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Removal of Cr(VI) and Humic Acid by Heterogeneous Photocatalysis in a Laboratory Reactor and a Pilot Reactor

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ABSTRACT: In this work heterogeneous photocatalysis has been used in order to eliminate Cr(VI) as well as humic acid in a laboratory reactor and in a pilot reactor. The reactors have been constructed with proportional geometric properties and similar nominal powers. In the laboratory reactor a kinetic study of the reduction of Cr(VI) to Cr(III) has been done for different concentrations of the catalyst at pH 4 and 7. The influence in the increase of the reduction of chromium(VI) that is obtained by the presence of humic acid has been determined. It has been verified that all the reactions possess pseudo-first-order kinetics, and the values of the apparent kinetic constants obtained for all systems studied have been compared. These values have allowed selection of the values of the variables to be used in the pilot reactor as it is desired to eliminate Cr(VI) by reduction and precipitation and humic acid by oxidation. A comparative evaluation of the efficiencies of the reactors was based on kinetic determinations.

■ INTRODUCTION

The accelerated growth of industry and the increasing worldwide concern for environmental conservation have revealed the great problem of water pollution by ions arising from metals. Metallic ions generally are not degradable and have an infinite lifetime. Also, while they increase their concentrations by numerous industrial processes, they produce a disturbing ecological imbalance in the environment. This situation occurs with chromium ions.[1]

Chromium is a heavy metal, naturally found in rocks, animals, plants, and soil, with multiple applications in industry. The three main forms of chromium are chromium(0), chromium(III), and chromium(VI). Chromium(III) is considered as necessary for human health in trace amounts, but the uptake of too much chromium(III) can cause adverse effects in human health as well, for instance, skin rashes. The International Agency for Research on Cancer (IARC) has listed chromium metal and its trivalent compounds within group 3 (The agent is not classifiable because of its carcinogenicity to humans.).[2]

Wastewater with chromium(VI) comes mainly from leather tanning, dyes from the textile industry, photoengraving processes, the electroplating industry, etc. It is dangerous for human health, and the International Agency for Research on Cancer (IARC) and the National Toxicology Program 11th Report on Carcinogens have classified chromium(VI) compounds as human carcinogens.[3]

Humic acids (HuAs) form yellow-brown aqueous solutions, and they are present in soils and natural waters. They are organic macromolecules with high structural complexity, and it has been determined that they possess multiple functional groups such as carboxylic, phenolic, hydroxyl, carbonyl, amine, amide, and others. Due to their polyfunctionality, HuAs are some of the most powerful chelating agents among natural organic substances. They are able to complex heavy metals[4,5] and halogens[6,7] and to form complexes with different solubilities and chemical and biochemical stabilities.

Nevertheless, they also can cause membrane plugging and fouling problems,[8] they can increase bacteria regrowth potential in distribution systems causing pipe corrosion,[9] and most importantly, they can react with chlorine (used for disinfection purposes) and originate mutagenic halogenated compounds.[10−12] It is, therefore, imperative that the concentration of humic substances is drastically reduced, and for this reason, to eliminate them from water, different technologies of treatment have been used such as enhanced coagulation, advanced oxidation,[13] adsorption,[14] biofiltration,[15,16] and membrane processes.[17] In general, biological treatment has been widely used for the removal of organic substances. However, this is limited in the case of removal of heavy metals and persistent organic compounds, which can give rise to a shock of load even at low concentrations.

Photocatalytic reduction of Cr(VI) has been widely studied in the presence of organic compounds. Most of the above studies reported that the reduction of Cr(VI) proceeds more quickly in the presence of organic compounds than that observed for Cr(VI) alone.[18−21]

Environmental problems from humic acids (HuAs) and fulvic acids are caused by the increased mobility of toxic heavy metals due to the complexation and formation of trihalomethane precursors during water treatment to produce potable water.

It has been demonstrated that UV/TiO_2 is a promising alternative purification and disinfection method for those systems.[17,19,22−25] Photocatalytic reactions have the advantage that they can simultaneously oxidize organic matter and reduce

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other contaminants, such as Cr(VI), as well as transform nonbiodegradable into biodegradable organic compounds.

Heterogeneous photocatalysis presents the interesting alternative of reducing Cr(VI) to Cr(III) that remains in solution and at high pH values is hydrolyzed and then precipitates[26−29] while mineralizing humic acid. In this technique UV radiation is absorbed by the catalyst TiO_2 particles with the production of electrons (e^-) transition from the valence band to the conduction band and the formation of holes (h^+). This is due to the UV irradiation of TiO_2 with an energy equal or superior to the band gap (>3.2 eV). This is followed by the formation of extremely reactive radicals (such as $OH^\bullet$) at the semiconductor surface and/or redox reactions.

In spite of the successful results obtained in the degradation of different contaminants, there is still much to do in technological applications, because photoreactor design is considerably more complex than the design of catalytic reactors.

In order to design a photoreactor, some structural elements, which rarely have ideal conditions, must be decided. For example, it must be decided if the catalyst used will be suspended or immobilized. The advantage of using immobilized catalysts is that separation and filtration processes after the photochemical treatment are saved. However, mass transfer is limited.

Frequently, to avoid radial gradients of concentration of reactants, turbulent flow or other designs such as bubbling are used. Undoubtedly, the geometry of the reactor will be strongly related to the irradiation source. In particular, the reactor must be designed in order to collect the maximum emitted light. The use of a lamp coaxial to the system has the advantage that there is no loss of the light dispersed by the catalyst as light reenters the system. Reactors with suspended catalysts have been studied in detail and, often, with flow in an annular space[30,31] around a linear lamp.

Developing an effective technology for the photocatalytic purification of water requires knowledge of optimal process conditions. This goal involves studying the kinetics that include the dependencies on the rate of photodegradation with different experimental conditions, e.g., the concentrations of the photocatalyst and reagent, light intensity, and reactor geometry.

In the present study, the order of the kinetic equation, the TiO_2 dosage, and the apparent rate constant (k_{app}) for the degradation of Cr(VI) with variation of the solution pH have been determined. Also, the effects of HuAs on the removal of Cr(VI) in the laboratory reactor have been studied. The obtained values have allowed selecting the values of the variables to be used in the pilot reactor, considering that it is desirable to eliminate the Cr(III) obtained by reduction of Cr(VI) and subsequent precipitation, and to eliminate humic acid by oxidation. The comparison of the performance of both reactors enables an approximation to the criterion of proportionality used in the construction of these reactors.

■ EXPERIMENTAL SECTION

Laboratory Reactor. A laboratory batch suspended solid reactor (LR) has been developed. It consists of a glass cylindrical recipient with a volume of 3 L and an internal diameter of 116 mm. The UV lamp (low pressure mercury lamp, 8 W at 253.7 nm) possesses a light intensity of 8×10^{-7} einstein/s (determined by actinometry, potassium ferrioxalate) and is protected by a quartz jacket, placed along the axis of the reactor. Particles remain in suspension by air bubbling. The temperature of operation was 24 ± 2 °C.

Pilot Reactor. After that, a column slurry pilot reactor (PR) was built. It consists of an acrylic cylindrical recipient with a volume of 15 L. The UV lamp (low pressure mercury lamp, 36 W at 253.7 nm) possesses a light intensity of 7×10^{-7} einstein/s (determined by the same methods used in the LR) and is protected by a quartz jacket, placed along the axis of the reactor.

Air from a porous plate placed at the bottom of the reactor was bubbled to keep particles in suspension. Sieve plates were placed along the reactor in order to keep a uniform size of bubbles (see Figure 1).

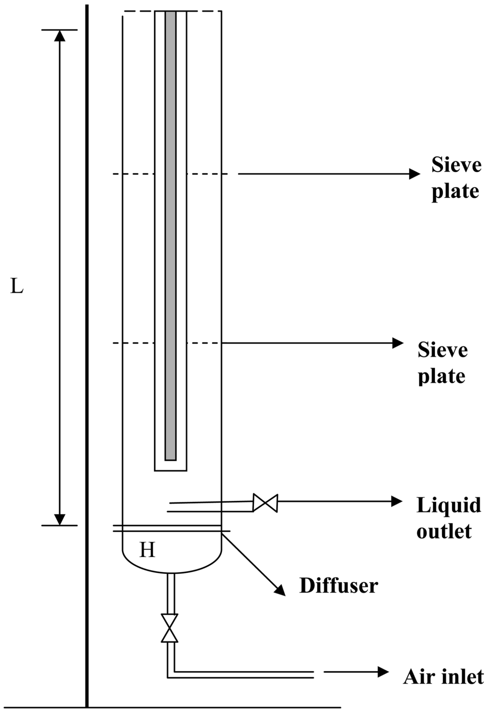

Figure 1. Column slurry 15 L pilot reactor, irradiated by an UV coaxial lamp enclosed within a quartz tube.

The LR and PR have similar geometric properties: the same relationship α of 1.4, with $\alpha = H/L$, where H is the height of the reactor and L is the lamp length, and the same geometric depth (0.043 m). The height and volume of the PR are 5-fold the height and volume of the LR.

Materials and Methods. Solutions of Cr(VI) were prepared from $K_2Cr_2O_7$ analytical grade (Fisher Scientific Co.) and deionized water (18 MΩ/cm). First, a 100 ppm stock solution of $K_2Cr_2O_7$ was prepared by weighing 0.2828 g of $K_2Cr_2O_7$ until 1 L of solution was measured. In all experiments, an initial Cr(VI) concentration of [Cr(VI)] = 10 ppm was used, and then an appropriate volume of stock solution was taken and diluted.

Humic acid (HuAs) (Fluka) solutions were prepared by dissolving 5 g of HuAs in 50 mL of a 0.025 M $NaHCO_3$ solution (analytical grade), and after it was sonicated for 30 min, an initial 100 ppm humic acid solution was obtained. Then, dilutions were made in order to obtain 10, 15, and 20 ppm HuAs solutions.

The photocatalyst used was P25 titanium dioxide, supplied by Evonik Degussa. It was dispersed in deionized water and sonicated for 20 min so that concentrations of 1, 1.5, 2, 2.5, 3, and 3.5 g/L TiO_2 were obtained.

The experiments were started by suspending the sonicated TiO_2. Then an appropriate volume of stock solution was taken in order to obtain an initial Cr(VI) concentration of [Cr(VI)] = 10 ppm. Water was added to complete the volume of the reactor, and the pH was adjusted with 0.1 N solution of $HClO_4$ (analytical grade) or 0.1 N solution of NaOH (analytical grade). Then, a lamp with its quartz jacket was placed inside the reactor and it was wrapped with an aluminum cover to avoid a radiation leak. A bubbler was connected for 60 min in darkness to ensure substrate−surface equilibration. The concentration of Cr(VI) in solution after equilibration was taken as the initial concentration.

The determination of the concentrations of both contaminants was carried out with a UV−vis Shimadzu UV2401 PC spectrophotometer. For Cr(VI), a colorimetric technique (APHA)[32] was used with a diphenylcarbazide solution. For the preparation of this solution 0.25 g of diphenylcarbazide (analytical grade) was weighed and was completed to a volume of 50 mL of solution with acetone (analytical grade). An absorbance of 305.6 nm was used for the humic acid, and a calibration curve was previously completed for concentrations from 0 to 20 ppm.

Samples for Cr(VI) analysis were taken from both reactors during irradiation at regular periods of 20 min up to 320 min. Each sample was filtered through a 0.2 μm pore size (MiniSart) membrane to remove titanium dioxide. After that, 10 mL of the filtrate was diluted 1:10 with deionized water up to 100 mL.

Immediately after, 95 mL of this dilution was taken, 2 mL of diphenylcarbazide solution was added, and the pH was adjusted to 2 ± 0.5 with a 10% aqueous solution of H_2SO_4 in order to produce the color development. Finally, the absorption spectra were recorded, and the absorbance values at 540 nm were taken. Previously, a calibration curve was done from solutions of known concentrations of Cr(VI). Also, a turbidity blank was prepared with a sample of Cr(VI) and kept at pH 2, without the addition of diphenylcarbazide.

Removal of Cr(III) has been done by precipitating $Cr(OH)_3$ at pH 9, and TiO_2 particles were eliminated by precipitating at pH 6.8. For the removal process, the reactor solution was transferred to a recipient. The solution was acidified to pH 6.8, so TiO_2 particles precipitated rapidly with chromium and humic acid adsorbed.

An aliquot of the supernatant solution was adjusted to pH 9 with 0.1 N solution of NaOH in order to precipitate Cr(III) as $Cr(OH)_3$. The solid particles were crystallized by water evaporation and dried, and the mass of $Cr(OH)_3$ was obtained by weighing.

The potassium ferrioxalate liquid chemical actinometer developed by Parker[33,34] was used in order to determine light intensities, whose values were 8×10^{-7} and 7×10^{-7} einstein/s for the laboratory reactor and the pilot reactor, respectively. All experiments were performed at 25 °C (±1 °C).

■ RESULTS AND DISCUSSION

Effect of Concentration of the Catalyst. The kinetics of Cr(VI) removal was studied using different concentrations of TiO_2 at pH 7. The following mass balance was used to understand and evaluate the concentration of Cr(VI) during the photocatalytic reaction:

$$[\mathrm{Cr(VI)}]_T = [\mathrm{Cr(VI)}]_S + [\mathrm{Cr(VI)}]_A + [\mathrm{Cr(III)}]_R \qquad (1)$$

where $[\mathrm{Cr(VI)}]_T$, $[\mathrm{Cr(VI)}]_S$, $[\mathrm{Cr(VI)}]_A$, and $[\mathrm{Cr(III)}]_R$ represent the total concentration of Cr(VI) used in the reaction, the concentration in solution, the concentration adsorbed, and the concentration of Cr(VI) reduced to Cr(III), respectively. The amount of Cr(VI) removed ($[\mathrm{Cr(VI)}]_{rem}$) was calculated by adding $[\mathrm{Cr(VI)}]_A$ and $[\mathrm{Cr(III)}]_R$.

At the beginning of the experiment a bubbler was connected for 60 min in darkness to ensure substrate−surface equilibration and the concentration of Cr(VI) in solution after equilibration was taken as the initial concentration. The concentration of chromium adsorbed is the difference between the total concentration and that obtained in this measurement. For this study, the concentration that exists at the time the lamp is turned on is considered the initial concentration.

The temporal concentration variation of Cr(VI) for the laboratory reactor is shown in Figure 2. As it is illustrated, the removal of Cr(VI) increases with the catalyst concentration up to the value of 1500 ppm, from which the degradation diminishes. The degradation increases with the concentration of TiO_2 due to the increasing availability of active sites up to a certain point, from which the blockage of the incident UV light increases and the catalysis decreases.

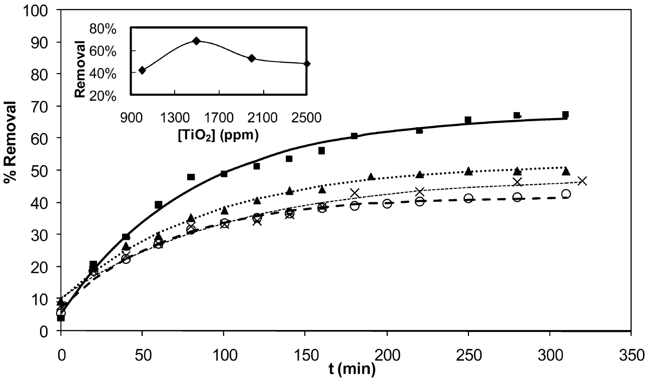

Figure 2. Removal of Cr(VI) as a function of illumination time. $[TiO_2]$ = (○) 1000, (■) 1500, (▲) 2000, and (×) 2500 ppm. (inset) Final removal (%) vs $[TiO_2]$ (ppm).

The determination of the kinetics of the reaction is an important datum for the design of reactors. Usually, the kinetic equation is expressed as

$$dC/dt = kC^n \qquad (2)$$

where dC/dt is the reaction rate, k is the kinetic constant, C is the substrate concentration, and n is the order of the reaction.

To obtain the reaction order and the kinetic constant of the reduction of Cr(VI) to Cr(III), the rates of removal ($d[\mathrm{Cr(VI)}]_R/dt$) as a function of concentration of Cr(VI) in solution ($[\mathrm{Cr(VI)}]_S$) for different concentrations of the catalyst have been graphed. As an example, Figure 3 shows the values obtained when $[TiO_2]$ = 1500 ppm. A computer fit of the data ($R^2 = 0.990$) indicates the pseudofirst order of the reaction and gives the apparent first-order rate constant $k_{app} = 0.012 \pm 0.001$ min^{-1}.

The pseudo-first-order kinetic equation can be written as follows:

$$-d[\mathrm{Cr(VI)}]/dt = k_{app}[\mathrm{Cr(VI)}] \qquad (3)$$

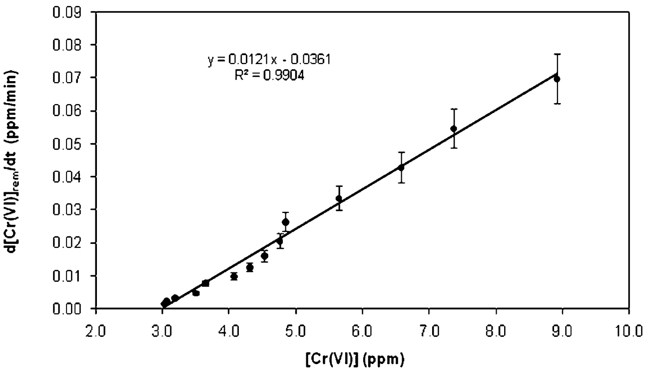

Figure 3. Rate of removal of Cr(VI) (d[Cr(VI)]$_{rem}$/d*t*) vs [Cr(VI)]$_{rem}$; [TiO_2] = 1500 ppm at pH 7.0.

The solution of eq 3 was graphed for the laboratory reactor using different concentrations of TiO_2 (Figure 4). The axis of the abscissa corresponds to the time of reaction, and the ordinate corresponds to ln([Cr(VI)](0)/[Cr(VI)](*t*)), which hereafter will be referred to as ln([Cr(VI)])(norm).

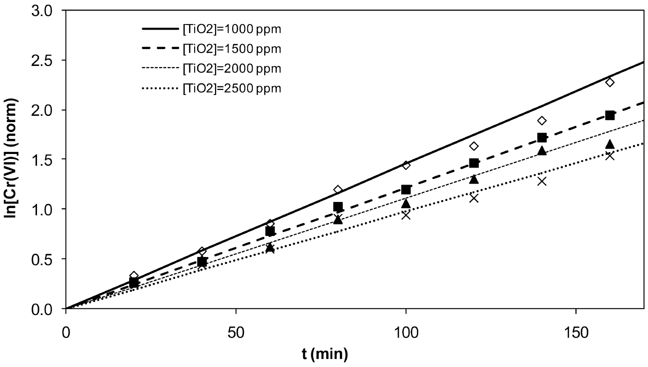

Figure 4. ln([Cr(VI)])(norm) as a function of time at pH 7 in the laboratory reactor. [TiO_2] = (○) 1000, (■) 1500, (▲) 2000, and (×) 2500 ppm.

It is demonstrated that the reaction is pseudofirst order for all concentrations of the catalyst, and the obtained k_{app} values are indicated in Table 1. The k_{app} values vary with the reactor geometry and operating conditions; however, the values that have been obtained have the same order of magnitude as those obtained in the literature.[35,36]

From the analysis of the values, for pH 7, we found that k_{app} decreases with [TiO_2] and for 1500 ppm the maximum removal of Cr(VI) (68%) is obtained, from which it decreases. This experimental observation is usually attributed to the increased blockage of the incident UV light used for the photocatalytic reaction.

Effect of pH. An important parameter in reactions taking place on semiconductor particulate surfaces is the pH of the suspensions, since this dictates the surface charge properties of the photocatalyst. The point zero charge (zpc) is at pH 6.5 for TiO_2.[37] Hence, at more acidic pH values, the particle surface is positively charged (Ti(IV)−OH + H^+ ↔ Ti(IV)−OH_2^+), while at pH values above 6.5, it is negatively charged (Ti(IV)−OH + HO^- ↔ Ti(IV)−O^- + H_2O).

This phenomenon significantly affect the adsorption−desorption properties of the catalyst surface, as well as the photoadsorption−photodesorption features of such surfaces.

The solution of eq 2 is graphed for different concentrations of the catalyst at pH 4 (Figure 5), which confirms that the reaction is pseudofirst order for all concentrations of TiO_2 tested. Figure 5 allows obtaining the values of k_{app} indicated in Table 1. At pH 4 the values of k_{app} reach a maximum value when [TiO_2] = 3000 ppm.

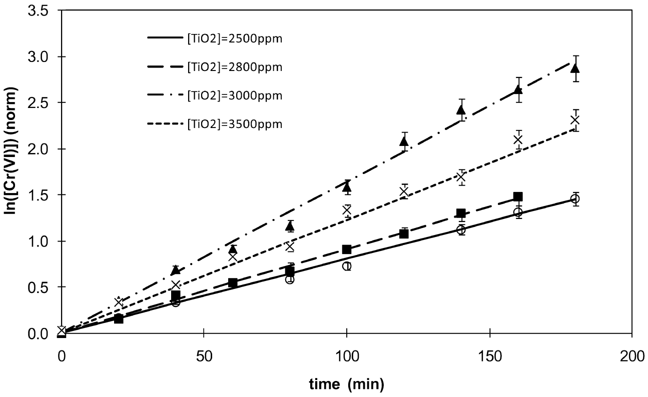

Figure 5. ln([Cr(VI)])(norm) as a function of time at pH 4 in the laboratory reactor. [TiO_2] = (○) 2500, (■) 2800, (▲)3000, and (×) 3500 ppm.

The higher percent removal of Cr(VI) at pH 4, compared with pH 7, is due to the fact that it increases the potential between the conduction band of TiO_2 and the potential of reduction of Cr(VI)/Cr(III).[26] Also, there is an effect of anionic adsorption of dichromate ion over the positively charged TiO_2 particles, while at pH 7 the particles of TiO_2 do not have net charge.[26]

Effect of Humic Acid in the Removal of Cr(VI) with Variation of pH. In order to accelerate the photocatalytic reduction of metal ions, many organic acids and alcohols were reported to be added in aqueous solution to serve as hole scavengers to inhibit the recombination of electrons and holes.[26] When HuAs are added to the photoreduction system, the possibility of capture of electrons by Cr(VI) can be promoted while part of the holes can be scavenged by HuAs and the photoreduction reaction rate of Cr(VI) is subsequently

Table 1. First Order Reaction Rate Constant (k_{app}) and Percent Removal of Cr(VI) Obtained for Different Catalyst Concentrations at pH 7 and pH 4

pH 7				pH 4			
[TiO_2] (ppm)	k_{app} (1/min)	R^2	Cr(VI) rem. (%)	[TiO_2] (ppm)	k_{app} (1/min)	R^2	Cr(VI) rem. (%)
1000	0.0146 ± 0.0010	0.991	42	2500	0.0081 ± 0.0006	0.997	99
1500	0.0122 ± 0.0010	0.990	68	2800	0.0091 ± 0.0002	0.998	98
2000	0.0111 ± 0.0005	0.996	52	3000	0.0164 ± 0.0010	0.996	99
2500	0.0098 ± 0.0011	0.982	48	3500	0.0123 ± 0.0020	0.997	99

increased. Therefore, heterogeneous photocatalysis possesses the advantage of reducing metallic ions and, simultaneously, oxidizing organic substances, in a simple and economical way.

For this system, the photocatalytic reaction of Cr(VI) at pH 4 and at pH 7 follows a pseudo-first-order kinetics for all concentrations of HuAs tested (Figure 6). The obtained k_{app} values are presented in Table 2, and it is noted that k_{app} and, hence, the reaction rate and the percent removal increase with HuAs concentration up to 15 ppm at pH 7 and up to 20 ppm at pH 4, from which they decrease. Similar effects have been observed in the literature.[26,38]

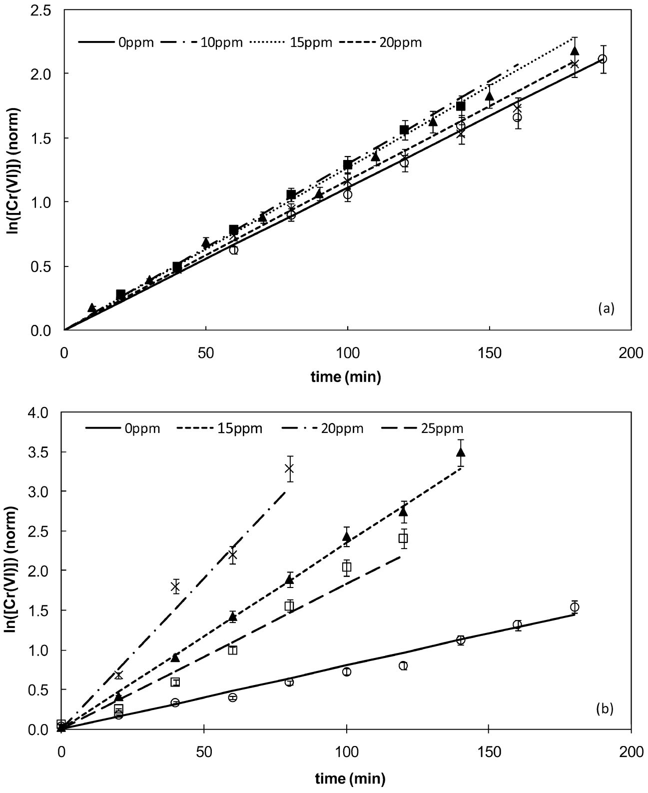

Figure 6. ln([Cr(VI)])(norm) as a function of time at (a) pH 7, $[TiO_2]$ = 2000 ppm, and (b) pH 4, $[TiO_2]$ = 2500 ppm, in the laboratory reactor. [HuAs] = (○) 0, (■) 10, (▲) 15, (×) 20, and (□) 25 ppm.

From the comparison of k_{app} values with and without HuAs at pH 7 and pH 4, the increase of kinetic constants of reaction produced by the increase of [HuAs] at both values of pH is evident, being more outstanding at pH 4. Thus, the rate increases since the kinetics is, in all cases, a first-order reaction.

The enhancement of the removal of Cr(VI) at both pH values in the presence of HuAs reveals the importance of HuAs acting as sensitizers in the photocatalytic reduction of Cr(VI) to Cr(III). The HuAs in solution or the HuAs adsorbed onto TiO_2 can be oxidized by oxidant radicals such as $OH^{\bullet}$ or positive holes (h^+). One of the ways accepted for HuAs oxidation is due to the reaction with positive holes. The direct oxidation of HuAs by positive holes and then the elimination of holes cause a reduction in the electron−hole recombination and thus an increase in the number of electrons that reduce chromium. This results in a photocatalytic efficiency increased in spite of the competition of HuAs and Cr(VI) for the active sites of TiO_2.[26]

The photocatalytic degradation and mineralization of HuAs adsorbed on TiO_2, mainly by carboxylate groups, also produce smaller molecules, one photodegraded and one photoresistant.[39]

Pilot Reactor. The values obtained in the laboratory reactor have allowed us to choose the concentrations of $[TiO_2]$ = 1500 ppm and [HuAs] = 15 ppm. Since it is desired to eliminate both contaminants and Cr(III) precipitates at pH 9, it was decided that it is more convenient to conduct the experiment at pH 7 in spite of the higher percent removal obtained at pH 4.

The obtained data are graphed in Figure 7. The value obtained R^2 = 0.976 indicates that the linear relation is correct.[41] Therefore, this reaction presents a pseudo-first-order kinetics with k_{app}= 0.014 min^{-1}.

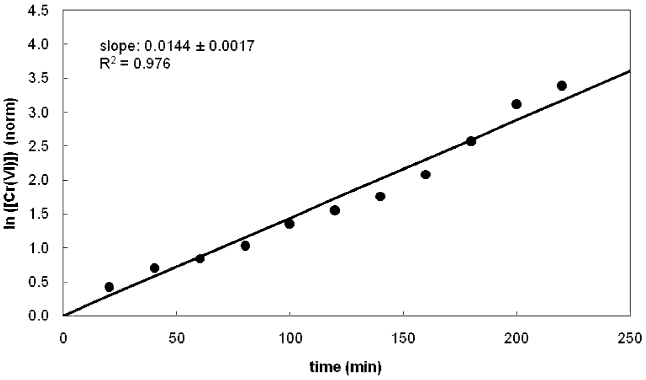

Figure 7. ln([Cr(VI)])(norm) as a function of time for the pilot reactor.

Cr(III) and TiO_2 were removed by precipitation, and the concentrations of Cr(VI) and HuAs in the solution were measured in both reactors. The following mass balance can be used in order to evaluate the removals of HuAs in the photocatalytic process.

$$[HuAs]_T = [HuAs]_S + [HuAs]_O + [HuAs]_A \tag{4}$$

Table 2. First Order Reaction Rate Constant (k_{app}) and Percent Removal of Cr(VI) Obtained for Different HuAs Concentrations at pH 7 and pH 4

pH 7, $[TiO_2]$ = 2000 ppm				pH 4, $[TiO_2]$ = 2500 ppm			
[HuAs] (ppm)	k_{app} (1/min)	R^2	Cr(VI) rem. (%)	[HuAs] (ppm)	k_{app} (1/min)	R^2	Cr(VI) rem. (%)
0	0.0111 ± 0.0005	0.996	52	0	0.0081 ± 0.0006	0.985	99
10	0.0130 ± 0.0030	0.995	78	10	0.0210 ± 0.0010	0.997	99
15	0.0127 ± 0.0008	0.995	91	15	0.0230 ± 0.0010	0.997	99
20	0.0117 ± 0.0005	0.996	82	20	0.0380 ± 0.0060	0.991	99
				25	0.0180 ± 0.0020	0.972	99

Table 3. Percent Removal of Cr(VI) and HuAs for Laboratory Reactor and Pilot Reactor

	$[\mathrm{Cr(VI)}]_S$ (ppm)	$[\mathrm{Cr(VI)}]_A$ (ppm)	$[\mathrm{Cr(VI)}]_R$ (ppm)	Cr(VI) rem. (%)	$[\mathrm{HuAs}]_S$ (ppm)	$[\mathrm{HuAs}]_{rem}$ (ppm)	Cr(VI) rem. (%)
laboratory reactor	0.19	0.88	8.93	98	1.24	13.08	87
pilot reactor	1.11	0.32	8.57	97	2.09	12.95	86

where $[\mathrm{HuAs}]_S$, $[\mathrm{HuAs}]_A$, and $[\mathrm{HuAs}]_O$ represent the concentrations of total HuAs, HuAs in the aqueous solution, HuAs adsorbed, and HuAs oxidized, respectively. The amount of HuAs removed, expressed as $[\mathrm{HuAs}]_{rem}$, was calculated by the summation of $[\mathrm{HuAs}]_A$ and $[\mathrm{HuAs}]_O$. Equations 1 and 4 allow calculation of the Cr(VI) adsorbed and HuAs removed, which are indicated in Table 3.

The values indicated in Table 3 show that $[\mathrm{Cr(VI)}]_A$ is greater for the LR (0.88 ppm) than for the RP (0.32 ppm), whereas the opposite effect is observed with respect to $[\mathrm{Cr(VI)}]_S$ (0.19 and 1.11 ppm, respectively). This is probably due to greater efficiency in the agitation of the PR. The same trend has been verified for the HuAs. For this compound the results confirm that the photodegradation leads to two kinds of smaller molecules, some easily photodegradable and other photoresistant.[39]

Comparing the values of Cr(VI) removal of 98 and 97% for the laboratory reactor and for the pilot reactor, and the values for HuAs of 87 and 86%, respectively, gives satisfactory results.

The reactors have been built with the same geometric path. Under the conditions of our work, the intensity for the LR and PR was 8×10^{-7} and 7×10^{-7} einstein/s, respectively. In these reactors the phenomena of absorption, reflection, and scattering are difficult to evaluate using the radiative transfer equation[40] due to the presence of air bubbles which keep TiO_2 in suspension. Similar values of pollutant removal in both reactors allow us to assume that excited catalyst particles are similarly distributed in both reactors, resulting in the high values of removal.

■ CONCLUSIONS

In order to study the degradation of Cr(VI) and HuAs, a laboratory reactor and a pilot reactor were constructed. They are tubular, noncontinuous, with mercury low pressure mercury lamps and coaxial with them, and have the same relationship between the height of the reactor and the lamp length. They possess the same geometric depth; the volume and height of the pilot reactor are 5-fold the volume and height of the laboratory reactor. The oxygenation and suspension of particles are achieved by air bubbling. As experimentally demonstrated, light intensities are similar in both reactors.

It was determined that the degradation of Cr(VI) in the laboratory reactor at pH 4 and pH 7 presents pseudo-first-order kinetics for all the $[TiO_2]$ studied. It was verified that the apparent rate constants (k_{app}) at pH 7 decrease with $[TiO_2]$ but the removal of Cr(VI) is maximum for $[TiO_2] = 1500$ ppm and from that they decrease. At pH 4 the highest value of k_{app} was obtained for $[TiO_2] = 3000$ ppm and the removal obtained was 99%. The greater removal obtained at pH 4 is due to a higher potential between the conduction band of TiO_2 and the potential of Cr(VI)/Cr(III) that exists at lower pH and to the effect of anionic adsorption of dichromate ion over positively charged particles of TiO_2.

Humic acids favor the efficiency and velocity of degradation of Cr(VI). At pH 4, where we obtained $k_{app} = 0.02$ min^{-1} for $[TiO_2] = 2500$ ppm, $[\mathrm{HuAs}] = 15$ ppm compared to $k_{app} = 0.008$ min^{-1} for the same $[TiO_2]$ without HuAs. At pH 7, for $[TiO_2] = 2000$ ppm, 91% of Cr(VI) was removed using HuAs and 52% of Cr(VI) was degraded without HuAs. This is because HuAs act as scavengers of h^+ and thus prevent the recombination of electrons.

The values obtained in the laboratory reactor allowed programming the experiment in the pilot reactor. We decided to carry out the removal at pH 7, because it is a more favorable condition for the precipitation of Cr(III). The values of removal of Cr(VI) in the laboratory reactor and in the pilot reactor were 98 and 97% and for HuAs they were 87 and 86%, respectively.

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Notes

The authors declare no competing financial interest.

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