCOONa) 99%, Potassium dichromate ($K_2Cr_2O_7$) 99%, Zinc Sulfate Heptahydrate ($ZnSO_4 \cdot 7H_2O$) 99%, Sulfuric acid (H_2SO_4) 98% w/v and Sodium hydroxide (NaOH) 98% were purchased from Sigma Aldrich.

Photocatalytic tests in batch systems

The photocatalytic reduction process from Cr^{+6} to Cr^{+3} and Zn^{+2} to Zn^0 in aqueous solutions with hexavalent Chromium or divalent Zinc initial concentrations of 5, 15 and 25 mg/L. It was performed in a batch reactor with a stipulated reaction volume of 250 mL, for the purpose it was provided a wooden box, which have a 20 W ultraviolet light lamp (Figure 1), installed in the chamber superior part. The tests were performed with pH initial conditions (2, 6 and 10 pH units) and photocatalyst doses (2.0, 2.5 y 3.0 g/L de TiO_2), from a multifactorial experimental design of three factor and three levels, following the exposed methodology in Figure 2 [12, 13, 14, 15].

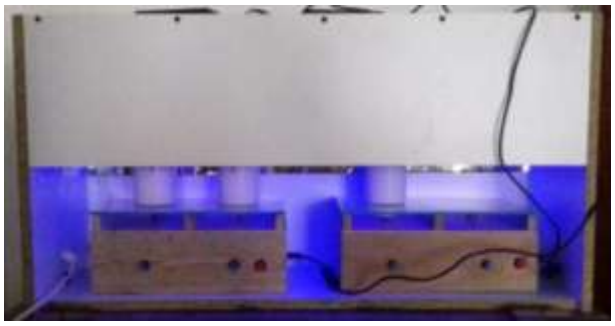

Figure 1. Experimental assembly.

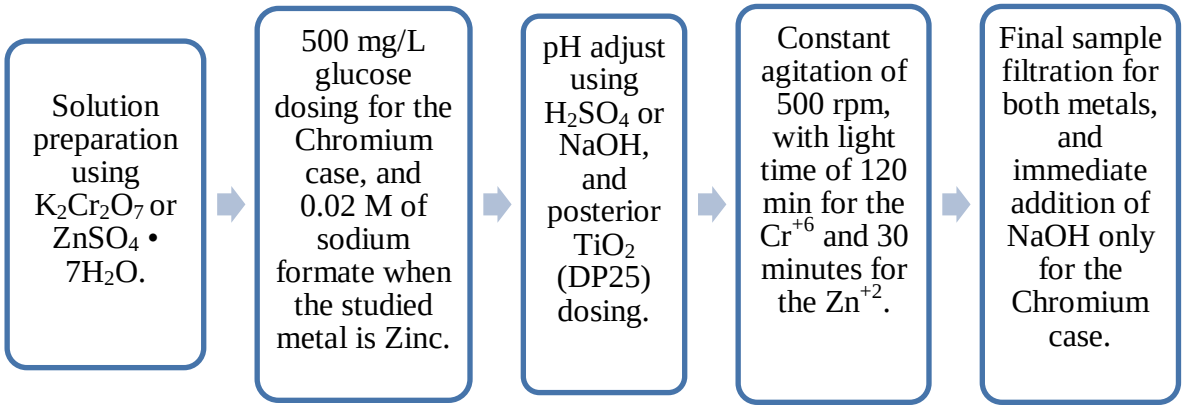

Figure 2. Experimental methodology for the Cr^{+6} y Zn^{+2} photocatalytic reduction.

Measurement of heavy metals

Throughout the experiment, the concentration in ppm of an initial sample and a final sample for both metals, using X-ray fluorescence, was measured in order to determine the amount of metal to reduce.

The equipment for measuring the concentration of Cr_{total} y/o Zn_{total} before and after the photocatalytic process was the x-ray fluorescence spectrophotometer of total reflection S2 Picofox.

For the measurement of all samples, a 100 µL aliquot was taken, which was mixed with 100 µL of a standardized gallium solution with a concentration of 10 mg / L. This final solution was mixed 1 minute on the vortex stirrer to achieve homogenization of said sample.

Subsequently, 10 µL of the mixture was deposited on a quartz disk (sample holder) and dried at 115 ° C for an approximate time of 1 minute. The disk is inserted into the PICOFOX S2 device so that it makes the readings corresponding to each experiment. All measurements were measured using the Standard method (Bayes), for a time of 300 seconds.

Results and discussion

Adsorption experiment in dark (Cr^{+6})

Figure 4 shows a strong influence of pH on the adsorption process of hexavalent chromium in the form of dichromate ion ($Cr_2O_7^{2-}$), which is based on the zero charge point pH of TiO_2 (6.25 units de pH). For pHs lower than this (2 and 6) the surface of the semiconductor is positively charged, favoring the electrostatic interaction between the photocatalyst and the dichromate ion, facilitating the absorption of the ion in question; While subjecting the TiO_2 to a basic medium (pH 10) brings with it a negative effect on the percentage of Cr^{6+} adsorption, since at this pH value the surface of the TiO_2 DP25 is negatively charged, causing repulsion between the particles and the $Cr_2O_7^{2-}$,Reason why the percentage of removal does not exceed14.2% [16, 17].

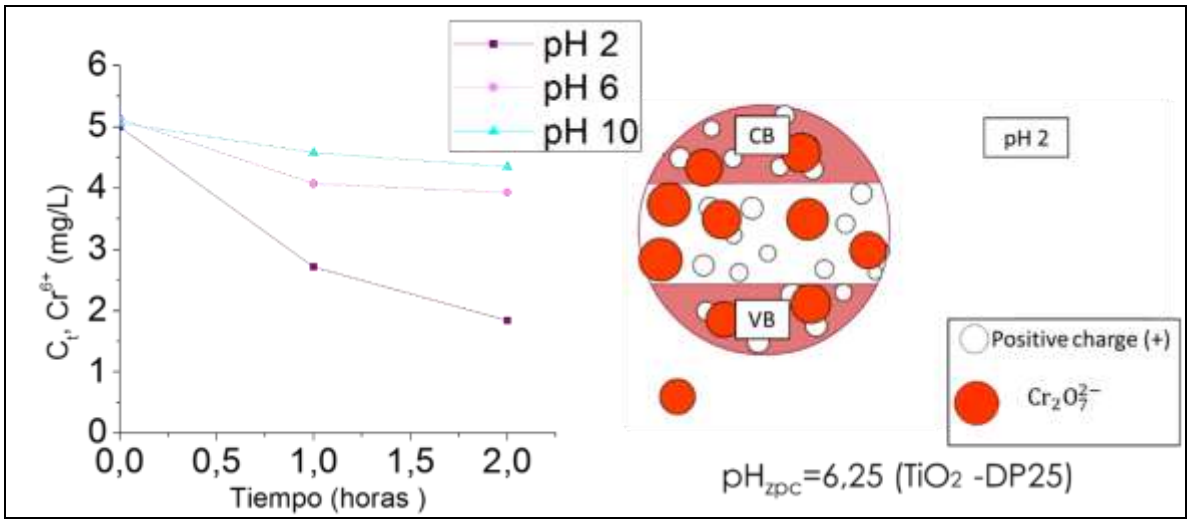

Figure 4. Adsorption experiment in dark for a Cr^{+6} initial concentration of 5 mg/L and 2.5g/L TiO_2 dosage.

Cr^{+6} Removal Using Heterogeneous Photocatalysis

Effect of initial pH

The mechanism of photocatalytic degradation of Cr (VI) requires a high consumption of protons (H^+) for the Cr (VI)-Cr (III) reduction process, according to equations 1 and 2, for acid and alkaline solutions, respectively[18]. Figure 5 shows that the best removal percentages were reached at pH 6, which is attributed to the inactivation of the photocatalyst pH 2 as a result of the large amount of $Cr_2O_7^{2-}$ adsorbed.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad (1)$$

$$CrO_7^{4-} + 20H^+ \rightarrow 4Cr^{3+} + 10H_2O + 3O_2 \quad (2)$$

Effects of TiO_2 dosage (Cr^{+6})

In the low concentration region illustrated in Figure 6 (0.1-1.0 g/L of TiO_2) the direct linear dependence of the removal percentage with the photocatalyst concentration is observed. On the other hand it was found that for relatively high concentrations (2.0-2.5 g/L of TiO_2) this behavior continues; Whereas for the highest concentration, which corresponds to 3.0 g/L of TiO_2, the removal percentage shows a tendency to decrease due to an excessive opacity of the solution which prevents titanium dioxide from the innermost part of the reactor being illuminated by directly affecting the reaction rate when the photocatalyst is in suspension Of shielding)[19].

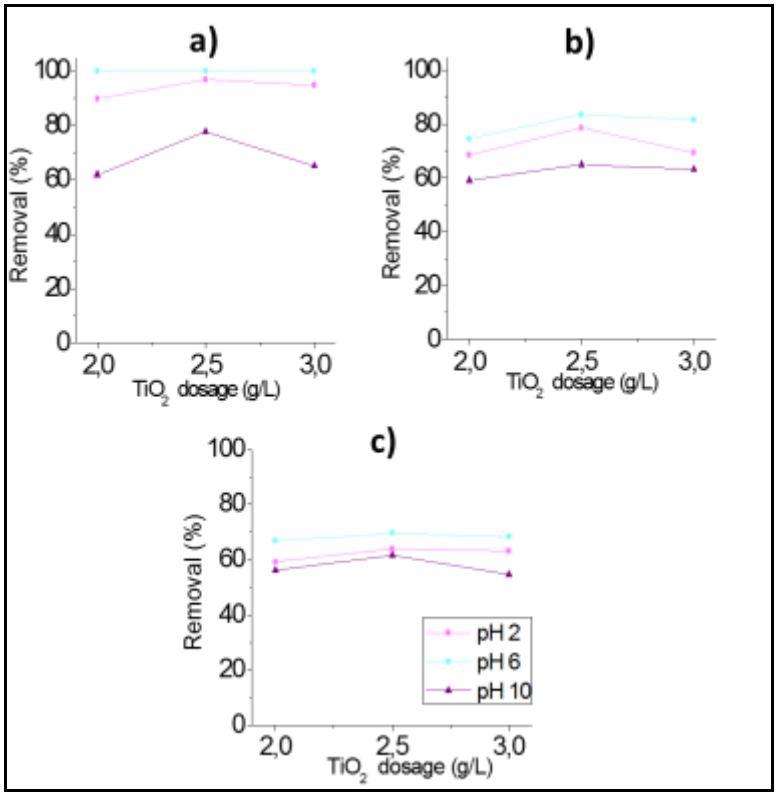

Figure 5. Removal percent for a Cr^{+6} initial concentration of: a) 5 mg/L, b) 15 mg/L, and c) 25 mg/L.

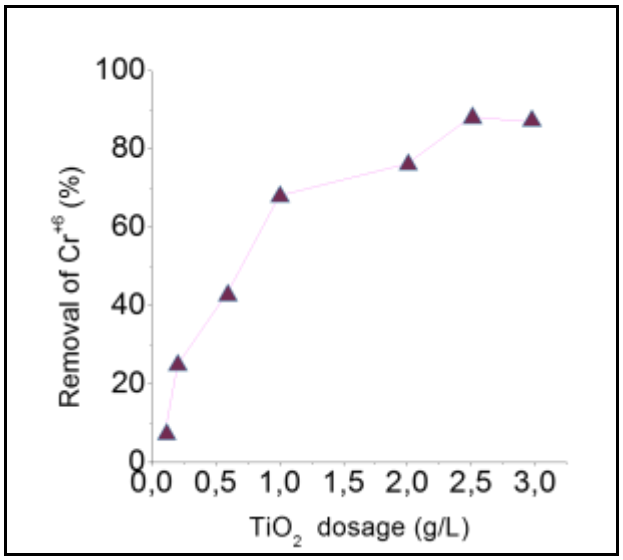

Figure 6. Removal percent based on TiO_2 dosage for an initial concentration of Cr (VI) equal to 5 mg/L and pH 2.

Effect of initial concentration (Cr^{+6})

Figure 7 shows the decrease in Cr (VI) concentration for different initial concentrations. It was also found that the lowest Cr (VI) initial concentration reaches a maximum removal percentage of 93.5% at 2 hours of photocatalytic treatment.

Langmuir-Hinshelwood Model (L-H) [20].

$$-\frac{dC_t}{dt} = r = k_r \frac{k_L k_t}{1 + k_L k_t} \qquad (3)$$

If,

$$k_L k_t \ll 1$$

$$-\frac{dC_t}{dt} = k_r\, k_L\, C_t \qquad (4)$$

If, t=0 and $C_t=C_0$, so:

$$Ln\left(\frac{C_0}{C_t}\right) = k_{Cr}\, t \qquad (5)$$

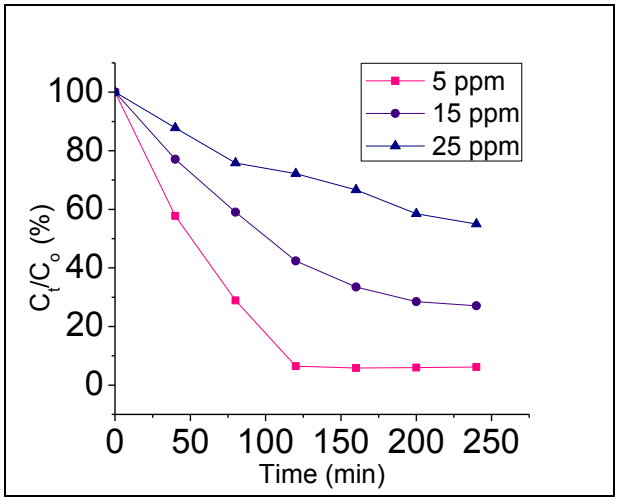

Figure 7. Cr^{+6} remaining at different illumination times for initial concentrations of 5 mg/L, 15 mg/L and 25 mg/L ppm, pH =2 and TiO_2 dosage = 2.5 g/L.

Figure 8 shows the Ln (C_o/C_t) as a function of lighting time. It is also possible to observe that the values of the rate constants decreased with the increase of the initial Cr (VI) concentration of 5 to 25 mg L^{-1}.

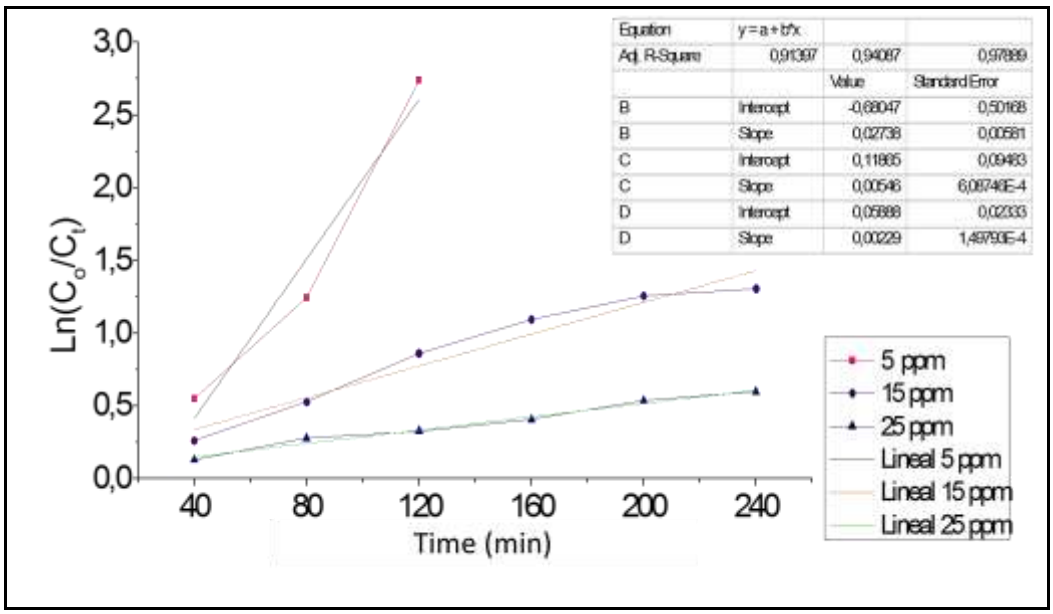

Figura 8. Ln (C_o/C_t) en función del tiempo de iluminación para el Cr^{6+}.

Adsorption experiment in dark (Zn^{+2})

Adsorption of divalent zinc for pHs 2 and 6 was negligible, with removal efficiencies close to 6.3% and 9.3%, respectively (Figure 9), which is attributed to the positive surface charge acquired by the TiO_2 DP25 In acid medium; This phenomenon generates repulsion forces that hinder the adsorption process of the divalent zinc on the surface of the TiO_2. On the other hand at pH 10 the adsorption phenomenon is not present but the precipitation of the ion due to its low solubility in basic medium.

Removal of Zn^{+2} using heterogeneous Photocatalysis.

The experimental data shown in Figure 10 reveals that the reduction of Zn^{+2} to zinc metal using sodium formate (formate ion) is negligible (<3% removal), since the standard potential for the reduction reaction of $Zn^{+2/0}$ is -0.76V, which means that the direct reduction of this metal ion (at its corresponding zero valence state) by the photogenerated electrons in TiO_2, is thermodynamically unfavorable[21].

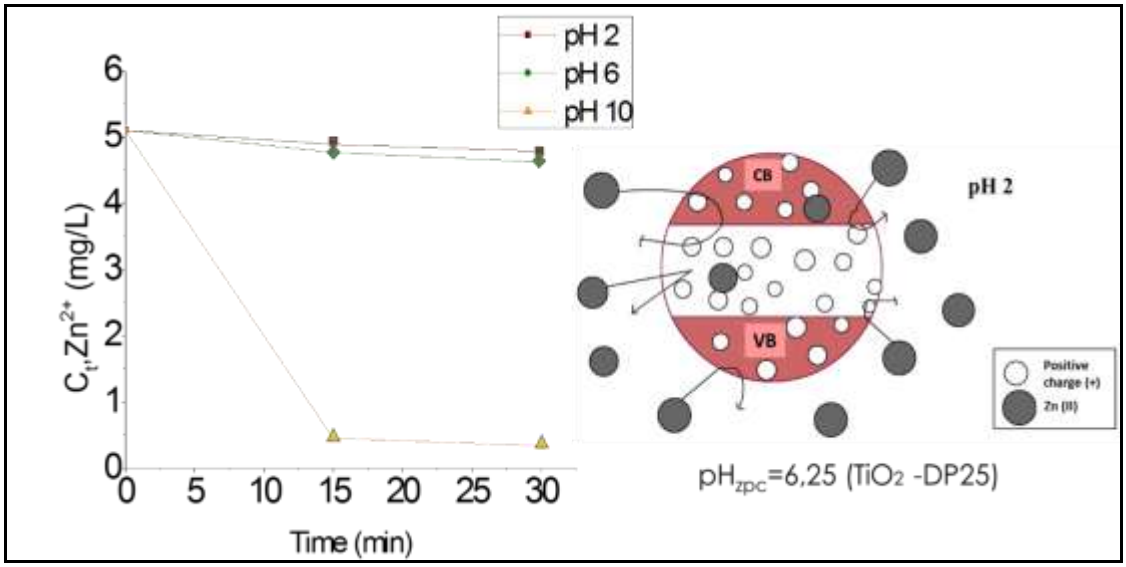

Figure 9. Adsorption experiment in dark for a Zn^{+2} initial concentration of 5 mg/L and 2.5 g/L TiO_2 dosage.

Conclusions

Heterogeneous photocatalysis is an excellent instrument for the removal of Cr^{6+} in aqueous solutions, when its concentration is relatively low, because for the initial concentration of 5 mg/L from Cr^{+6} is possible its total removal, while heterogeneous photocatalysis is not a good instrument for the removal of Zn^{2+}.

The catalyst dosing was found than the intermediate dose (2.5 g/L of TiO_2) is the most effective for the chromium case, due that the higher dosing (3.0 g/L) produces a shield effect made by the catalyst particles.

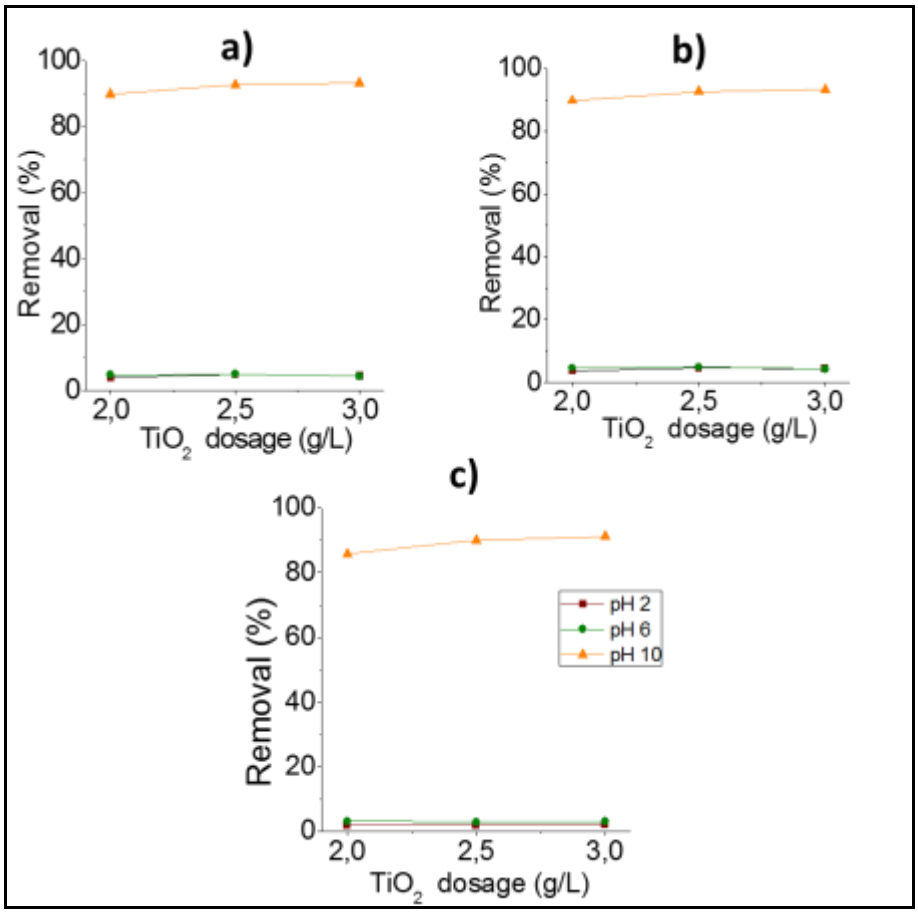

Figure 10. Removal percent for a Zn^{+2} initial concentration of: a) 5 mg/L, b) 15 mg/L and c) 25 mg/L.

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