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Photo-reduction of hexavalent chromium in aqueous solution in the presence of zinc oxide as semiconductor catalyst

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ABSTRACT

Common sources of chromium in wastewater are electroplating and leather industries. Hexavalent chromium is more toxic and carcinogenic compared to its trivalent counterpart. Conversion of Cr(VI) to Cr(III) in an aqueous medium by photocatalytic reduction using UV radiation and ZnO semiconductor catalyst has been investigated using potassium dichromate as the model compound. Effects of the process parameters such as ZnO loading (0–3 g/L) and intensity of UV radiation (0–125 W medium pressure Hg vapour lamp) on photocatalytic reduction were investigated. Initial concentration of substrate solution was varied from 40 to 120 mg/L. A comparison of the performance of the ZnO photocatalyst achieved in this study with that reported in the literature for photocatalytic and conventional processes is presented. The initial rate of the photochemical method was found to be independent of the concentration of potassium dichromate. Methanol was added as a hole scavenger for enhancement of the photo-reduction. Initial rate of photo-reduction was found to be independent of the concentration of methanol above a particular value. A probable mechanism and the corresponding kinetic model have been proposed for the photo-reduction and tested by experimental results. An alternative rate equation based on the LHHW model compares well with the mechanistic rate equation.

1. Introduction

Chromium occurs in two common oxidation states—Cr(III) and Cr(VI). Hexavalent chromium is carcinogenic and toxic. But Cr(III) is less toxic and can be readily precipitated or sorbed on a variety of inorganic and organic substances at alkaline or neutral pH [1,2]. Industrial sources such as chrome plating, electronic, metallurgical, wood processing and leather tanning industries release Cr(VI) in effluent streams. These effluents must be treated before discharge to surface water. The methods generally used to treat wastewater containing hexavalent chromium are adsorption [3], ion exchange [4] and reduction by chemical methods using zero-valent iron or ferrous salts followed by coagulation–precipitation [5,6]. In fact, use of ferrous sulfate at an acidic pH [7,8] followed by alkali precipitation has been a common method of removal of hexa- and also tri-valent chromium. Reduction with sodium sulfite or metabisulfite [9] is another conventional method of treating hexavalent chromium in wastewater. In addition to requirement of excess chemicals to ensure complete conversion of Cr(VI), formation of sludge or release of sulfur dioxide are the major problems associated with the above two conventional methods. Recently, Kulkarni et al. [10] explored the emulsion liquid membrane technique to concentrate Cr(VI) in an aqueous alkaline strip phase followed by reduction using $FeSO_4$ in an acid medium at about 100 °C. This technique involves a number of steps and eventually relies on $FeSO_4$ to reduce Cr(VI). The problems associated with the classical techniques have been the important reasons behind the attempts of developing alternative clean technologies for chromium remediation.

An alternative clean route of treating Cr(VI) that has received considerable attention is photocatalytic reduction in the presence of a semiconductor material such as ZnO, TiO_2, CdS or WO_3 under visible or UV radiation [2,4,11–13]. The photocatalytic method is based on the reactive properties of an electron–hole pair generated in the semiconductor when irradiated by UV/vis light having energy greater than the band-gap energy of the semiconductor. This method is widely used for treatment of the drinking water and industrial wastewater by oxidizing the organic pollutants. The reducing capacity of the semiconductor photocatalyst which uses the electrons generated on the semiconductor surface is, however, less explored. It is more attractive compared to the conventional

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processes since it works at near-neutral pH thereby requiring less alkali during coagulation–precipitation. This method, if conducted with solar radiation as the source of activation energy, can be more economical and eco-friendly [14]. Among the photocatalysts, WO_3 is less available, cadmium itself is a toxic heavy metal and CdS is prone to easy deactivation and photocorrosion [15].

Application of the photocatalytic technique for remediation of inorganic and organic pollutants in wastewater has been reviewed by Kabra et al. [12]. Ciesla et al. [16] have made an exhaustive survey of the work on environmental photocatalysis by transition metal complexes. Photo-reduction of a metal ion is accelerated if it is accompanied by simultaneous oxidation of an organic molecule that plays the role of a ligand or a 'sacrificial electron donor'. Concurrent generation of one or more of the species $O_2^\bullet$, $HO_2^\bullet$, $OH^\bullet$, H_2O_2 and HO_2^- during the photo-reduction process has been reported. This occurs because of the fact that the medium (water) acts as the electron donor simultaneously with the sacrificial organic species. The phenomenon has been called 'ligand to metal charge transfer' (LMCT).

A number of investigations on photo-reduction of Cr(VI) have been reported in the recent years. Ku and Jung [17] studied photo-reduction of Cr(VI) in an irradiated suspension of TiO_2 (up to 12 g/L). Khalil et al. [18] studied the same using an irradiated suspension of ZnO, WO_3 and two varieties of TiO_2. The effects of pH and initial concentration of Cr(VI) were reported. Use of a sacrificial organic to enhance photo-reduction of Cr(VI) has been reported in several recent publications. Schrank et al. [11] used 'Luranzol S Kong' dye in the presence of TiO_2 photocatalyst at pH values ranging from 2.5 to 7.0. Mytych et al. [19–21] studied photo-reduction of Cr(VI) with simultaneous degradation of aliphatic alcohols, phenols, chloro- and bromo-phenols and oxalate ligands. Carbon tetrachloride in the presence of a non-ionic surfactant used as hole absorbers from suspended TiO_2 irradiated with visible light was reported by Cho et al. [22]. The degradation was visualized to proceed through the formation of CCl_3^- which got further degraded. Photo-reduction in the presence of algae, *Chlorella vulgaris*, was studied by Deng et al. [23]. An empirical rate equation based on data fitting was proposed. Bisphenol A was used by Liu et al. [24] for the reduction of Cr(VI) as the ligand.

Photo-reduction of hexavalent chromium in an aqueous medium using ZnO as semiconductor catalyst in the presence of a 125-W medium pressure Hg lamp as a source of UV radiation has been carried out in the present study. Though the band-gap energy of both TiO_2 and ZnO are the same (3.2 eV) it has been reported that in many cases the initial reaction rate is higher for ZnO compared to that for TiO_2 under otherwise identical experimental conditions [25]. It may be noted further that only the anatase form of TiO_2 has the characteristics of a semiconductor photocatalyst and Degussa P-25 TiO_2 is a few times costlier than the laboratory reagent grade ZnO powder used in this work. However, only a few researchers investigated the potential of ZnO and this prompted us to select ZnO as semiconductor photocatalyst for the reduction of hexavalent chromium. Methanol has been used as the hole scavenger. Methanol is a very well known sacrificial electron donor [26–28] and photo-reduction is very often facilitated by the presence of the sacrificial electron donors, mostly organic compounds. As a sacrificial electron donor, methanol readily consumes the hole and/or the $OH^\bullet$ radical generated so that the holes and electrons cannot recombine and the electrons become available for the reduction of Cr(VI). It has a higher reduction capacity and is cheaper compared to other reagents reported in the literature (e.g., formic acid and humic acids). The objective of the present work is to explore photocatalytic reduction of Cr(VI) and to investigate the influence of the major process parameters such as the initial concentration of the substrate, loading of ZnO, intensity of UV radiation on the rate of photo-reduction and the hole scavenger as well as to develop a rate equation for the process based on a mechanistic model. The experiments have been carried out at the slightly acidic pH (4.5) of the solution.

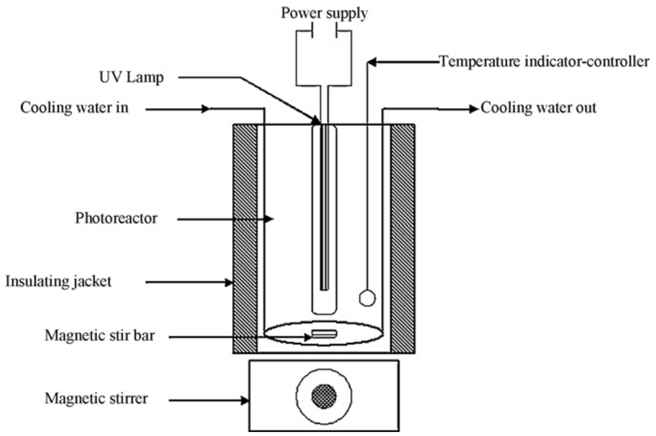

Fig. 1. Experimental set-up for the photocatalytic reduction of hexavalent chromium.

2. Materials and methods

Materials: Potassium dichromate and zinc oxide (GR grade) were received from LOBA Chemie, India. Methanol (GR) was from SD Chemicals, India. Freshly prepared double distilled water was used to prepare solutions. The mean particle size of the ZnO catalyst was 146.7 nm (Zeta Plus, Brookhaven Instrument Corporation) and the BET surface area was 3.23 m^2/g. The true density of the solid is 5600 kg/m^3 whereas the bulk density is 880 kg/m3. Illuminance of the UV lamp at different electrical power supply was measured using Metravi 1330 digital lux meter.

Analytical methods: The concentration of potassium dichromate in solution was determined at $\lambda_{max} = 349$ nm [29] using a 1-cm quartz cell in a UV–vis spectrophotometer (Shimadzu UV-160A).

2.1. Experimental set-up and procedure

Photo-reduction experiments were carried out in a cylindrical stainless steel reactor (Fig. 1), 0.12 m in diameter and 0.25 m in height, fitted with a stainless steel cooling coil. A 125-W medium pressure Hg vapour lamp was inserted in a quartz sleeve at the center of the reactor as the source of UV radiation. The reactor temperature was maintained constant at 20 ± 1 °C by circulating chilled water at 10 °C. The ZnO particles were kept suspended by using a magnetic stirrer. It was confirmed by visual inspection that no settling of the ZnO particles occurred in the reactor. The total suspension volume was 2000 mL. Liquid samples were withdrawn at 15 min interval, filtered and analyzed to monitor the progress of the reaction.

A set of experiments on adsorption of Cr(VI) and of methanol on the ZnO photocatalyst was carried out in the absence of UV radiation (dark experiment). A measured amount of ZnO (0.2 and 5 g) was kept stirred overnight in a solution of Cr(VI) or methanol (525 and 150 mL liquid volume), samples of the liquid were withdrawn and the change of concentration was measured after separation of the solid.

3. Results and discussions

Adsorption of dichromate on the ZnO particles was negligible as indicated by measurement of solution concentration before and after contacting with the solid. In order to confirm the result, EDS

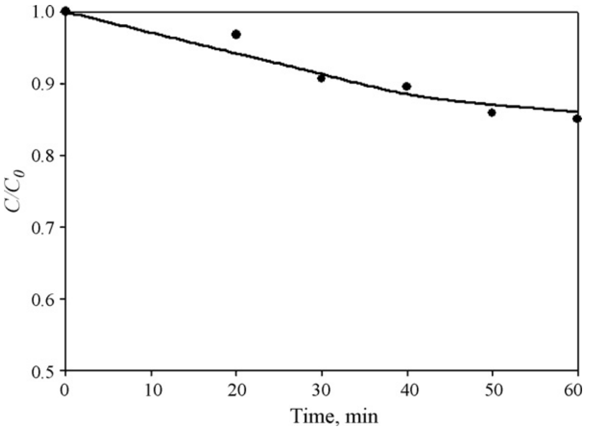

Fig. 2. Adsorption of methanol on ZnO catalyst [volume of solution: 150 mL; initial concentration: 2.53 gmol/L; ZnO loading: 5 g; pH: 5; temperature: 20 °C].

analysis of the spent ZnO was done but the picture (not shown here) also did not indicate the presence of chromium on ZnO surface. Blank experiments carried out without any photocatalyst did not indicate any photolysis or photochemical change in the substrate. It is to be noted that there is considerable disagreement among researchers on adsorption of Cr(VI) on ZnO. In most of the papers [13,18,30] very small to negligible adsorption is reported. Wang et al. [4] reported low but non-zero adsorption at around the same pH selected for this work. However, substantial adsorption of methanol on ZnO was observed. The methanol adsorption results are shown in Fig. 2.

3.1. Influence of process parameters on the photocatalytic reduction

The major parameters that influence the rate and conversion of Cr(VI) to Cr(III) are the initial concentration of the substrate, Cr(VI), the loading of the semiconductor catalyst, the intensity of the UV radiation and the concentration of the sacrificial electron donor (here methanol). The effects of the parameters were studied over reasonable ranges of their values.

The time evolution of the dimensionless concentration (C/C_0) for different initial concentrations (C_0) of the substrate is shown in Fig. 3. The extent of photo-reduction decreases with increasing initial concentration of the substrate. Since the absorbance of the solution increases with the $K_2Cr_2O_7$ concentration, a higher fraction of the UV radiation is intercepted before it reaches the surface of the photocatalyst thereby diminishing the conversion. Similar phenomena were reported before by Ku and Jung [17], Iwata et al. [31] and Chakrabarti and Dutta [32]. Though the extent of photo-reduction was found to decrease with increasing initial concentration of dichromate solution, the initial rates obtained from the time–concentration plots were found to be nearly independent of the initial concentration of dichromate solution (Fig. 3, inset). This appears to be because of more abundant presence of dichromate ions at the beginning that readily consumes the electrons available from the excitation of the semiconductor. As a result, the initial reaction order with respect to the substrate becomes virtually zero.

Both the extent and rate of degradation were found to increase with the increase in ZnO loading from 0 to 3 g/L of suspension volume (Fig. 4). Increase in the amount of ZnO or the catalyst concentration enhances the interception of UV radiation by the particles and the rate of reduction of Cr(VI) increases.

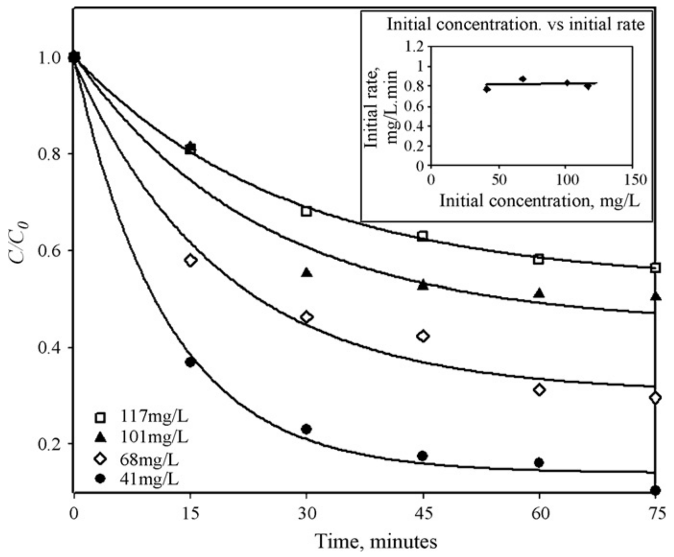

Fig. 3. Dimensionless time–concentration plots for different initial concentrations of dichromate solution [ZnO loading: 3 g/L; temperature: 20 °C; pH: 4.5; UV radiation: 388 lx; concentration of methanol: 1.25 mol/L]. Inset: initial rate vs. initial concentration of dichromate solution.

The power of the UV lamp could be varied from 0 to 125 W and the corresponding illuminance was measured in lux using a digital lux meter. No reduction of the dichromate in the absence of UV radiation was observed. An increasing UV intensity enhanced both the rate and the extent of degradation. The time–concentration plots at different UV dosage are presented in Fig. 5.

The pH of the solution is an important parameter in photocatalytic processes. We conducted a few experiments for 75 min at different pH values. The corresponding fractional reduction of Cr(VI) is presented in Fig. 6. It appears that the conversion is maximum (about 90%) at a pH 4.5 but decreases rapidly with increasing pH. The range of pH for the photocatalytivc reduction of Cr(VI) using ZnO is rather limited. The catalyst dissolves at a low pH; a high pH is detrimental to both the catalyst and the oxidizing species (i.e., $^\bullet$OH or H_2O_2 generated in course of irradiation of the catalyst as discussed later). This observation has been supported by other researchers also [31,32]. Wang et al. [4] reported low conversion of Cr(VI) as well as 'photcorrosion' of ZnO at neutral to basic pH. It may be mentioned that TiO_2 is more resistant to lower solution pH and Cr(VI) reduction has been reported at a pH as low as 2 [33,34]. We performed the experiments at a constant pH of 4.5 which is a little below the neutral pH.

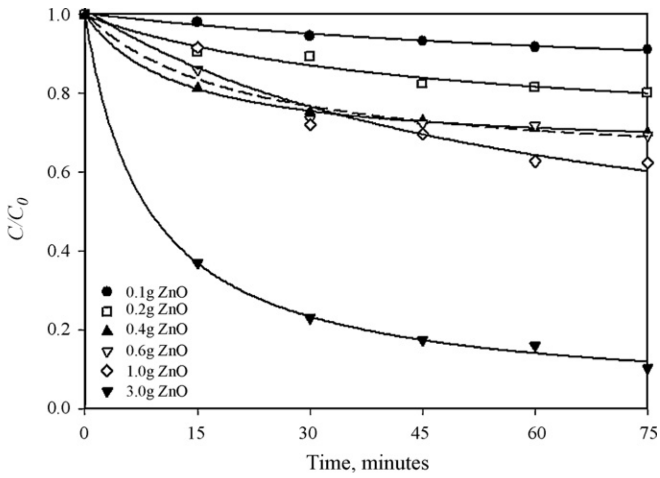

Fig. 4. Dimensionless time–concentration plots for different loadings of ZnO catalyst. [Initial concentration: 50 mg/L; temperature: 20 °C; pH: 4.5; UV radiation: 388 lx; concentration of methanol: 1.25 mol/L].

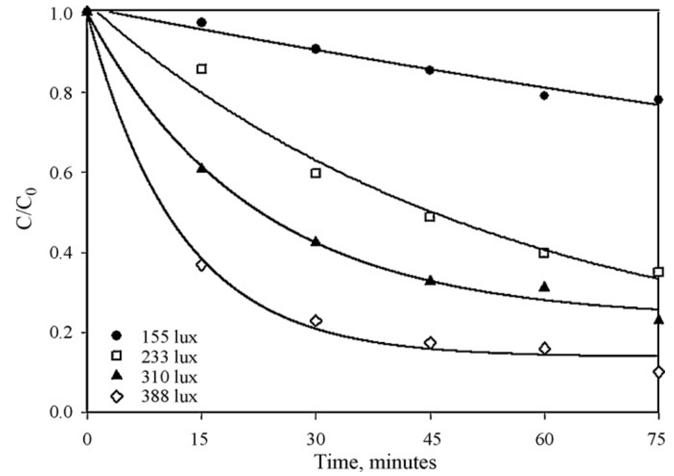

Fig. 5. Dimensionless time–concentration plots for different intensities of UV radiation [initial concentration: 50 mg/L; temperature: 20 °C; pH: 4.5; ZnO loading: 3 g/L; concentration of methanol: 1.25 mol/L].

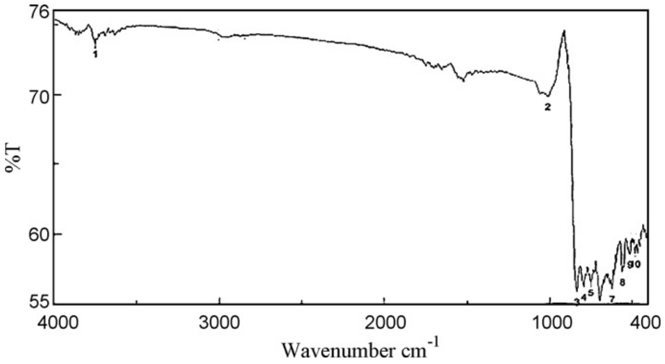

Fig. 7. FTIR spectra of the solution after 75 min irradiation in the presence of ZnO photocatalyst.

The photocatalytic Cr(VI) reduction rate is less sensitive to temperature change than a typical catalytic reaction. This has been amply established by several researcher including Domènech and Muñoz [13] and Bhatkhande et al. [35]. The former workers reported activation energy of only 3.6 kJ/mol, and 25% increase in the reaction rate for a change of temperature from 25 to 88 °C. We carried out the work at a constant temperature of 20 °C.

The enhancing role of a sacrificial electron donor for photocatalytic reduction of Cr(VI) has been amply established in the literature. If an organic(s) is incidentally present in the Cr(VI)-containing effluent and can act as the sacrificial agent, external addition of a reagent may not be necessary. But such a synergy is likely to be uncommon and addition of a sacrificial agent is necessary to enhance the reaction rate and to exploit the potential of the technique fully. Methanol has been used as a reagent of choice in a few recent studies [26–28]. Other reagents reportedly used are humic acids [30] and formic acid [4]. We used methanol since it is cheaper than other sacrificial agents reported in the literature and also because it has a much higher capacity of electron donation by way of oxidation to formaldehyde, formic acid and eventually to CO_2 and H_2O. One disadvantage of methanol is its toxicity. But by adjusting the process conditions, it may be possible to identify the right dose of methanol to avoid the toxic effect yet exploiting its ability of electron donation. A typical FTIR spectra (Jasco FTIR-670 Plus) of the reaction mixture after an exposure of 75 min to UV radiation (Fig. 7) showed peaks at 1009 cm^{-1} (69% transmission) and 835 cm^{-1} (55% transmission). These peaks are characteristic of a saturated aldehyde which is formaldehyde in this case. Further oxidation would expectedly occur to formic acid and then to CO_2 and H_2O if an appropriate dose of methanol is used after optimizing the process conditions. Time–concentration profiles for the reduction with different methanol dosing are shown in Fig. 8. It was observed that the initial rate was very low without methanol; the extent of photo-reduction reaction becomes slow in the absence of a sacrificial electron donor. However, the concentration of this sacrificial donor does not appear to affect the initial rate substantially after a certain critical value presumably because of an excess methanol present in the solution. Fig. 8 also shows that at a methanol concentration of 0.625 mol/L, the initial rate was enhanced by more than 100% of its value without alcohol. There was no appreciable increase in the initial rate with further addition of the reagent (Fig. 8, inset). About 90% conversion of Cr(VI) for 3 g/L catalyst loading could be achieved over a reaction time of 75 min. Our results are compared with those reported in the literature for photocatalytic (Table 1a) as well as with conventional methods of Cr(VI) reduction (Table 1b). The ZnO photocatalyst has been used by a few other researchers over a pH range of 4.5–6.5 and a maximum reduc-

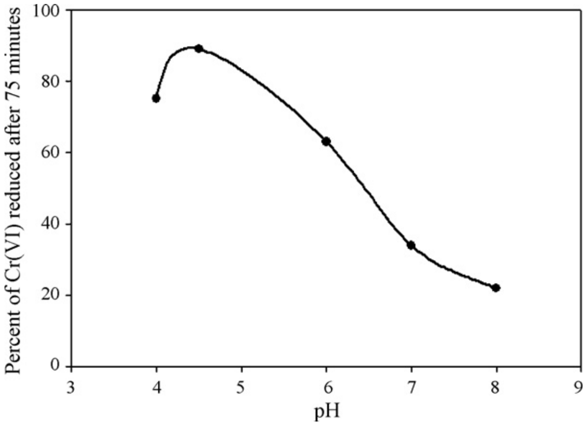

Fig. 6. Percent Cr(VI) reduced vs. pH [initial concentration: 50 mg/L; temperature: 20 °C; ZnO loading: 3 g/L; concentration of methanol: 1.25 mol/L, UV radiation: 388 lx].

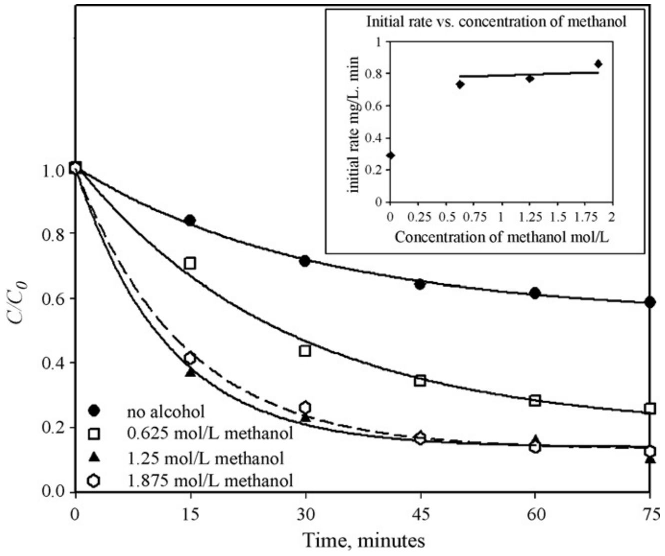

Fig. 8. Dimensionless time–concentration plots for different concentrations of methanol [initial concentration: 50 mg/L; temperature: 20 °C; pH: 4.5; ZnO loading: 3 g/L; UV radiation: 388 lx]. Inset: initial rate vs. concentration of methanol.

Table 1a
Comparison of photocatalytic Cr(VI) reduction results.

Ref.	Initial Cr(VI) conc. (ppm)	Catalyst	Catalyst loading (g/L)	pH	Temperature (°C)	UV dose	Time (min)	Sacrificial reagent	Cr(VI) reduction
Domènech and Muñoz [13]	300	ZnO	12	6	25	125 W/40 mL	15	–	50%
Khalil et al. [18]	40	ZnO	12	4.5	–	740 W/L	20	–	60%
	100	ZnO	12	4.5	–	740 W/L	120	–	50%
Selli et al. [30]	1.5	ZnO	2	6.5	20	–	30	Humic acid	70%
Ku and Jung [17]	10	TiO_2	1	2	25	7 W/L	300	–	70%
	10	TiO_2	1	4	25	7 W/L	300	–	50%
Wang et al. [4]	150	TiO_2	2	2.5	22	450 W/150 mL	60	Formic acid	95%
	150	TiO_2	2	4.5	22	-do-	60	-do-	90%
	150	ZnO	2	7.3	22	-do-	60	-do-	60%
Jiang et al. [33]	150	TiO_2	2.5	2.5		500 W/500 mL	180	–	80%
Siemon et al. [38]		TiO_2	1	3.0	2.5	1200 W/L	120	EDTA	90%
Present work	40–120	ZnO	3	4.5	20	62.5 W/L	75	Methanol	90%

tion of 70% is reported. In contrast, 90% reduction at a pH 4.5 has been achieved in the present work. A little higher reduction (95%) was claimed by Wang et al. [4] with TiO_2 catalyst and formic acid as the hole scavenger at a pH 2.5. Also a much higher UV dosage has been used in most of the previous work. It is also seen from Table 1b that the conventional techniques of reduction by using ferrous sulfate or using sulfite (sodium bisulfate or meta-bisulfite) removes Cr(VI) to a higher extent (97% to nearly 100%) but only by using 25 times or more of the theoretical amount of the reagent. It is expected that the performance of the photocatalytic reduction process may be improved by suitably adjusting and optimizing the process parameters and allowing a longer reaction time. A hybrid process in which most of the Cr(VI) is reduced photocatalytically and the residual, together with Cr(III), removed by the conventional reduction–co-precipitation may be a more attractive strategy for chromium remediation.

3.2. *A mechanistic rate equation for the photo-reduction*

The proposed reaction pathway for the reduction of chromium in aqueous medium in the presence of ZnO photocatalyst is discussed below. The first step is the generation of a hole–electron pair upon irradiation with UV light—the hole is responsible for oxidation and the electron is responsible for reduction:

$$\text{photo-excitation}: \quad \mathrm{ZnO} + h\nu \xrightarrow{k_1} \mathrm{ZnO}(\mathrm{h}^+ + \mathrm{e}^-) \qquad (1)$$

Turchi and Ollis [36] suggested four modes of photocatalytic reactions, of which one described reaction occurring between two free species in the fluid phase forming H_2O_2. Since there was no appreciable adsorption of Cr(VI) on ZnO surface, it is possible that homogeneous reduction of Cr(VI) in solution occurs by photogenerated H_2O_2 [18] Dissolved oxygen acts as the hole scavenger and generates H_2O_2 which reduces Cr(VI) as shown in Eq. (4) below:

$$\text{generation of } \mathrm{H_2O_2}: \quad \mathrm{O_2} + \mathrm{H}^+ + \mathrm{ZnO}(\mathrm{e}^-) \xrightarrow{k_2} \mathrm{H_2O_2} \qquad (2)$$

A parallel reduction reaction occurs through adsorbed methanol which gives rise to methoxy radicals upon hole scavenging:

$$\text{hole scavenging by methanol}: \quad \mathrm{CH_3OH} + \mathrm{ZnO}(\mathrm{h}^+) \xrightarrow{k_4} \mathrm{CH_3O}^{\bullet} \qquad (3)$$

The reduction reaction of Cr(VI) with hydrogen peroxide generated in situ by photo-excited ZnO as well as with the methoxy radicals generated by hole scavenging leads to Cr(III) are given below. Khalil et al. [18] suggested homogeneous reduction of hexavalent chromium by photogenerated H_2O_2 responsible for supply of electron to the hexavalent chromium in solution. In spite of the powerful oxidizing ability of hydrogen peroxide, it acts as a reductant ($E_0 = +0.68$ V) when reacting with stronger oxidizing agents such as chlorine ($E_0 = 1.77$ V), potassium permanganate ($E_0 = 1.52$ V), and potassium dichromate ($E_0 = 1.33$ V):

$$\text{reduction of Cr(VI)}: \quad \mathrm{Cr(VI)} + \mathrm{H_2O_2} + \mathrm{H}^+ \xrightarrow{k_3} \mathrm{Cr(III)} + \mathrm{H_2O} + \mathrm{O_2} \qquad (4)$$

$$\mathrm{Cr(VI)} + \mathrm{CH_3O}^{\bullet} \xrightarrow{k_5} \mathrm{Cr(III)} + \text{products} \qquad (5)$$

A mechanistic rate expression for photo-reduction can be developed on the basis of the above reaction steps. Generation and consumption of H_2O_2 and methoxy radicals are assumed to occur at pseudo-steady state:

$$\frac{d}{dt}[\mathrm{H_2O_2}] = k_2[\mathrm{O_2}][\mathrm{H}^+][\mathrm{e}^-] - k_3[\mathrm{Cr(VI)}[\mathrm{H_2O_2}][\mathrm{H}^+] = 0 \qquad (6)$$

$$\frac{d}{dt}[\mathrm{CH_3O}^{\bullet}] = k_4[\mathrm{CH_3OH}][\mathrm{h}^+] - k_5[\mathrm{Cr(VI)}][\mathrm{CH_3O}^{\bullet}] = 0 \qquad (7)$$

The initial rate of reduction [from Eqs. (4) and (5)] is

$$-\frac{d[\mathrm{Cr(VI)}]}{dt} = k_3[\mathrm{Cr(VI)}[\mathrm{H_2O_2}][\mathrm{H}^+] + k_5[\mathrm{Cr(VI)}][\mathrm{CH_3O}^{\bullet}] \qquad (8)$$

Combining Eqs. (6)–(8),

$$\text{initial rate} = k_2[\mathrm{O_2}][\mathrm{H}^+][\mathrm{e}^-] + k_4[\mathrm{CH_3OH}][\mathrm{h}^+] \qquad (9)$$

Table 1b
Chromium (VI) reduction by conventional techniques.

Ref.	Initial Cr(VI) conc.	Reducing agent	Dosage	Percent Cr(VI) reduced
McGuire et al. [8]	100 μg/L	$FeSO_4$	Fe(II)/Cr(VI) = 25	98%
-do-	100 μg/L	$NaHSO_3$ + NaOCl	Large excess (23.6 g/L + 1.5 g/L)	99%+
Patterson et al. [9]	540 mg/L	$Na_2S_2O_5$	100% excess	97%

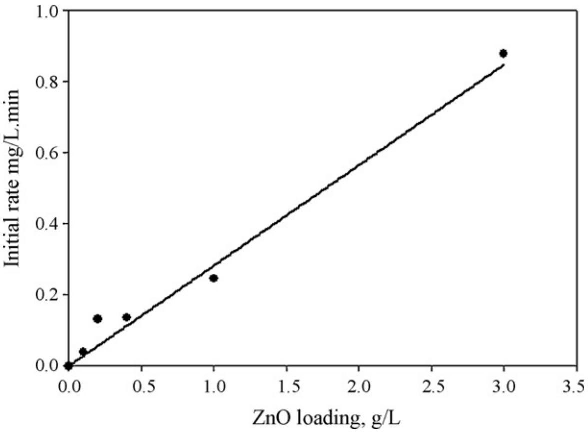

Fig. 9. Plot of Eq. (12) for different values of ZnO loading [initial concentration: 50 mg/L; temperature: 20 °C, pH: 4.5; UV radiation: 388 lx].

Again, the pseudo-steady state assumption applied to the generation of holes and the electrons leads to

$$\frac{d}{dt}[\mathrm{h}^+] = k_1[\mathrm{ZnO}][h\nu] - k_4[\mathrm{CH_3OH}][\mathrm{h}^+] = 0 \tag{10}$$

and

$$\frac{d}{dt}[\mathrm{e}^-] = k_1[\mathrm{ZnO}][h\nu] - k_2[\mathrm{O_2}]^{1/2}[\mathrm{H}^+][\mathrm{e}^-] = 0 \tag{11}$$

Combining Eqs. (9)–(11), the final form of the rate equation becomes

$$\text{initial rate of reduction,}\ r_i = 2k_1[\mathrm{ZnO}][h\nu] = k \tag{12}$$

The above rate equation indicates a zero order reduction reaction with respect to the concentration of the substrate as well as to that of methanol over the range of parameter values used in this study. A very recent article by Wang et al. [37] reports that the rate of reduction is independent of the substrate concentration; this supports our Eq. (12) as deduced from the present model. This is also in conformity with the experimental findings presented in insets of Figs. 3 and 8. The rate equation has been tested by plotting the initial rates against the catalyst (ZnO) concentration as well as UV dosage. The linear plots of the experimental data presented in Figs. 9 and 10 validates the rate Eq. (12) derived above for the initial rate. The above rate equation gives the overall rate as a result of reduction of Cr(VI) by H_2O_2 generated in situ as well as by the methoxy radicals.

The value of the rate constant, k_1, was obtained from Fig. 9 as 3.6572×10^{-4} [mg Cr(VI)/(L)(min)] [mg ZnO/L]$^{-1}$ [lx]$^{-1}$ considering a total of 125 W UV (388 lx) input in a 2-L liquid volume. If we plot initial rates against UV radiation in lux (Fig. 10), we get the value of k_1 as 3.833×10^{-4} [mg Cr(VI)/(L)(min)] [mg ZnO/L]$^{-1}$ [lx]$^{-1}$ considering the same photoreactor configuration. This revalidates the kinetic model of Eq. (12). However, the fitting of data in Figs. 9 and 10 shows that correlation of initial rate and ZnO loading is better compared to the correlation of initial rate and intensity of UV radiation. Fig. 11 shows a parity diagram showing the experimental and predicted values of the initial rates at different loading of ZnO photocatalyst.

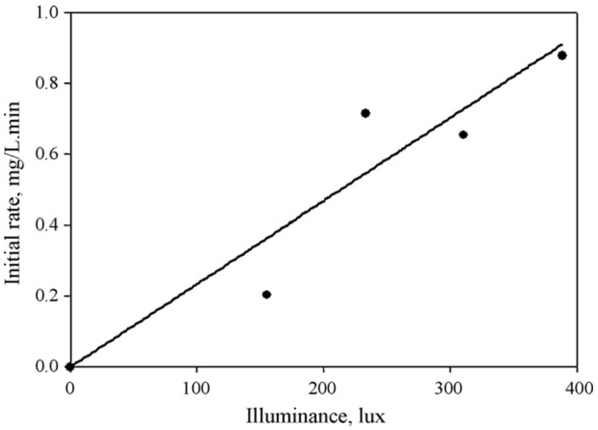

Fig. 10. Plot of Eq. (12) for different intensities of UV radiation [initial concentration: 50 mg/L; temperature: 20 °C; pH: 4.5; ZnO loading: 3 g/L].

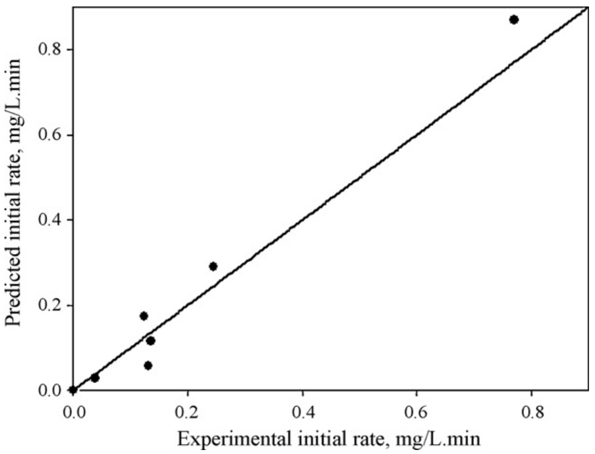

Fig. 11. Parity diagram of experimental and predicted values of initial rates [ZnO loading: 3 g/L; UV radiation: 388 lx; pH: 4.5; temperature: 20 °C].

3.3. An alternative rate equation—the Langmuir–Hinshelwood–Hougen–Watson (LHHW) model

Several researchers proposed the LHHW rate equation to determine the rate constant for photocatalytic reduction. For example, Ku and Jung [17], in their work on photo-reduction of Cr(VI) using TiO_2, suggested a Langmuir–Hinshelwood type rate equation which was approximated by a pseudo-first order equation at low Cr(VI) concentration. The rate constant was found to be linear in the UV intensity similar to our observation. Schrank et al. [11] also suggested a Langmuir–Hinshelwood rate equation in their work on photo-reduction of Cr(VI) using the same catalyst. Although we did not observe any appreciable adsorption of Cr(VI) on the ZnO catalyst, adsorption of methanol could lead to a LHHW-type pathway of the reduction reaction through the formation of the methoxy radicals [Eq. (3)]. To test this possibility we selected the following form of the LHHW equation for the initial rate:

$$\text{rate,}\ r_i' = \frac{k' C_A}{1 + K C_A} \tag{13}$$

The corresponding linearized form of the equation is

$$\frac{C_A}{r_i'} = \frac{1}{k'} + \frac{K}{k'} C_A \tag{14}$$

The fitting of data with the above equation ($R^2 = 0.99$) has been shown in Fig. 12. The values of k' and K obtained from the slope and intercept are 3.29 min^{-1} and 3.99 (mg/L)$^{-1}$ respectively. At the concentrations (C_A in mg/L) of Cr(VI) used in this work, $KC_A \gg 1$ and hence Eq. (13) reduces to

$$\text{initial rate,}\ r_i' = \frac{k'}{K} = k_0 \tag{15}$$

That is the initial reaction rate is zero order—it is independent of the initial concentration of the substrate as well as of the concentration of methanol added. This also matches the rate equation

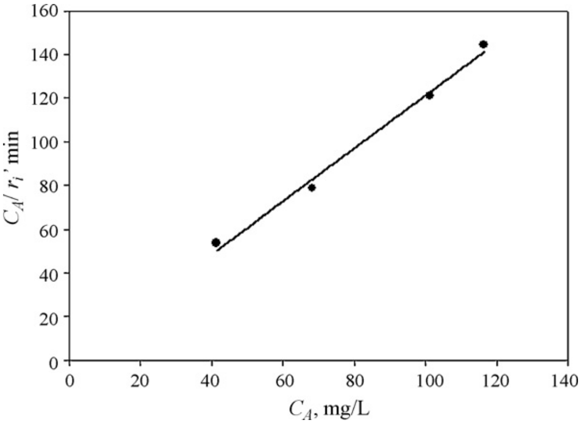

Fig. 12. LHHW fitting of the photocatalytic reduction of potassium dichromate with ZnO [ZnO loading: 3 g/L; UV radiation: 388 lx; pH: 4.5; temperature: 20 °C].

[Eq. (12)] developed on a mechanistic basis and the experimental findings as indicated in the insets of Figs. 3 and 8. The value of the rate constant from the LHHW model [k_0 in Eq. (15)] is 0.8245 mg L^{-1} min^{-1}. Using intensity of UV radiation as 388 lx and ZnO loading as 3 g/L, the value of rate constant from our proposed model [k in Eq. (12)] comes to be 0.8512 mg L^{-1} min^{-1} (from Fig. 9) and 0.8922 mg L^{-1} min^{-1} (from Fig. 10), which are all in good agreement.

4. Conclusion

Hexavalent chromium in aqueous solutions can be effectively reduced to the trivalent state using ZnO as the semiconductor photocatalyst under UV radiation in the presence of a sacrificial electron donor. The extent of degradation as well as its initial rate increased with the loading of the photocatalyst and intensity of UV radiation. About 90% reduction of the substrate could be achieved over a reaction time of 75 min. This shows the better performance of the ZnO catalyst in the presence of methanol as the sacrificial electron donor. The initial reaction rate was practically independent of the concentration of the substrate as well as of the sacrificial electron donor but showed a linear dependence on the catalyst in suspension as well as on the UV dosage. A kinetic model has been suggested based on a possible sequence of reactions. The model fits in the initial rate calculated from the experimental data. The values of the rate constants have been determined. An alternative rate equation based on the LHHW model led to the same zero order form as the mechanistic rate equation. The rate constants derived by the two models are comparable.

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References

[1] L.A.G. Rodenas, A.D. Weisz, G.E. Magaz, M.A. Blesa, Effect of light on the electrokinetic behaviour of TiO_2 particles in contact with Cr(VI) aqueous solutions, J. Colloid Interface Sci. 230 (2000) 181–185.
[2] B. Sun, E.P. Reddy, P.G. Smirniotis, Visible light Cr(VI) reduction and organic chemical oxidation by TiO_2 photocatalysis, Environ. Sci. Technol. 39 (2005) 6251–6259.
[3] A.R. Bowers, C.P. Huang, Activated carbon process for treatment of automotive application for chromium wastewaters containing hexavalent chromium, Prog. Water Technol. 12 (1980) 629.
[4] X. Wang, S.O. Pehkonen, A.K. Ray, Removal of aqueous Cr(VI) by a combination of photocatalytic reduction and coprecipitation, Ind. Eng. Chem. Res. 43 (2004) 1665–1672.
[5] A.H. El-Shazly, A.A. Mubarak, A.H. Konsowa, Hexavalent chromium reduction using a fixed bed of scrap bearing iron spheres, Desalination 185 (2005) 307–316.
[6] S.-S. Chen, C.-Y. Cheng, C.-W. Li, P.-H. Chai, Y.-M. Chang, Reduction of chromate from electroplating wastewater from pH 1 to 2 using fluidized zero-valent iron process, J. Hazard. Mater. 142 (2007) 362–367.
[7] D. Wichern, A quick look at waste treatment with ferrous sulfate, Met. Finish. 102 (2004) 39.
[8] M.J. McGuire, N. Blute, C. Seidel, G. Qin, A.L. Fong, Pilot-scale studies of hexavalent chromium removal, J. Am. Water Works Assoc. 98 (2006) 134–143.
[9] J.W. Patterson, E. Gasca, Y. Wang, Optimization for reduction/precipitation treatment of hexavalent chromium, Water Sci. Technol. 29 (1994) 275–284.
[10] P.S. Kulkarni, V. Kalyani, V.V. Mahajani, Removal of hexavalent chromium by membrane-based hybrid processes, Ind. Eng. Chem. Res. 46 (2007) 8176–8182.
[11] S.G. Schrank, H.J. José, R.F.P.M. Moreira, Simultaneous photocatalytic reduction and dye oxidation in a TiO_2 slurry reactor, J. Photochem. Photobiol. A: Chem. 147 (2002) 71–76.
[12] K. Kabra, R. Chaudhary, R. Sawhney, Treatment of hazardous organic and inorganic compounds through aqueous phase photocatalysis: a review, Ind. Eng. Chem. Res. 43 (2004) 7683–7696.
[13] J. Domènech, J. Muñoz, Photocatalytical reduction of Cr(VI) over ZnO powder, Electrochim. Acta 32 (1987) 1383–1386.
[14] P. Mohapatra, S.K. Samantaray, K. Parida, Photocatalytic reduction of hexavalent chromium in aqueous solution over sulphate modified titania, J. Photochem. Photobiol. A: Chem. 170 (2005) 189–194.
[15] L.B. Reuterglrdh, M. langphasuk, Photocatalytic decolourization of reactive azo dye: a comparison between TiO_2 and CdS photocatalysis, Chemosphere 35 (1997) 585–596.
[16] P. Ciesla, P. Kocot, P. Mytych, Z. Stasicka, Homogeneous photocatalysis by transition metal complexes in the environment, J. Mol. Catal. A: Chem. 224 (2004) 17–33.
[17] Y. Ku, I. Jung, Photocatalytic reduction of Cr (VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide, Water Res. 35 (1) (2001) 135–142.
[18] L.B. Khalil, W.E. Mourad, M.W. Rophael, Photocatalytic reduction of environmental pollutant Cr(VI) over some semiconductors under UV/visible light illumination, Appl. Catal. B: Environ. 17 (1998) 267–273.
[19] P. Mytych, A. Larocki, Z. Stasicka, Mechanism of photochemical reduction of chromium(VI) by alcohols and its environmental aspects, J. Photochem. Photobiol. A: Chem. 160 (2003) 163–170.
[20] P. Mytych, Z. Stasicke, Photochemical reduction of chromium(VI) by phenol and its halogen derivatives, Appl. Catal. B: Environ. 52 (2004) 167–172.
[21] P. Mytych, P. Cielsa, Z. Stasicka, Photoredox processes in the Cr(VI)–Cr(III)-oxalate system and their environmental relevance, Appl. Catal. B: Environ. 59 (2005) 161–176.
[22] Y. Cho, H. Kyung, W. Choi, Visible light activity of TiO_2 for the photoreduction of CCl_4 and Cr(VI) in the presence of nonionic surfactants (Brij), Appl. Catal. B: Environ. 52 (2004) 23–32.
[23] L. Deng, H. Wang, N. Deng, Photoreduction of chromium(VI) in the presence of algae, *Chlorella vulgaris*, J. Hazard. Mater. B 138 (2006) 288–292.
[24] Y. Liu, L. Deng, Y. Chen, F. Wu, N. Deng, Simultaneous photocatalytic reduction of Cr(VI) and oxidation of bisphenol A induced by Fe(III)–OH complexes in water, J. Hazard. Mater. B 139 (2007) 399–402.
[25] I. Poulios, A. Avranas, E. Rekliti, A. Zouboulis, Photocatalytic oxidation of Auramine O in the presence of semiconducting oxides, J. Chem. Technol. Biotechnol. 75 (2000) 205–212.
[26] P. Cuendet, K.K. Rao, M. Grätzel, D.O. Hall, Light induced H_2 evolution in a hydrogenase-TiO_2 particle system by direct electron transfer or via rhodium complexes, Biochimie 68 (1968) 217–221.
[27] F. Aulenta, J.M. Gossett, M. Petrangeli Papini, S. Rossetti, M. Majone, Comparative study of methanol, butyrate, and hydrogen as electron donors for long-term dechlorination of tetrachloroethene in mixed anerobic cultures, Biotechnol. Bioeng. 91 (2005) 743–753.
[28] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J.M. Carlsson, K. Domen, M. Antonietti, A metal-free polymeric photocatalyst for hydrogen production from water under visible light, Nat. Mater. 8 (2009) 76–80.
[29] S. Goeringer, C.R. Chenthamarakshan, K. Rajeswar, Synergistic photocatalysis mediated by TiO_2: mutual rate enhancement in the photoreduction of Cr(VI) and Cu(II) in aqueous media, Electrochem. Commun. 3 (2001) 290–292.
[30] E. Selli, A. De Giorgi, G. Bidoglio, Humic acid sensitized photoreduction of Cr(VI) on ZnO particles, Environ. Sci. Technol. 30 (1996) 598–604.
[31] T. Iwata, M. Ishikawa, R. Ichino, M. Okido, Photocatalytic reduction of Cr(VI) on TiO_2 film formed by anodizing, Surf. Coat. Technol. 169–170 (2003) 703–706.
[32] S. Chakrabarti, B.K. Dutta, Photocatalytic degradation of textile dyes in aqueous solutions using ZnO as semiconductor catalyst, J. Hazard. Mater. B 112 (2004) 269–278.
[33] F. Jiang, Z. Zheng, Z. Xu, S. Zheng, Z. Guo, L. Chen, Aqueous Cr(VI) photo-reduction catalyzed by TiO_2 and sulfated TiO_2, J. Hazard. Mater. B 134 (2006) 94–103.
[34] J.A. Navio, J.J. Testa, P. Djedjeian, J.R. Padron, D. Rodriguez, M.I. Litter, Iron-doped titania powder prepared by a sol–gel method. Part II. Photocatalytic properties, Appl. Catal. A: Gen. 178 (1999) 191–203.

[35] D.S. Bhatkhande, V.G. Pangarkar, A.A.C.M. Beenackers, Photocatalytic degradation for environmental application—a review, J. Chem. Technol. Biotechnol. 77 (2001) 102–116.
[36] C.S. Turchi, D.F. Ollis, Photocatalytic degradation of organic water contaminants: mechanism involving hydroxyl radical attack, J. Catal. 122 (1990) 178–192.
[37] S.-L. Wang, C.-C. Chen, Y.-M. Tzou, C.-L. Hsu, J.-H. Chen, C.-F. Lin, A mechanism study of light-induced Cr(VI) reduction in an acidic solution, J. Hazard. Mater. 164 (2009) 223–228.
[38] U. Siemon, D. Bahnemann, J.J. Testa, D. Rodriguez, M.I. Litter, N. Bruno, Heterogeneous photocatalytic reactions comparing TiO_2 and Pt/TiO_2, J. Photochem. Photobiol. A: Chem. 148 (2002) 247–255.