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# Photocatalytic treatment of industrial wastewater containing chromium as a model pollutant-effect on process parameters and kinetically studies

Rubina Chaudhary<sup>a)</sup> and Rajendra Singh Thakur<sup>b)</sup>

School of Energy and Environmental Studies, Devi Ahilya University, Takshshila Campus, Khandawa Road, Indore, Madhya Pradesh 452001, India

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This study has focused on treatment of the metal ions, which have infinite lifetimes and build up their concentrations in food chains to toxic levels. Many researches have been performed about use of photocatalysis processes in treatment of industrial wastewater. The additional advantage is coming from sensitivity of the Cr(VI) photo reduction to the surface catalytic effects or to the presence of an additional electron donor and acceptors; then, a synergistic effect was observed in two- or multicomponent systems. The efficiency of total chromium reduction by photo catalytic treatment under UV-light in different degradation systems, UV, TiO<sub>2</sub>/UV, H<sub>2</sub>O<sub>2</sub>/UV, TiO<sub>2</sub>/citric acid/UV, and TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV, was studied and compared. Even when the TiO<sub>2</sub>/citric acid/H<sub>2</sub>O<sub>2</sub>/UV reaction happened to be the most efficient process, both homogeneous and heterogeneous photocatalysis can be considered as suitable methods to reach the complete mineralization of the solutions. Maximum treatment efficiency of total chromium reduction with increasing citric acid concentration from 20 to 80 mg/l was reduced to 62%, 76.7%, 77.91%, and 100%, and with increasing H<sub>2</sub>O<sub>2</sub> concentration from 20 to 100 ml/l was reduced to 40.57%, 41.84%, 50.77%, 61.03%, and 100%, which is more efficient than the H<sub>2</sub>O<sub>2</sub>/UV process. Finally, the combination of TiO2/citric acid/H2O2/UV result was observed more efficient than the TiO<sub>2</sub>/citric acid and TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV processes in the solutions. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4757629]

#### I. INTRODUCTION

The photochemical degradation of pollutants using semiconducting powders as catalysts is a subject of current interest. The photo catalytic method is based on the reactive properties of electron–hole pairs generated in the semiconductor particles under illumination by light of energy greater than the semiconductor band gap. These charge carriers can reach the particle surface and react with species in solution with suitable redox potentials.<sup>1</sup> The process has a potential of accomplishing two decontamination reactions, i.e., conversion of organics to water, carbon dioxide and dilute mineral acids, and reduction of the metals to their non-toxic forms.<sup>2</sup> This has been successfully applied to the degradation of organic or inorganic pollutants. The photo catalytic degradation technology might be feasible for the treatment of wastewater containing hazardous contaminants at medium or low pollutant concentrations when biological treatment is impossible. The use of advanced oxidation process (AOP) for wastewater treatment has been studied extensively, but generation of UV radiation by lamps. Therefore, research is focusing more and more on those AOPs, which can be driven by UV irradiation, i.e., light with a wavelength longer than 300–400 nm, heterogeneous, homogenous catalysis, and photo-fenton. Whenever different semiconductor or materials have been tested under comparable conditions

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<sup>&</sup>lt;sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: rubina\_chaudhary@yahoo.com. Telephone: +91-731-2460309. Fax: +91-731-2460737.

<sup>&</sup>lt;sup>b)</sup>Email address: rsthakur.sees@gmail.com. Telephone: +91-9977480205.

for the degradation of the same compounds,  $TiO_2$  has generally been demonstrated to be the most active.<sup>3</sup> There are few papers concerning decontamination of complex systems, which, however, are the actual situation of the real environmental pollution.<sup>1</sup> Metal ions have infinite lifetimes and build up their concentrations in food chains to toxic levels. As a result, in today's highly industrialized society, we are living in an environment with a multitude of potentially harmful toxic metal ions.<sup>4</sup> Cr(VI) is a very toxic pollutant, which is present in a great variety of industrial wastes.<sup>1</sup> The environmental importance of this process derives from the variety of sources which generate Cr(VI) in effluent streams: chrome plating, electronic, metallurgical, pigment, paint, timber, and leather tanning industries. Chromium occurs in two common oxidation states in nature, Cr(III) and Cr(VI). Cr(VI) is toxic and carcinogenic. On the other hand, Cr(III) is readily precipitated or absorbed on a variety of inorganic and organic substrates at neutral or alkaline *p*H.

The catalytic photo-reduction of Cr(VI) to Cr(III) has been proved to be a practical and clean alternative. The catalytic materials usually used for Cr(VI) photo-reduction are metal oxides and metal sulphates, including ZnO, TiO<sub>2</sub>, WO<sub>3</sub>, and CdS.<sup>5</sup> Moreover, photo reduction of the Cr(VI) species is accompanied by oxidation of the electron donor, which creates a possibility of photo degradation of many organic pollutants. The additional advantage is coming from the sensitivity of the Cr(VI) photo reduction to the surface catalytic effects or to the presence of an additional electron donor and acceptors; then, a synergistic effect was observed in two- or multi-component systems.<sup>4,6</sup> The nature of the carboxylic acid used as the sacrificial agent seems to play a very important role in the photo reduction of Cr(VI). Citric acid leads to higher conversion rates without deactivation of the catalyst.<sup>7</sup>

There are many works based on supported  $TiO_2$  catalysts, in which a variety of supporting materials, coating methods, and reactor arrangements have been investigated from both engineering and fundamental points of view.<sup>8</sup> Therefore, the purpose of this study has emphasized on the capability of UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> process to meet the discharge standards for the disposal of spent reactive dye effluents into water courses.<sup>9</sup> The study focused on the identification of possible intermediate products and on the determination of inorganic ions formed during the process. Although many researches have been performed about use of photocatalysis processes in treatment of industrial wastewaters, this study should be regarded novel, because the efficiency of UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> process has been determined for the first time in simultaneous removal of phenol as an organic pollutant and heavy metals as inorganic pollutants under different conditions of treatment.<sup>10,11</sup> Among these AOPs, the combined systems UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> and UV/Fe<sup>3+</sup>/H<sub>2</sub>O<sub>2</sub> are most utilized for environmental applications since they use the UV component of UV light. A wide range of applications have been reported for different compounds using these systems, i.e., direct UV, TiO<sub>2</sub>/UV, TiO<sub>2</sub>/(citric acid)/UV, H<sub>2</sub>O<sub>2</sub>/UV (photo-fenton), and TiO<sub>2</sub>/UV/H<sub>2</sub>O<sub>2</sub> processes.

A brief outline of the redox process of photo catalytic reduction of dissolved metal ions is as follows: Metal ions are reduced by capturing the photo-excited conduction band electrons and water is oxidized by the valence band holes.<sup>15</sup> If organics are absent, water will be slow oxidized. This is a kinetically slow four-electron process, and the competing recombination of the photo generated holes and electrons plays an active inhibiting role.<sup>10</sup> Some studies have found that the addition of organic acids can enhance the photo catalytic reduction rate. When citric acid was added into the reduction system, the possibility of electron capture by chromium was promoted because hole was scavenged by additive and photo catalytic reduction rate of chromium was subsequently increased for TiO<sub>2</sub>/citric acid/ UV.<sup>17</sup> The possibility is that the initial oxidation of the organic additives by the photo generated holes in  $TiO_2$  (or by the •OH radicals) generates radical species with strong reducing power.<sup>18</sup> For example, the reduction potential of  $HCOO \cdot /CO_2$ , formed due to oxidation of formic acid, is -1.7 V vs. Standard Hydrogen Electrode (SHE),<sup>19</sup> which is negative enough to reduce Cr(VI).<sup>20</sup> This could also be a possible route for metal reduction in the presence of organics.  $H_2O_2$  may also be split photolytically to produce •OH radicals directly. It should be taken into consideration that photo catalytic oxidation will be inhibited via the reaction of excess  $H_2O_2$  with OH radicals and  $h_{VB}+$ .<sup>21</sup>

#### **II. MATERIALS AND METHODS**

The industrial wastewater was obtained from a chrome plating industry, and the samples were obtained from the collection tank before entering the treatment cycle. The major wastewater contaminate was chromium. Titanium dioxide (Merck) was used as a photo catalyst in this study. The kinetics of the reduction and oxidation processes for obtaining efficient detoxification of the chromium in the presence and in the absence of a hole scavenger, hydrogen peroxide, and factors affecting the photo catalytic reaction were studied.<sup>22</sup> Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was used as an oxidant and citric acid (Merck) as a hole scavenger for increasing the reaction rate. Besides its low cost and non-toxic nature, the choice of citric acid was made, because it does not form any harmful complexes, which could cause catalyst deactivation unlike aromatic compounds.<sup>23</sup> These aspects were considered during the experimental design. The TiO<sub>2</sub> catalyst dose was varied in the concentration of 2 g/l. The dose of citric acid was varied in the concentration of 2 g/l. The dose of citric acid was varied in the concentration of 2 g/l. The dose of citric acid was varied in the concentration of 2 g/l.

Thereafter, dark adsorption photolytic and photo catalytic reduction was also investigated. The experiments were carried out at natural pH for both adsorption and photo catalytic reduction. No attempt was made to adjust the pH of industrial wastewater. The results of this study facilitated the designing of further experiments.

Fig. 1 shows a schematic diagram of the setup consists of a UV lamp box type reactor made up of wooden insulated by thermo coal sheet having dimensions of  $3 \text{ ft} \times 3 \text{ ft} \times 3 \text{ ft}$  consisting inside of two UV lamps, input power of each lamp was 15 W (F15T8/GL/WS, Philips) of wavelength ( $\lambda < 380 \text{ nm}$ ), fitted in parallel on the back side wall and top of the box. In order to reveal the photo catalytic degradation behaviour, the photo degradation reaction was conducted under ambient condition in a lamp-housing box. The photo reactor and the UV lamps were enclosed in a box to ensure safe operation and to prevent the entrance of extraneous light. Measurement of UV light intensity was done by digital lux meter (DLM2). The obtained intensity was at approximately  $30 \text{ W/m}^2$ .

Batch type reactor was carried out in six 500 ml capacity conical flask. The experiments were performed in day time. Constant stirring of solution had been operated continuously by using simple magnetic stirrers for proper mixing. Temperature and pH levels were measured using a digital temperature indicator and pH meter (digital pH-systronics model-335). The metal concentration was analysed using atomic absorption spectrophotometer (Shimadzu AA 6300). Chemical oxygen demand (COD) was measured before and after the treatment according to close reflux method followed by standard methods. The same photo catalytic experimental set up was employed in industrial and synthetic wastewater treatment. During the experiment, wastewater was suitably diluted in order to facilitate light penetration.

	Testing variables					
Objective of the experiment	Catalyst: T	Hole scavenger: CA	Oxidant: HP			
To determine the kinetic	2 g/l	0 mg/l	0 ml/l			
parameters total chromium		20 mg/l	20 ml/l			
reduction based on the L-H		40 mg/l	40 ml/l			
model by increasing the opti- mum dose of hole scavenger and oxidant used in single and with combinations		60 mg/l	60 ml/l			
		80 mg/l	80 ml/l			
		100 mg/l	100 ml/l			
		120 mg/l				
		140 mg/l				

TABLE I. Study of the experimental plan and variation dose (where  $T = TiO_2$  photocatalyst, CA = citric acid,  $HP = H_2O_2$ ).



FIG. 1. The apparatus of UV light irradiation. 1. Wastewater without any catalyst, 2. Wastewater with  $TiO_2$  catalyst, 3. Wastewater with  $H_2O_2$  oxidant, 4. Wastewater with  $TiO_2$  catalyst and citric acid as hole scavengers, 5. Wastewater with  $TiO_2$  catalyst and  $H_2O_2$  oxidant, 6. Wastewater with  $TiO_2$  catalyst,  $H_2O_2$  oxidant and citric acid as hole scavengers. T-1.Thermometer (settled in canter side), T-2. Thermometer (settled in right side). (a) 15 W UV Lamp (settled in centre side on roof in horizontal direction) and (b) 15 W UV Lamp (settled in back side in vertical direction).

#### **III. RESULTS AND DISCUSSION**

#### A. Dark adsorption

Study of chromium dark adsorption was performed in the presence of  $TiO_2$  catalyst, citric acid, and  $H_2O_2$ . This process was used for similar to all the experiments and before an initiation period of 1 h (in dark, i.e., UV light irradiation was started after 1 h). However, the time and experimental conditions of adsorption and photo reduction were identical. No more effect on this process but beneficial role of citric acid and  $H_2O_2$  in photo reduction was found to be remarkable. For example, the amount of chromium initially adsorbed on  $TiO_2$  (in the dark) was affected as the citric acid (Fig. 2) and  $H_2O_2$  (Fig. 3) were added. The results showed that adsorption of total chromium on  $TiO_2$  surface in the presence of citric acid was found to increase initially but decreased after a particular concentration of citric acid. The experiment



FIG. 2. Dark adsorption of chromium with different ratios of citric acid:  $TiO_2 = 2 g/l$ ,  $H_2O_2 = 60 ml/l$ , citric acid = variable.



FIG. 3. Dark adsorption of chromium with different ratios of  $H_2O_2$ :  $TiO_2 = 2 g/l$ , citric acid = 60 mg/l,  $H_2O_2$  = variable.

with  $H_2O_2$  was same to citric acid reaction. It can be seen that the concentration at which maximum adsorption was occurred on citric acid concentration of 40–60 mg/l and  $H_2O_2$  of 60 ml/l. The adsorption, therefore, clearly is not the single key to securing high photo catalytic conversion yields. In terms of mg/l of total chromium adsorbed, the adsorption was more for higher initial concentration of citric acid and  $H_2O_2$ . The adsorption was reduced due to decrease in *p*H at higher concentration of citric acid and  $H_2O_2$ .

#### B. Photolytic interactions of chromium

In order to investigate any other reactions like, photolytic interactions, among total chromium, were carried out blank experiments in the absence of photo catalyst, citric acid, and  $H_2O_2$ . The results for total chromium reduction for photolytic experiments in the absence of citric acid and  $H_2O_2$  are depicted in Figs. 4 and 5. It can be observed that UV radiations reduce total chromium to 5.82% and show that reaction was found very slow on 5 h without TiO<sub>2</sub>. In



FIG. 4. Percentage reduction of chromium with time for different ratios of citric acid:  $TiO_2 = 2 g/l$ ,  $H_2O_2 = 60 ml/l$ , citric acid = variable.



FIG. 5. Percentage reduction of chromium with time for different ratios of  $H_2O_2$ :  $TiO_2 = 2 g/l$ , citric acid = 60 mg/l,  $H_2O_2 = variable$ .

addition, pH remained unchanged throughout the irradiation. It can be affirmatively said that the process was satisfactory, which results with photo catalytic and nonphotolytic.

#### C. TiO<sub>2</sub>-UV system for reduction of chromium

After assuring that the process is truly photo catalytic, experiment was performed for total chromium reduction on  $TiO_2$  surface. The experiments performed in the absence of citric acid supported that the electron hole recombination predominated with water as a reducing agent. The results for total chromium reduction during experiments are depicted in Figs. 4 and 5. In the absence of citric acid and in the presence of  $TiO_2$ , total chromium was found to reduce 12.92% in UV exposure throughout 5 h. Although the average UV irradiation in this experimental run was similar to other experiments, yet the reaction rate was significantly enhanced with the addition of  $TiO_2$ . The electron hole recombination acted as an active inhibitor in absence of a hole scavenger.

#### D. H<sub>2</sub>O<sub>2</sub>-UV system for reduction of chromium

Light absorbed by a molecule can result in electronic excitation, which increases the molecule's ability to lose or gain electrons. This makes the excited state more suitable as an oxidizing or reducing agent, which in turn makes it more likely and a highly reactive species such as the hydroxide radical (OH•) can be produced from an electron transfer process between the excited state and the contacting medium.<sup>24</sup> The results obtained by treating the sample with UV alone and in combination with  $H_2O_2/UV$  are reported. From Figs. 4 and 5, it is possible to observe that the action of UV alone did not show any reduction capacity, although  $H_2O_2$  can be a relatively powerful oxidant. The combination  $H_2O_2/UV$  was found to be effective in the reduction of total chromium in wastewater than UV alone. The rate of photo catalytic reduction of total chromium, adding 18.98% of  $H_2O_2$  concentration from 20 to 100 ml/l reduces 9.52%, 12.19%, 33.44%, 41.84%, and 47.50%, respectively, and it observed that reaction was found satisfactory on 5 h of UV irradiation without TiO<sub>2</sub> dose. In addition, *p*H remained unchanged throughout the irradiation period.

#### E. TiO<sub>2</sub>-citric acid-UV for reduction of chromium

Citric acid used in this study had a pronounced effect on reduction rate and probably attenuated the electron-hole recombination by donating electrons, which directly fill the

valence band. The beneficial role of the organic additive was quite striking. With the addition of citric acid, the reduction rate was significantly enhanced. On increasing the citric acid concentration further, the rate of reduction was also significantly enhanced. The faster degradation can be attributed to minimum electron-hole recombination due to sufficient concentration of hole scavenger. The reaction apparently followed partial order for low citric acid concentration and zero order for higher citric acid concentration indicating that the role of citric acid for lowering the solution pH was more effective at higher concentrations thereby making the conditions favourable for total chromium reduction. The results for total chromium reduction during experiments for the initial concentration: the percentage of increase was from 12.92% (without citric acid) to above concentration of 20-100 mg/l for 58.56%, 73.51%, 75.73%, 88.29%, and 100%, for the UV exposure throughout 5 h shown in Fig. 4. The citric acid concentration of 100 mg/l showed that complete reduction of total chromium was achieved in 5 h. There was a steep decrease in the total chromium concentration in the first 2-3h, which contributed a maximum reduction to the UV, TiO<sub>2</sub>/UV, and H<sub>2</sub>O<sub>2</sub>/UV. Citric acid also decreases the solution pH, thereby favouring total chromium reduction. Almost complete reduction of Cr(VI) in the presence of citric acid is also reported by Colon et  $al.^{23}$ The trends of reduction were similar but the quantity of citric acid required for complete reduction of total chromium was found to increase with increasing concentration. The total chromium concentration in the solution was obtained below permissible limit after photo catalytic reduction.

#### F. TiO<sub>2</sub>-H<sub>2</sub>O<sub>2</sub>-UV system for reduction of chromium

In both homogenous and heterogeneous processes, the •OH radicals are the main responsible for the redox reaction. This clearly indicates that photocatalysis can also be regarded as an applicable process for metals treatment. The efficiency of chromium reduction could be improved to a certain extent by addition of more H<sub>2</sub>O<sub>2</sub> and TiO<sub>2</sub>. Introducing TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV process improves mineralization rates, as H<sub>2</sub>O<sub>2</sub> addition increases OH production. After 5 h, a 78% total organic carbon (TOC) removal is achieved.<sup>13</sup> The experimental studies with UV alone, TiO<sub>2</sub>/UV, and H<sub>2</sub>O<sub>2</sub>/UV in combination with TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV are reformed. The same trend was also considered for metal treatment and metals were removed much better when UV light was combined with  $TiO_2/H_2O_2$ . The study, depicted in Figs. 4 and 5, reveals maximum treatment efficiency of total chromium reduction with citric acid, 24.84% and increasing H<sub>2</sub>O<sub>2</sub> concentration up to 20–100 ml/l to reduce 15.12%, 32.64%, 40.57%, 58.70%, and 61.03%, that is more efficient than the H<sub>2</sub>O<sub>2</sub>/UV process. Even when the TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV reaction happened to be the most efficient process, both homogeneous and heterogeneous photocatalysis can be considered as suitable methods to reach the complete mineralization of the solutions. The efficiency of TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV systems for the removal of hazardous heavy metals is much greater using  $H_2O_2$  as an oxidant. The removal of total chromium in the TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV process compared with the TiO<sub>2</sub>/UV, H<sub>2</sub>O<sub>2</sub>/UV, and TiO<sub>2</sub>/citric acid/UV processes at the optimal conditions increased about 4.7, 1.8, and 2.3 times, respectively. As shown in the equations,  $H_2O_2$  reacts with conduction band electrons and with superoxide radicals produced between oxygen and electron to generate •OH radicals. Also, H<sub>2</sub>O<sub>2</sub> produces •OH radicals directly by the photolytic split.<sup>22</sup> The same results were also obtained in previous works and it had been reported that photo catalytic oxidation of same organics as well as reduction of few metals is possible by coupling TiO<sub>2</sub> with UV light.<sup>10</sup> The performance of TiO<sub>2</sub>/UV and UV/TiO<sub>2</sub>/chemical oxidant processes for the removal of Cr(VI) in aqueous TiO<sub>2</sub> suspensions was compared. The reaction rate of hazardous heavy metals by TiO<sub>2</sub>/UV was higher than that of UV alone or  $TiO_2$  alone, indicating that the  $TiO_2/UV$  system was a more practical method than either UV illumination or TiO<sub>2</sub>. In the TiO<sub>2</sub>/UV system, the removal efficiency for Cr(VI) in acid or neutral pH was higher than that in basic pH. The addition of  $H_2O_2$  in the TiO<sub>2</sub>/UV system increased the degradation efficiency for the treatment of hazardous heavy metals. Finally, the degradation efficiency of the TiO<sub>2</sub>/oxidant/UV systems was much greater when  $H_2O_2$  was used as the oxidant.<sup>22</sup>

#### G. TiO<sub>2</sub>-citric acid-H<sub>2</sub>O<sub>2</sub>-UV system for reduction of chromium

The efficiency of total chromium reduction by photo catalytic treatment under UV light in different degradation systems, UV, TiO<sub>2</sub>/UV, H<sub>2</sub>O<sub>2</sub>/UV, TiO<sub>2</sub>/citric acid/UV, and TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV, was studied and compared. Even when the TiO<sub>2</sub>/citric acid/H<sub>2</sub>O<sub>2</sub>/UV reaction happened to be the most efficient process, both homogeneous and heterogeneous photocatalysis can be considered as suitable methods to reach the complete mineralization of the solutions. In chromium reduction, percentage was given in Figs. 4 and 5; the addition of citric acid to the TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV system enhances its photo reduction rate. This may be due to the production of a greater amount of OH radicals in the TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/citric acid/UV system compared with the production in other systems. The time in which complete reduction was obtained decreased to 2 h rather than 5 h as in the earlier experimental runs. The faster degradation can be attributed to minimum electron-hole recombination due to sufficient concentration of hole-electron scavenger. Fig. 4 shows the maximum treatment efficiency of total chromium reduction with increasing citric acid concentration from 20 to 80 ml/l which reduces to 62.00%, 76.70%, 77.91%, and 100%, and Fig. 5 shows as that increasing H<sub>2</sub>O<sub>2</sub> concentration from 20 to 100 ml/l reduces 40.57%, 41.84%, 50.77%, 61.03%, and 100%, which is more efficient than the H<sub>2</sub>O<sub>2</sub>/UV process.

#### H. Adsorption and deposition of total chromium

As mentioned in Figs. 6 and 7, the pH has a great influence on the reaction rate of reduction of total chromium. A decrease in the pH has two combined effects. On the one hand, the Nernst redox potential for chromate reduction increases. On the other hand, the positive charge of titania particles increases. This, in fact, could increase the adsorption of chromate by electrostatic attraction. Furthermore, the desorption of the product formed (Cr(III) species) could be favoured. At pH > 4.5, the catalyst surface is negatively charged. Under these conditions, the adsorption of anions, such as chromate, is more difficult which is due to the electrostatic repulsion. Otherwise, in these conditions the product formed (insoluble chromium hydroxide) could be adsorbed more easily on the titania surface, decreasing the active surface of the catalyst.<sup>25</sup> The total chromium present in the industries was initially in the hexavalent form. However, after reduction and conversion to trivalent state, total chromium is used as a measure to assess chromium deposition. The decreased concentration of total chromium is an indicative of Cr(III) hydroxide deposition on the catalyst surface found to occur at around pH 6. A series of experiments were conducted at different combination systems (UV, TiO<sub>2</sub>/UV, H<sub>2</sub>O<sub>2</sub>/UV, TiO<sub>2</sub>/citric acid/UV, TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV, and TiO2/citric acid/H2O2/UV) and pH values ranging, containing total chromium in order to investigate photo catalytic reactions. Photolysis tests showed that no more reduction of total chromium was 1.68% observed either without catalyst and oxidant. Fig. 6 shows that the depositions for the TiO<sub>2</sub>/UV, H<sub>2</sub>O<sub>2</sub>/UV, TiO<sub>2</sub>/citric acid/UV, TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV, and TiO<sub>2</sub>/citric acid/H<sub>2</sub>O<sub>2</sub>/UV systems were 3.49%, 5.49%, 25.55%, 7.18%, and 25.55%, respectively, for citric acid and Fig. 7 shows that 2.26%, 8.33%, 4.52%, 10.70%, and 10.70%, respectively, with H<sub>2</sub>O<sub>2</sub> concentrations. This close to the total percentage which is between 2%-25% of total chromium reduced. In the presence of citric acid and  $H_2O_2$ , the deposition was higher for the experimental run in which more reduction was observed and final pH was closer to 6. Maximum deposition occurred in TiO<sub>2</sub>/citric acid/H<sub>2</sub>O<sub>2</sub>/UV systems for concentrations (citric acid 88.29% and H<sub>2</sub>O<sub>2</sub> 61.03%) with final pH 7.24 and 8.06, depicted in Table II. It can be observed that the deposition was also affected by initial pH. The deposition decreased with decreasing initial pH. At lower pH, Cr(III) hydroxide formation was expected to be less and Cr(III) remained in its cationic form thereby being repelled by the positive charged TiO<sub>2</sub> surface.

#### I. Effect of process parameters

#### 1. Effect of the pH on the photocatalytic reduction of total chromium

A series of experiments were performed by adding citric acid and  $H_2O_2$  conducted at *p*H 7, containing chromium and catalysts (TiO<sub>2</sub>) in order to investigate photo catalytic reactions.



FIG. 6. Milligrams of total chromium deposited per gram of  $TiO_2$  for different ratios citric acid,  $TiO_2 = 2 g/l$ ,  $H_2O_2 = 60 ml/l$ , citric acid = variable.

Under illumination with the UV lamp, the chromium solution gradually lost its original yellow color, while the originally white TiO<sub>2</sub> turned pale green. Figs. 4 and 5 show that the effect of pH 7 was studied for the reduction of total chromium in industrial effluent at a TiO<sub>2</sub> loading of 2 g/l, with the variable of citric acid dosage of 60 mg/l and H<sub>2</sub>O<sub>2</sub> dosage of 60 ml/l. The results for pH change during the temporal profiles of total chromium reduction by UV, TiO<sub>2</sub>/UV, H<sub>2</sub>O<sub>2</sub>/UV, TiO<sub>2</sub>/citric acid/UV, TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV, and TiO<sub>2</sub>/citric acid/H<sub>2</sub>O<sub>2</sub>/UV reactions are depicted in Table II. The initial pH 7.12, decreasing with increasing citric acid and increasing with increasing H<sub>2</sub>O<sub>2</sub> dosing, and at the end of reaction the pH was found to be increasing. Figs. 4 and 5 show the change of concentration for the photo catalytic reduction only (i.e., the results shown are obtained after it was ascertained that an adsorption equilibrium has been attained and the lamp was turned on) and indicate that the reduction rates increase with acidic or alkaline pH.<sup>26</sup> Maximum pH change was found to occur during the first 3 h of reaction



FIG. 7. Milligrams of total chromium deposited per gram of  $TiO_2$  for different ratios  $H_2O_2$ ,  $TiO_2 = 2 g/l$ , citric acid = 60 mg/l,  $H_2O_2 = variable$ .

		(1)	(1) (2)		(4)	(5)	(6)	
		S	S + T	S + HP	S + T + CA	S + T + HP	S + T + HP + CA	
Citric acid	Initial <i>p</i> H	Final <i>p</i> H	Final <i>p</i> H	Final <i>p</i> H	Final pH	Final <i>p</i> H	Final <i>p</i> H	
0	7.12	8.58	8.44	6.48		7.66		
20	7.12	8.58	8.44	6.48	7.47	7.66	7.64	
40	7.12	8.58	8.44	6.48	8.42	7.66	7.88	
60	7.12	8.58	8.44	6.48	8.03	7.66	6.71	
80	7.12	8.58	8.44	6.48	8.29	7.66	6.88	
100	7.12	8.58	8.44	6.48	8.62	7.66	6.54	
120	7.12	8.58	8.44	6.48	8.16	7.66	6.49	
140	7.12	8.58	8.44	6.48	8.39	7.66	6.64	
$H_2O_2$	Initial <i>p</i> H	Final pH	Final pH	Final pH	Final <i>p</i> H	Final <i>p</i> H	Final <i>p</i> H	
0	7.32	8.47	8.55		8.03			
20	7.32	8.47	8.55	8.65	8.03	8.28	8.04	
40	7.32	8.47	8.55	7.82	8.03	7.47	7.91	
60	7.32	8.47	8.55	8.75	8.03	8.79	8.02	
80	7.32	8.47	8.55	7.01	8.03	7.98	6.58	
100	7.32	8.47	8.55	7.96	8.03	8.3	7.98	

TABLE II. The corresponding *p*H change in variation of citric acid and  $H_2O_2$  concentration (where  $T = TiO_2$  (g/l) Photocatalyst, CA = citric acid (mg/l),  $HP = H_2O_2$  (ml/l)).

which also corresponds to the maximum reduction of chromium. The *p*H increase was not significant in the UV alone and runs in which chromium also has minimum reduction. There was an overall increase in about *p*H 8 units for maximum samples. The change in *p*H is due to the formation of  $OH^-$  ions. The samples, in which the *p*H was lower due to high citric acid concentration, showed higher reduction of chromium, which is expected as the reduction of chromium is favoured at acidic *p*H. The deposition of reduced chromium was lower at low *p*H due to repulsion of cationic Cr(III) species by TiO<sub>2</sub>. No more adsorption was observed at *p*H 7.0. This result agrees with no adsorption was detected at *p*H above 6.0, due to the negative charge on the photo catalyst surface at *p*H 7.0 repels the dichromate ion.<sup>4</sup>

#### 2. Determination of COD

The study of COD was also applied for the solutions, treated by  $H_2O_2$  and citric acid combination with variation of concentration. Experimental results demonstrate that the COD removal efficiency is higher at initially increasing  $H_2O_2$  and citric acid concentration. The citric acid and  $H_2O_2$ oxidation is the counterpart reaction of chromium reduction. COD decrease was measured to trace the oxidation of citric acid and  $H_2O_2$ . Citric acid and  $H_2O_2$  in the reaction system were found to degrade completely as well as increasing concentration in about 5 h of UV exposure. The exhaustion of citric acid ceased the reaction. The results show in Fig. 8 maximum COD reduction with H<sub>2</sub>O<sub>2</sub>/UV system with  $H_2O_2$  increasing concentration from 0 to 100 ml/l for an increase with 6.66%, 30%, 44.44%, 57.77%, 64.44%, and 80% and H<sub>2</sub>O<sub>2</sub>/TiO<sub>2</sub>/UV system 33.33%, 51.11%, 57.77%, 66.66%, 82.22%, and 92.22%. The combination with TiO<sub>2</sub>/citric acid/H<sub>2</sub>O<sub>2</sub>/UV system was 33.33%, 60%, 61.11%, 77.77%, 94.44%, and 98.88% that is more efficient than the H<sub>2</sub>O<sub>2</sub>/UV and H<sub>2</sub>O<sub>2</sub>/TiO<sub>2</sub>/UV processes. Similarly, Fig. 9 shows maximum COD reduction with TiO2/citric acid/UV was increasing citric acid concentration from 20 to 140 ml/l for the increase with 37.77%, 46.66%, 55.55%, 60%, 62.22%, 65.55%, and 66.66% and H<sub>2</sub>O<sub>2</sub>/UV and H<sub>2</sub>O<sub>2</sub>/TiO<sub>2</sub>/UV system 68.88%, 71.11%, 77.77%, 83.33%, 86.66%, 85.55%, and 86.66%, that is more efficient than the TiO<sub>2</sub>/citric acid/UV process. The combination was observed with COD removal efficiency improvement in the treated solutions. When the concentration of citric acid and H<sub>2</sub>O<sub>2</sub> was increased further, complete reduction of total chromium was achieved. It is observed that COD was reduced maximum in the time period



FIG. 8. Reduction trends of COD with time for the different ratios of combinations and  $H_2O_2$ : Ti $O_2 = 2 g/l$ , citric acid = 60 mg/l,  $H_2O_2 =$  variable.

in which total chromium reduction was more. This shows that there is a synergism in the redox reactions and the absence of any of the species leads to dominant electron hole recombination and shows that the moles of citric acid/ $H_2O_2$  consumed per mole of total chromium. As discussed earlier, the fast reduction of COD indicates that the oxidation of citric acid and  $H_2O_2$  was by donating electrons, which directly fill the valence band, and not through an indirect pathway. The COD reduction in percentage was different for all the samples due to initial concentrations of citric acid and  $H_2O_2$  added.

#### 3. Effect of the photo catalyst loading

It is observed that irradiation time required for degradation of effluent decreases with increasing catalyst concentration, until 2 g/l. Further increase in catalyst concentration decreases



FIG. 9. Percentage of the COD values at different irradiation time with different combinations and citric acid:  $TiO_2 = 2 g/l$ ,  $H_2O_2 = 60 ml/l$ , citric acid = variable.

the degradation rate. As seen in Figs. 4 and 5, the addition of  $TiO_2$  increases the initial reaction rate constant for the  $TiO_2/UV$  and  $TiO_2/H_2O_2/UV$  processes and reaches an apparent at about 2 g/l of photo catalyst. For comparison, the initial reaction rate constant for  $TiO_2/citric$  acid/  $H_2O_2/UV$  is also given in Figs. 4 and 5. The  $TiO_2/citric$  acid/ $H_2O_2/UV$  system has a higher initial reaction rate constant at all levels of catalyst loading by 6%–20%, depending on the  $TiO_2$ concentration. Moreover, in the absence of citric acid and  $H_2O_2$ , no optimum value of photo catalyst is observed, instead the reaction rate increases continuously with  $TiO_2$  addition.

#### Effect of H<sub>2</sub>O<sub>2</sub> concentration

Reduction rates increase with  $H_2O_2$  concentration, which is explained by the effect of the additionally produced •OH radicals. However, above a certain H<sub>2</sub>O<sub>2</sub> concentration, the reaction rate levels off and sometimes is negatively affected by the progressive increase of the  $H_2O_2$ . This may be due to auto-decomposition of  $H_2O_2$  to oxygen and water and recombination of •OH radicals. Therefore,  $H_2O_2$  should be added at an optimal concentration to achieve the best degradation. This optimal  $H_2O_2$  concentration depends on the nature and concentration of the compound to treat.<sup>8</sup> It can be concluded that the reduction rate of the dark reaction is far lower than that of the photo catalytic reaction. The results showed that the homogeneous photochemical reaction of total chromium after 5 h irradiation is so small to be negligible, which is in agreement with a previous report.<sup>27</sup> The effect of  $H_2O_2$  concentration was varied systematically in the reaction solutions. This phenomenon indicates that competing mechanisms are present in this system. In fact, according to the available literatures,  $H_2O_2$  and citric acid in the TiO<sub>2</sub>/UV system could act as (a) the electron acceptor, (b) the scavenger of positive holes, (c) the scavenger of •OH radicals, or (d) the producer of •OH radicals. In the presence of UV and TiO<sub>2</sub>, the degradation rate increased by adding H<sub>2</sub>O<sub>2</sub>. The degradation rates, however, were lower in the presence of  $H_2O_2$  but in the absence of TiO<sub>2</sub>. As shown in Figs. 10(a)-10(c)), a significant enhancement of degradation efficiency is demonstrated when H<sub>2</sub>O<sub>2</sub> concentrations are increased from 0 to 100 ml/l. Above this concentration, the rate of COD reduction is negatively affected by the progressive increase of  $H_2O_2$ .

#### 5. Effect of initial concentration of total chromium

The absorption of light by the solution increases with the chromium concentration and the expected reaction rate decreases, since less radiation reaches to the catalyst because chromates absorb light in the range of 300–400 nm. Therefore, the amount of light reaching the photo catalyst depends on the amount of chromate in solution. This could be a possible reason for low reduction rates of total chromium obtained. Another effect of initial concentration of chromium in the lower concentration was that the quantity of citric acid and  $H_2O_2$  required for complete reduction. The trend of Figs. 11(a) and 11(b) shown as well as increasing concentration of CA:H<sub>2</sub>O<sub>2</sub> provided corresponding reduction rates which were quite similar. Citric acid and  $H_2O_2$  was, respectively, 60 mg/l and 60 ml/l, optimum with variable for each other for the reduction of total chromium.

#### 6. Kinetically analysis of photocatalytic reduction of total chromium

The photo catalytic oxidation of total chromium in aqueous solutions has been successfully modelled using Langmuir-Hinshelwood (L-H) kinetics. According to the L-H model, confirming the heterogeneous catalytic character of the system with the rate "r" varying proportionally with the surface coverage  $\theta$  as<sup>28</sup>

$$\mathbf{r} = \mathbf{k}\theta = (\mathbf{k}(\mathbf{K}\mathbf{C}))/(1 + \mathbf{K}\mathbf{C}),\tag{1}$$

where "r" is the rate of reaction, "K" is the adsorption constant, "k" is the rate constant, and "C" is the concentration of the species.







(b): TiO2=2g/l, Citric Acid=0mg/l, H2O2=Variable



(c): TiO2=2g/l, Citric Acid=60mg/l, H2O2=Variable

FIG. 10. Reduction trends of chromium with time for the different ratios of combinations and H<sub>2</sub>O<sub>2</sub>.



(a): TiO2=2g/l, H2O2=0ml/l, Citric Acid=Variable



(b). TiO2=2g/l, H2O2=60ml/l, Citric Acid=Variable

FIG. 11. Reduction trends of chromium with time for the different ratios of combinations and citric acid.

The degradation rate constant (k) is determined and evaluated at different citric acid and  $H_2O_2$  concentrations to find out the values at which maximum efficiency ( $k_{max}$ ) is obtained. In all the following experiments, it is described assuming a pseudo-first order reaction. Then, an approximation of L-H expression can be used<sup>8</sup>

$$(-d(C))/dt = k(C),$$
 (2)

where k is the pseudo-first order reaction rate constant. Integration of Eq. (3) leads to

$$(\ln(C))/Co = -kt, \tag{3}$$

from where the slope of the plot ln(C)/Co vs. t (time of irradiation) renders the reaction rate constant (k).

The reaction apparently followed partial order for low citric acid concentration and zero order for higher citric acid concentration, indicating that the role of citric acid for lowering the solution pH was more pronounced at higher concentrations thereby making the conditions more favourable for total chromium reduction. The zero order kinetics could also be interpreted by



FIG. 12. Initial rate of chromium reduction for different ratios of citric acid,  $TiO_2 = 2 g/l$ ,  $H_2O_2 = 60 ml/l$ , citric acid = variable.

assuming a saturation of surface sites by all the organic molecules. However, it was not possible to determine the rate constant due to varying reaction conditions throughout the day. Therefore, the initial rates of reaction were determined for the first 2 h of reaction for all the experimental runs given in Figs. 12 and 13. Since the rate of reduction was found to be varied with the initial concentration of citric acid and  $H_2O_2$ , the initial rate (in first 2 h) determined for total chromium reduction is compared with the increasing concentration. The L-H plots the values of slope (R<sup>2</sup>) and equation for the trend line with respect to increase in citric acid and  $H_2O_2$  concentrations. A straight line was obtained on plotting the 1/rate versus 1/concentration of TiO<sub>2</sub> and citric acid separately, the trend line is depicted on Fig. 14(a). It can be observed that the L-H mechanism was followed with respect to increasing citric acid shown in Figs. 14(a)–14(c) and  $H_2O_2$  shown in Figs. 14(d)–14(f) concentrations in the wastewater shown in linearized higher value of correlation coefficient (r2=0.935, 0.977, 0.785,0.972, and 0.902, respectively).



FIG. 13. Initial rate of chromium reduction for different ratios of  $H_2O_2$ ,  $TiO_2 = 2 g/l$ , citric acid = 60 mg/l,  $H_2O_2$  = variable.



FIG. 14. Langmuir-Hinshelwood plot of chromium reduction at the different ratios of combinations with citric acid and  $H_2O_2$ .

#### 7. Effect of UV irradiance

A comparison of total chromium reduction % under UV light, Figs. 4 and 5, shows that complete total chromium reduction was achieved in 5 h under  $30 \text{ W/m}^2$  UV irradiation, whereas, under UV light, total chromium was reduction completely in 3 h only depicted in Table III.

It has been reported that degradation rate is proportional to light intensity, which confirms the photo-induced nature of the catalytic process activation, with the participation of photo induced electrical charges (electrons and holes) in the reaction mechanism. The optimal light power utilization corresponds to the domain where the degradation rate is proportional to light intensity.<sup>8</sup> The corresponding ultraviolet light intensity of  $4.488 \times 10^{-6}$  W/cm<sup>-2</sup> was thereby found to be adequate for the catalyst activation and reduction of Cr(VI). Ku and Jung *et al.*<sup>29</sup> reported similar light intensity to be sufficient for reduction of similar concentrations of total chromium. Another reason for faster reduction could be the availability of more active sites during the initial reaction time, which were occupied later by the deposition of reaction products. It is reported<sup>28</sup> that above a certain value (estimated to be 25 W/m<sup>2</sup> of UV in laboratory experiments), the reaction rate becomes proportional to the square root of UV intensity. The optimal light power utilization corresponds to the domain where rate is directly proportional to UV intensity. Therefore, the average solar irradiation during winter months with a maximum of about 900 W/m<sup>2</sup> in the study area, corresponding to 27 W/m<sup>2</sup> of UV, (assuming to be 3% of the total radiation) would also be sufficient for photoreaction.

	Citric acid concentration							
Time in minutes	1:0	1:20	1:40	1:60	1:80	1:100	1:120	1:140
0	30	30	33	33	33	30	30	30
60	40	40	39	39	39	40	40	40
120	46	46	39	39	39	44	44	44
180	49	49	42	42	42	49	49	49
240	47	47	48	48	48	49	49	49
300	47	47	48	48	48	48	48	48
UV irradiance (W/m <sup>2</sup> )	30	30	30	30	30	30	30	30
$H_2O_2$ concentration								
Time in minutes	1:0	1:20	1:40	1:60	1:80	1:100		
0	33	35	33	33	35	33		
60	43	38	43	37	38	37		
120	44	43	44	47	42	47		
180	47	45	47	48	45	48		
240	49	50	49	49	50	49		
300	49	50	49	49	50	49		
UV irradiance (W/m <sup>2</sup> )	30	30	30	30	30	30		

TABLE III. Hourly attained maximum temperature (°C) and UV irradiance (W/m<sup>2</sup>) during various experiments.

#### 8. Temperature change

Most of the photoreactions are not sensitive to small variations in temperature. Very few cases have shown Arrhenius dependence during detoxification. The *p*H of the aqueous solution significantly affects the particle size, the surface charge, and the band edge positions of the TiO<sub>2</sub> due to its amphoteric character. The zero point charge ( $pH_{ZPC}$ ) or *p*H at which the surface of an oxide is uncharged, for TiO<sub>2</sub> is around 7. Above and below this value, the catalyst is negatively or positively charged according to Eqs. (4) and (5). In consequence, the photo catalytic degradation of organic compounds is affected by the *p*H,<sup>8</sup>

$$\text{TiOH}_{2+} \leftrightarrow \text{TiOH} + \text{H}^+,$$
 (4)

$$\text{TiOH} \leftrightarrow \text{TiO}^- + \text{H}^+.$$
 (5)

However, at very low temperatures  $(-40 \,^{\circ}\text{C}$  to  $0 \,^{\circ}\text{C})$ , the activity decreases and Ea becomes positive. This behaviour can be easily explained within the framework of the L-H mechanism, which is the suggested mechanism for photo catalytic reaction. The decrease in temperature favours adsorption, which is a spontaneous exothermic phenomenon. Additionally, the lowering temperature also favours adsorption of final reaction products.

#### **IV. CONCLUSIONS**

The major conclusions of the metals tested for which photocatalytic reduction occurs, all but chromium was deposited in the metallic state onto the photo catalyst. Cr(VI) is only reduced to Cr(III). The dark adsorption of total chromium is differ significantly from the reduction trends showing that the adsorption is not the only key factor to secure high photocatalytic reductions. The total chromium reduction rates increase in the TiO<sub>2</sub>/UV process with the increase of TiO<sub>2</sub> loading, especially up to about 2 g/l. The deposition of total chromium mg/l for TiO<sub>2</sub> g/l increases with increase in reduction was maximum at optimum concentration. At the range pH 7–8, the deposition with final pH, the total chromium reduction results in H<sub>2</sub>O<sub>2</sub>/UV process faster than TiO<sub>2</sub>/UV process. The TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV process results in the fastest total chromium reduction. Finally, the degradation efficiency of the TiO<sub>2</sub>/oxidant/UV systems was much greater when H<sub>2</sub>O<sub>2</sub>

was used as the oxidant. Citric acid is not proper chromium reduction with photolytic, so the reaction is photocatalytic in nature. The rate of reduction absence of citric acid is very less and is significantly enhanced on addition of citric acid. Citric acid is an efficient hole scavenger and reduces  $Cr_T$  completely, in the initial and higher concentration of citric acid that is given in experimental conditions. Finally, the combination of TiO<sub>2</sub>/citric acid/H<sub>2</sub>O<sub>2</sub>/UV result is observed more efficient than the TiO<sub>2</sub>/citric acid and TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV processes in the solutions. The L-H plots of total chromium reduction with respect to citric acid show that linearity increased with increasing concentration (R<sup>2</sup> = 0.935 and 0.977 for TiO<sub>2</sub>/citric acid/UV and TiO<sub>2</sub>/citric acid/H<sub>2</sub>O<sub>2</sub>/UV systems). The H<sub>2</sub>O<sub>2</sub> reaction apparently followed partial order for low concentration and zero order for higher concentration. The L-H plots of chromium reduction with respect to H<sub>2</sub>O<sub>2</sub> concentration show a linear fit (R<sup>2</sup> = 0.785, 0.972, and 0.902 for H<sub>2</sub>O<sub>2</sub>/UV, TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV, and TiO<sub>2</sub>/citric acid/H<sub>2</sub>O<sub>2</sub>/UV systems, respectively).

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<sup>&</sup>lt;sup>1</sup>G. Colón, M. C. Hidalgo, and J. A. Navio, "Photocatalytic deactivation of commercial TiO<sub>2</sub> samples during simultaneous photoreduction of Cr(VI) and photooxidation of salicylic acid," J. Photochem. Photobiol. A **138**, 79–85 (2001).

<sup>&</sup>lt;sup>2</sup>M. R. Prairie and B. M. Stange, in *Proceedings from The Annual AIChE Heat Transfer Conference, Symposium on Innovative Applications of Solar Energy, Atlanta, August 1993 (1993), pp. 8–11, status report.* 

<sup>&</sup>lt;sup>3</sup>J. Blanco, P. Fernández, and S. Malato, "Solar photocatalytic detoxification and disinfection of water: Recent overview," J. Sol. Energy Eng. **129**(1), 1–12 (2007).

<sup>&</sup>lt;sup>4</sup>S. G. Schrank, H. J. José, and R. F. P. M. Moreira, "Simultaneous photocatalytic Cr(VI) reduction and dye oxidation in a TiO<sub>2</sub> slurry reactor," J. Photochem. Photobiol. A 147, 71–76 (2002).

<sup>&</sup>lt;sup>5</sup>S. Zheng, Z. Xu, Y. Wang, Z. Wei, and B. Wang, "On the enhanced catalytic activity of TiO<sub>2</sub>-supported layered compounds for Cr(VI) photo-reduction," J. Photochem. Photobiol. A **137**, 185–189 (2000).

<sup>&</sup>lt;sup>6</sup>M. Piotr, K. Andrzej, and S. Zofia, "Mechanism of photochemical reduction of chromium(VI) by alcohols and its environmental aspects," J. Photochem. Photobiol. A **160**, 163–170 (2003).

<sup>&</sup>lt;sup>7</sup>G. Colon, M. C. Hidalgo, and J. A. Navío, "Influence of carboxylic acid on the photocatalytic reduction of Cr(VI) using commercial TiO<sub>2</sub>," Langmuir **17**, 7174–7177 (2001).

<sup>&</sup>lt;sup>8</sup>S. P. Parra Cardona, "Coupling of photocatalytic and biological processes as a contribution to the detoxification of water: catalytic and technological aspects," Doctoral Theses no. 2470 (EPFL, Lausanne, 2001), online at http://library.epfl.ch/theses/?nr=2470.

<sup>&</sup>lt;sup>9</sup>S. Sreedhar Reddy and B. Kotaiah "Decolorization of simulated spent reactive dye bath using solar/TiO<sub>2</sub>/H<sub>2</sub>O2," Int. J. Environ. Sci. Technol. **2**(3), 245–251 (2005), online at http://www.bioline.org.br/pdf?st05034.

<sup>&</sup>lt;sup>10</sup>M. R. Samarghandi, J. Nouri, A. R. Mesdaghinia, A. H. Mahvi, S. Nasseri, and F. Vaezi, "Efficiency removal of phenol, lead and cadmium by means of UV/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> processes," Int. J. Environ. Sci. Technol. 4(1), 19–25 (2007), online at http://www.sid.ir/en/VEWSSID/J\_PDF/92220070103.pdf.

<sup>&</sup>lt;sup>11</sup>S.-M. Lee, Y.-G. Kim, and I.-H. Cho, "Treatment of dyeing wastewater by TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>/UV process: experimental design approach for evaluating total organic carbon (TOC) removal efficiency," J. Environ. Sci. Health A40, 423–436 (2005).

<sup>&</sup>lt;sup>12</sup>L. Kos, J. Perkowski, and S. Bzdon, "Application of photocatalytic oxidation in the presence of TiO<sub>2</sub> in small sewage treatment plants," Sep. Sci. Technol. 42, 1553–1563 (2007).

<sup>&</sup>lt;sup>13</sup>A. Rigaa, K. Soutsas, K. Ntampegliotis, V. Karayannisa, and G. Papapolymerou "Effect of system parameters and of inorganic salts on the decolorization and degradation of Procion H-exl dyes. Comparison of H<sub>2</sub>O<sub>2</sub>/UV, Fenton, UV/Fenton, TiO<sub>2</sub>/UV and TiO<sub>2</sub>/UV/H<sub>2</sub>O<sub>2</sub> processes," Desalination **211**, 72–86 (2007).

<sup>&</sup>lt;sup>14</sup>K. Kabra, R. Chaudhary, and R. L. Sawhney, "Application of solar photocatalytic treatment to industrial wastewater from a chrome plating unit," Int. J. Green Energy **6**, 83–91 (2009).

<sup>&</sup>lt;sup>15</sup>D. Chen and A. K. Ray, "Removal of toxic metal ions from wastewater by semiconductor photocatalysis," Chem. Eng. Sci. 56, 1561 (2001).

<sup>&</sup>lt;sup>16</sup>J. A. Navio, G. Colon, M. Trillas, J. Peral, X. Domenech, J. J. Testa, J. Padron, D. Rodriguez, and M. I. Litter, "Heterogeneous photocatalytic reactions of nitrite oxidation and Cr(VI) reduction on iron-doped titania prepared by wet impregnation method," Appl. Catal. B 16, 187 (1998).

<sup>&</sup>lt;sup>17</sup>S. X. Liu, "Removal of copper (VI) from aqueous solution by Ag/TiO<sub>2</sub> photocatalysis," Bull. Environ. Contam. Toxicol. **74**, 706–714 (2005).

<sup>&</sup>lt;sup>18</sup>P. Wardman, "Reduction potentials of one-electron couples involving free radicals in aqueous solutions," J. Phys. Chem. Ref. Data 18, 1637 (1989).

<sup>&</sup>lt;sup>19</sup>C. R. Chenthamarakshan and K. Rajeshwar, "Photocatalytic reduction of divalent zinc and cadmium ions in aquous TiO<sub>2</sub> suspensions: An interfacial induced adsorption-reduction pathway mediated by formate ions," Electrochem. Commun. 2, 527 (2000).

<sup>&</sup>lt;sup>20</sup>X. Wang, S. O. Pehkonen, and A. K. Ray, "Removal of aqueous Cr(VI) by a combination of photocatalytic reduction and coprecipitation," Ind. Eng. Chem. Res. 43, 1665–1672 (2004).

- <sup>21</sup>J.-T. Jung, J.-Y. Choi, J.Chung, Y.-W. Lee, and J.-O. Kim, "UV/TiO<sub>2</sub> and UV/TiO<sub>2</sub>/chemical oxidant processes for the removal of humic acid, Cr and Cu in aqueous TiO<sub>2</sub> suspensions," Environ. Technol. **30**(3), 225–232 (2009). <sup>22</sup>S. Malato, J. Blanco, A. Vidal, and C. Richter, "Photocatalysis with solar energy at a pilot plant scale: an overview,"
- Appl. Catal. B 37, 1 (2002).
- <sup>23</sup>G.Colon, M. C. Hidalgo, and J. A. Navio, "Influence of carboxylic acid on the photocatalytic reduction of Cr(VI) using commercial TiO<sub>2</sub>," Langmuir 17, 7174 (2001). <sup>24</sup>F. Al-Momani, *Directed by Dr. Santiago Esplugas Combination of Photo-oxidation Processes with Biological Treatment*
- (Universitat De Barcelona Facultat De Química Departament D' Enginyeria Química I Metal Lúrgia, Barcelona, 2003).
- <sup>25</sup>J. Gimknez, M. A. Aguado, S. Cervera-March "Photocatalytic reduction of chromium (VI) with titania powders in a flow system. Kinetics and catalyst activity," J. Mol. Catal. A: Chem. 105, 67–78 (1996). <sup>26</sup>X. Wang, S. O. Pehkonen, and A. K. Ray, "Photocatalytic reduction of Hg(II) on two commercial TiO<sub>2</sub> catalysts," Elec-
- trochimica. Acta. **49**, 1435–1444 (2004). <sup>27</sup>L. B. Khalil, W. E. Mourad, and M. W. Rophael, "Photocatalytic reduction of environmental pollutant Cr(VI) over some
- semiconductors under UV/visible light illumination," Appl. Catal. B 17, 267-273 (1998).
- <sup>28</sup>J. M. Herrmann "Heterogeneous photocatalysis: Fundamentals and applications to the removal of various types of aqueous pollutants," Catal. Today 53, 115 (1999).
- <sup>29</sup>Y. Ku and I. Jung, "Photocatalytic reduction of Cr(VI) in aqueous solutions by uv irradiation with the presence of titanium dioxide," Water Res. **35**(1), 135 (2001).