

Photocatalytic reduction of hexavalent chromium in aqueous solution over titania pillared zirconium phosphate and titanium phosphate under solar radiation

Dipti Prakashini Das^a, Kulamani Parida^{a,*}, Bhudev Ranjan De^b

^a BP and EM Department, Regional Research Laboratory (CSIR), Bhubaneswar 751013, Orissa, India

^b Department of Chemistry and Chemical Technology, Vidyasagar University, Midnapur, West Bengal, India

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Abstract

The photo-reduction of hexavalent chromium was carried out varying different parameters such as pH, titania loading on zirconium phosphate (ZrP) and titanium phosphate (TiP), initial substrate concentration, irradiation time and catalyst dose. The reduction rate of chromium was favorable under acidic pH than in the alkaline pH. The dissolved oxygen imparts the minimum effect on the reduction of Cr(VI) as oxygen competes with the hexavalent chromium for the electron in the acidic solutions. Hexavalent chromium was completely reduced over titania pillared ZrP and TiP under solar radiation. This process of photo-reduction follows approximately pseudo first-order kinetics.

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1. Introduction

The presence of heavy metals in aquatic bodies has been known to cause pollution problem. The major source of heavy metals is the improper discharge of various industrial wastewaters. These metal ions are generally non-degradable. They have got infinite life times and build up their concentrations in food chains to toxic levels. Among these inorganic pollutants chromium is an important industrial metal that is considered a priority pollutant by US Environmental protection agency. Chromium occurs in two common oxidation states in nature, Cr(III) and Cr(VI), out of which hexavalent chromium is 100 times more toxic than the other (for concentrations higher than 0.05 ppm). This form of chromium is known to be human carcinogen [1] and is generally associated with the development of various chronic health disorders including organ damage, dermatitis and respiratory impairment [2]. In the environment hexavalent chromium salts do not readily precipitate or become bound to components of soil [3]. It is soluble in water and

forms divalent oxyanions: chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$). Cr(VI) is mobile in nature and is only weakly sorbed onto inorganic surface. Cr(III) is readily precipitated or sorbed on inorganic and organic substrates.

Cr(VI) is an important contaminant in wastewaters arising from industrial processes such as electroplating, leather tanning or paint making, due to its carcinogenic properties, it has been controlled in many countries. The preferred treatment is to reduce the harmful Cr(VI) to Cr(III) which is less harmful. Again the removal from wastewater is generally accomplished by employing various chemical and physical means such as hydroxide precipitation, ion exchange, adsorption, and membrane process. Recently, a new technology, based on photo-catalysis to eliminate Cr(VI) ions, a toxic pollutant in the environment was applied using solar energy [4,5]. The photocatalytic process was used for rapid and efficient destruction of environmental pollutants.

Reduction by semiconductor photocatalysis technology [6] is a relatively new technique for the removal or recovery of dissolved metal ions in wastewater. Ultraviolet and visible light have sufficient energy to overcome the band gap of semiconductors and form electron-hole pairs (e^-h^+) [7–11]. These charge carriers, which migrate to the semiconductor surface, are

* Corresponding author. Tel.: +91 674 2581636x305; fax: +91 674 2581637.

E-mail addresses: kmparida@yahoo.com (K. Parida), das.diptiprakashini@rediffmail.com (D.P. Das).

capable of reducing or oxidising species in solution. The metal is reduced on the semiconductor particle surface. The photocatalytic reduction of chromium using semiconductor particles has been widely studied. This photo-reduction takes place at low pH because the net reaction consumes protons. The photocatalysts used are mainly CdS [12,13], ZnS [12], WO_3 [12,14], various types of TiO_2 [14,15], ZnO [16], titania supported layered compounds (SLCs) [17], titania modified mesoporous silicate MCM-41 [18], sulphated titania [19]. Heterogeneous catalysis and photochemistry principles were used to explain these processes.

The current paper deals with photo-reduction of Cr(VI) using the titania pillared zirconium phosphate and titanium phosphate under solar radiation. The activities of this catalyst was studied under different reaction conditions such as titania load, catalyst dose, substrate concentration, pH, effect of sacrificial electron donors like EDTA, 4-nitrophenol, effect of presence of N_2 , O_2 , air and were correlated with surface properties.

2. Experimental

2.1. Preparation of the material

Titania pillared ZrP and TiP were prepared from Na-exchanged ZrP and TiP following the procedure reported by Yamanaka et al. [20]. First titania sol was prepared by dropwise addition of titanium(IV) isopropoxide to a vigorously stirred 1 M HCl solution. The resulting slurry was stirred for 3 h to give a clear titania sol and then aqueous suspension of sodium exchanged ZrP or TiP was added to the sol. The suspension was further stirred for 3 h at 50°C . It was filtered and washed thoroughly with deionised water and dried at different temperatures for further studies.

2.2. Physicochemical characterisation

The X-ray powder diffraction pattern was taken in Philips PW 1710 diffractometer with automatic control. The patterns were run with monochromatic Cu $\text{K}\alpha$ radiation, with scan rate of 2°min^{-1} .

UV–vis DRS was taken in Varian UV–vis spectrophotometer in the range of 200–800 nm. The spectra were recorded against boric acid reflectance standard as base line. The computer processing of spectra with CARY 1E software consisted of calculation of Kubelka–munk function $F(R_\infty)$ from the absorbance.

The BET-surface area analysis was carried out using Quantasorb instrument (Quantachrome, USA) by nitrogen adsorption–desorption isotherms at liquid nitrogen temperature (-196°C). Prior to adsorption–desorption measurements, samples were degassed at 110°C and 10^{-5} Torr for 5 h in vacuum.

FT-IR spectra were taken using Jasco FT-IR-5300 in KBr phase in the range $400\text{--}4000 \text{ cm}^{-1}$.

2.3. Experimental procedure

The photo-reduction of Cr(VI) ($\text{K}_2\text{Cr}_2\text{O}_7$, BDH) was performed in batch process by taking 20 mg/L of the substrate

(fresh solution of $\text{K}_2\text{Cr}_2\text{O}_7$) and 0.2 g/L of catalyst. The solution was exposed to sunlight in closed pyrex flasks at room temperature with constant stirring. The observations were compared with the blank, which was done in dark. The effect of EDTA, 4-nitrophenol, N_2 , O_2 and air were studied keeping all other parameters fixed. After irradiation, the suspension was filtered and analysed for Cr(VI) quantitatively by measuring the absorbance at 348 nm using CARY 1E Spectrophotometer (Varian). The detail method of measurement is found in the literature [21].

3. Results and discussion

3.1. Physicochemical characterisation

The XRD patterns (Fig. 1, the values of crystallite size were pointed out in the figure) show that the crystallite size was found to be less in case of 4 wt.% of titania loaded TiP (104.56 \AA) support than that of neat TiP (206.624 \AA) calcined at 500°C and similar case was observed in case of 2 wt.% titania loaded ZrP

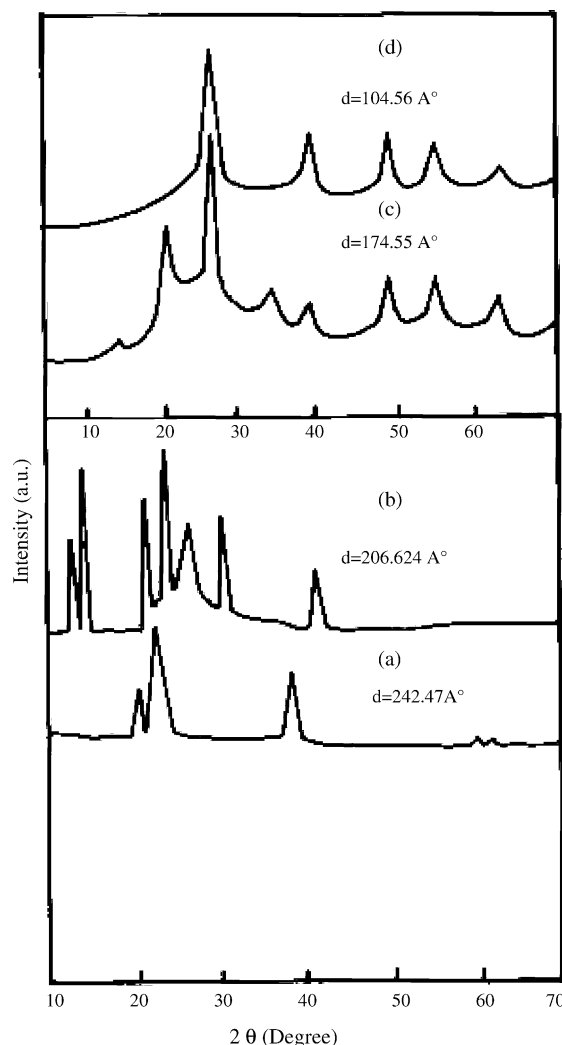


Fig. 1. The XRD pattern of 500°C calcined (a) ZrP, (b) TiP, (c) ZrP/ TiO_2 2 wt.%, (d) TiP/ TiO_2 4 wt.% (d = crystallite size in \AA).

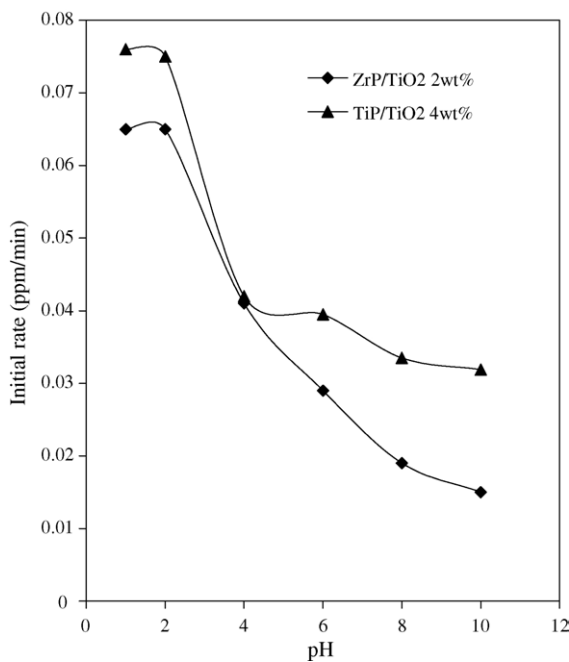


Fig. 2. Effect of pH on the initial rate of Cr(VI) photo-reduction: catalyst dose = 0.6 g/L; [Cr(VI)] = 20 mg/L; time = 240 min.

(174.55 Å) and neat ZrP (242.47 Å) calcined at 500 °C. The decrease in the crystallite size in presence of titania species could possibly due to the interaction of titania species with ZrP and TiP.

Again the values of basal spacing, UV–vis DRS spectra, FT-IR spectra and surface area confirms pillaring, the details of which has been published elsewhere [22].

3.2. Photo-reduction of Cr(VI)

3.2.1. Effect of pH

The photo-reduction of hexavalent chromium was strongly dependent on pH. The highest reaction rate was obtained at lower pH (Fig. 2). Fig. 2 depicts the initial rate (ppm/min) values of 2 and 4 wt.% titania pillared ZrP and TiP, respectively in the pH range 1–10. Initial rate of photo-reduction was found to be maximum in the acidic pH (pH ≈ 1–2). With further increase in the pH decreases the initial rate of the process from 0.065 to 0.015 and 0.075 to 0.0319 ppm/min for 2 wt.% titania pillared ZrP and 4 wt.% titania pillared TiP, respectively. This can be explained on the basis of pH_{pzc} of the catalyst. Since pH_{pzc} of titania pillared ZrP and TiP is around 5–6 and consequent negative surface charge which probably repels the Cr(VI) species at pHs higher than pH_{pzc} [16]. Probably a similar mechanism is operating here. The initial photo-reduction rate was dropped markedly with increase in pH. The catalysed effect of the acidified pH values is in agreement with the reported results that the photo-reduction of $K_2Cr_2O_7$ solutions, using platinumised titania (Pt/P25) as photocatalyst, is more adequate for acidic solutions [23,24].

It is significant that results obtained by Lin et al. [25] for pH effect in case of Cr(VI)/TiO₂ suspension is in conflict with that

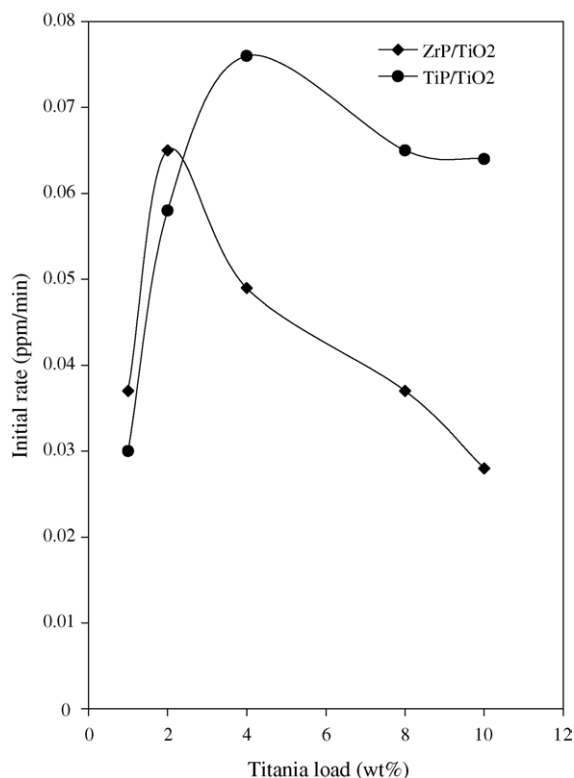


Fig. 3. Effect of titania loading on the initial rate of Cr(VI) photo-reduction: catalyst dose = 0.6 g/L; [Cr(VI)] = 20 mg/L; pH 2.0; time = 240 min.

of Munoz et al. [26] who observed a decrease in the conversion level of Cr(VI) with increasing pH in the range 4–8 using TiO₂. A different trend was observed by the same author for ZnO [16], where they found a maximum at pH 7.0 with the Cr(VI) photo-reduced falling off at lower and higher pH values in the range 6–9. Due to so many inconsistencies in the previous papers, it is preferable not to make any further comparison based on pH effects.

3.2.2. Effect of titania load

From Fig. 3, with increase in the titania loading up to 2 wt.% for ZrP and 4 wt.% for TiP, the initial rate of the Cr(VI) photo-reduction increases to 0.065 and 0.076 ppm/min, respectively and thereafter it decreases to 0.028 and 0.064 ppm/min range. This promoting effect of titania on the activity of ZrP and TiP could be understood by considering the following factors:

- (1) Pillaring of titania resulted in higher surface area, which allows more Cr(VI) molecules to be adsorbed on the surface and thereby facilitating the photo-reduction process.
- (2) Pillaring of titania leads to lowering of crystallite size which in turn increases the surface area and adsorption of hexavalent chromium and ultimately the photo-reduction of Cr(VI).

3.2.3. Effect of initial concentration

The rate of photo-reduction of Cr(VI) over titania pillared ZrP and TiP was studied by taking the initial concentration of Cr(VI) in the range of 2–50 mg/L. Almost all Cr(VI) was reduced for initial concentration of 2–5 mg/L of Cr(VI) in case of both the

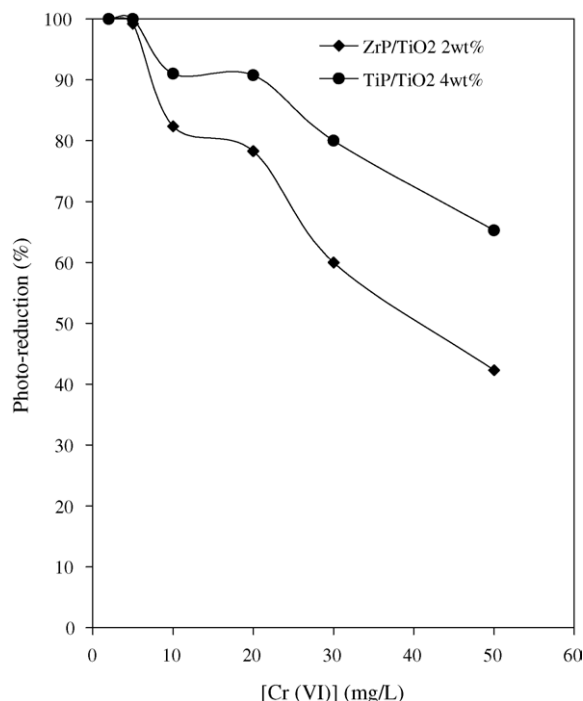


Fig. 4. Effect of initial concentration of Cr(VI) on the percentage of photo-reduction: catalyst dose = 0.6 g/L; pH 2.0; time = 240 min.

catalysts (Fig. 4). But it gradually decreases with increasing the initial concentration of Cr(VI) from 10 to 50 mg/L. The percentage of Cr(VI) photo-reduction decreases from 100 to 42.5 and 65.28% for 2 and 4 wt.% titania loaded ZrP and TiP, respectively with a fixed amount of catalyst dose. This may be due to the fact that at higher substrate concentration, the light absorbed by the substrate is more than that of the catalyst which may not be effective in bringing about the photo-reduction of Cr(VI). Since the catalyst amount was fixed, the active sites remaining the same, the substrate concentration increases for which there may be a decrease in the initial rate of photo-reduction of Cr(VI) (Fig. 4).

3.2.4. Kinetic analysis

The variation of initial chromium concentration in the range of 2–50 mg/L on the photo-reduction process was studied under constant conditions of pH, catalyst dose. The photo-reduction process at low concentration of Cr(VI) followed pseudo first-order kinetics. Some authors reported [27,28] that below pH 4.0 the Cr(VI) photo-reduction follows half-order kinetics. Some

Table 1
Rate constant values for photo-reduction of Cr(VI) over titania pillared ZrP (2 wt.%)

Time (min)	Concentration, 20 mg/L ($k = 0.0064 \text{ min}^{-1}$)		Concentration, 30 mg/L ($k = 0.0038 \text{ min}^{-1}$)		Concentration, 50 mg/L ($k = 0.0025 \text{ min}^{-1}$)	
	Photo-reduction (%)	$\log C_0/C$	Photo-reduction (%)	$\log C_0/C$	Photo-reduction (%)	$\log C_0/C$
30	27.33	0.138	15.92	0.075	10.23	0.046
90	35.2	0.188	24.3	0.12	17.9	0.085
120	49.35	0.295	32.5	0.17	25.39	0.127
240	78.3	0.663	60	0.39	42.5	0.24
300	79	0.677	60.5	0.40	42.98	0.243

k is the apparent rate constant.

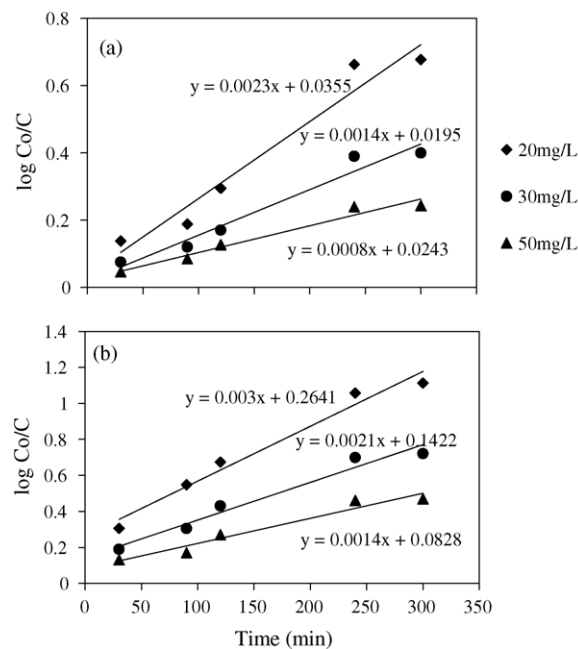


Fig. 5. Plot of $\log C_0/C$ vs. time for photo-reduction of Cr(VI): (a) for 2 wt.% titania pillared ZrP, (b) for 4 wt.% titania pillared TiP; catalyst dose = 0.6 g/L; pH 2.0; [Cr(VI)] = 20 mg/L.

authors [16,29] reported this process to be first-order. In the present work and experimental conditions, a linear relationship was observed between Cr(VI) concentration and irradiation time as shown in Fig. 5(a) and (b) ($\log C_0/C$ versus time, where C_0 is initial Cr(VI) concentration and C is the Cr(VI) concentration at time t) for titania pillared ZrP and TiP, respectively. The data calculated for pseudo first-order rate constants " k " at different Cr(VI) concentration were given in Tables 1 and 2 for titania pillared ZrP and TiP, respectively. The rate constant values in both the cases were found to decrease with increase in initial Cr(VI) concentration from 20 to 50 mg/L.

3.2.5. Effect of catalyst dose

The effect of catalyst dose on the initial rate of photo-reduction was studied in the range of 0.2–1.6 g/L of the catalyst. Fig. 6 shows the variation of initial rate of photo-reduction of Cr(VI) as a function of catalyst dose (g/L). The values indicated that with increase in the catalyst dose, the initial rate of photo-reduction of Cr(VI) increases from 0.0375 to 0.065 and 0.052 to 0.076 ppm/min for 2 wt.% titania loaded ZrP and

Table 2
Rate constant values for photo-reduction of Cr(VI) over titania pillared TiP (4 wt.%)

Time (min)	Concentration, 20 mg/L ($k = 0.0137 \text{ min}^{-1}$)		Concentration, 30 mg/L ($k = 0.0086 \text{ min}^{-1}$)		Concentration, 50 mg/L ($k = 0.0055 \text{ min}^{-1}$)	
	Photo-reduction (%)	$\log C_0/C$	Photo-reduction (%)	$\log C_0/C$	Photo-reduction (%)	$\log C_0/C$
30	50.48	0.3052	35.29	0.189	26.29	0.132
90	71.71	0.548	50.35	0.304	32.38	0.169
120	78.77	0.673	62.9	0.43	46.42	0.27
240	90.75	1.057	80	0.699	65.28	0.46
300	92.3	1.113	81	0.721	66.05	0.469

k is the apparent rate constant.

4 wt.% titania loaded TiP, respectively. Thereafter, it remains almost constant. This is mainly because with increase in the catalyst dose, there is an increase in the active sites which in turn increases the adsorption of Cr(VI) and ultimately increases the rate of photo-reduction. The initial Cr(VI) concentration remaining same further increasing the catalyst amount did not make any difference to photo-reduction of hexavalent chromium. So with further increase in the catalyst dose the initial rate of photo-reduction of Cr(VI) remains constant.

3.2.6. Effect of time

Fig. 7 shows that with increase in the irradiation up to 4 h, the percentage of Cr(VI) photo-reduction increases from 27.33 to 78.3% and 50.48 to 90.75% for 2 wt.% titania pillared ZrP and 4 wt.% titania pillared TiP, respectively. Then it remains almost

constant. This may be due to increase in the photon flux with increase in the contact time which leads to more reduction of Cr(VI).

3.2.7. Effect of reductants

In absence of any organic species, the conjugate oxidation reaction of metal ion reduction is the electrochemical oxidation of water. This is a kinetically slow four-electron process according to Chen and Ray [30] and inhibited by recombination of photo-generated holes and electrons [31]. So we can expect the addition of sacrificial electron donors such as suitable organic substrates may accelerate the photocatalytic reduction of Cr(VI). Hence we can say the reduction of organics-titania pillared ZrP/TiP must be more efficient than simply titania loaded ZrP/TiP. The organic species such as EDTA, methanol, salicylic acid and 4-nitrophenol accept holes from the valence band either directly or indirectly and subsequently oxidized and thereby suppressing the electron-hole recombination process, increasing the reduction efficiency. In this work the effect of

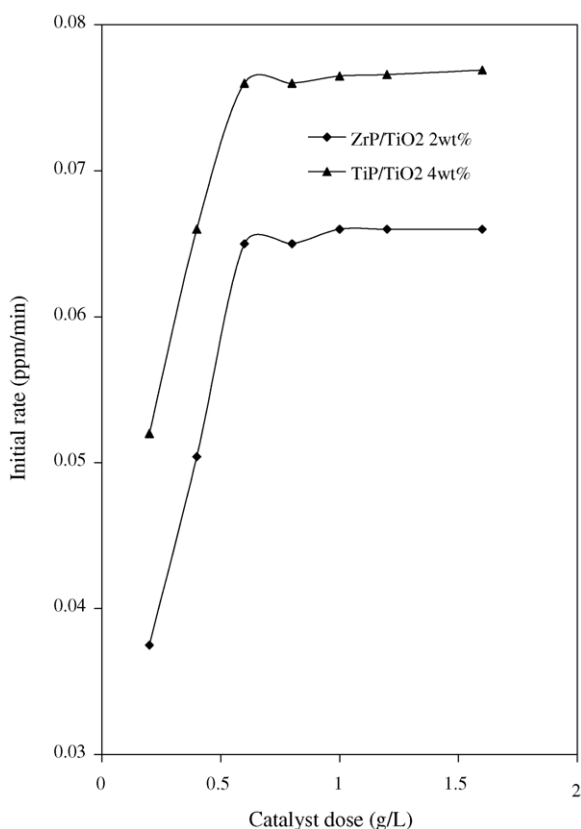


Fig. 6. Effect of catalyst amount on the initial rate of photo-reduction of Cr(VI): [Cr(VI)] = 20 mg/L; pH 2.0; time = 240 min.

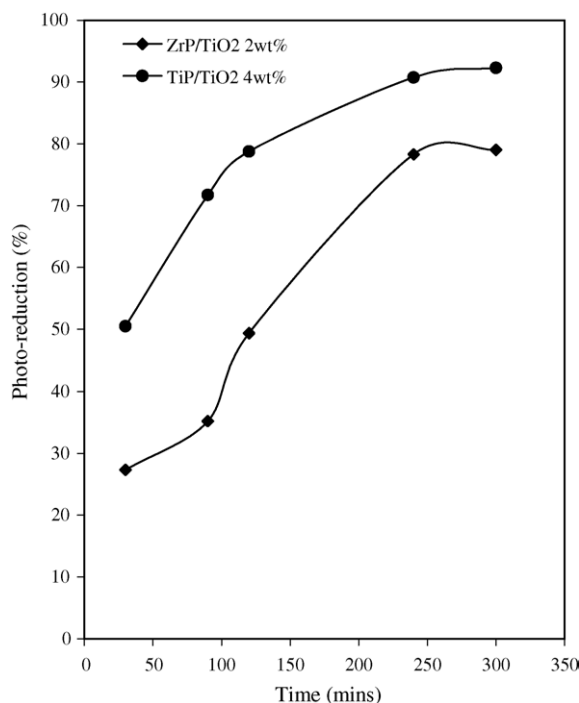


Fig. 7. Effect of irradiation time on the percentage of photo-reduction of Cr(VI): catalyst dose = 0.6 g/L; [Cr(VI)] = 20 mg/L; pH 2.0.

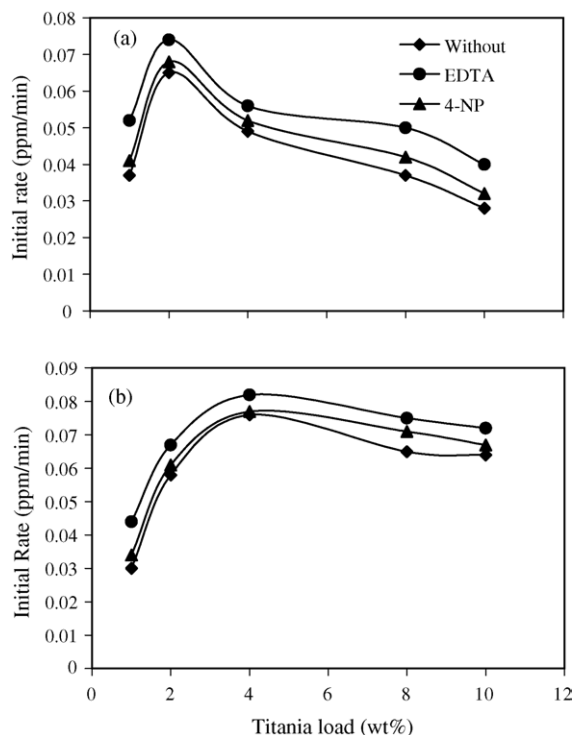


Fig. 8. Effect of reductants on the initial rate of Cr(VI) photo-reduction: (a) 2 wt.% titania pillared ZrP; (b) 4 wt.% titania pillared TiP; catalyst dose = 0.6 g/L; [Cr(VI)] = 20 mg/L; pH 2.0; time = 240 min.

sacrificial electron donors such as EDTA and 4-nitrophenol were investigated. Fig. 8 shows that both reductants promote the photo-reduction of Cr(VI), but in case of EDTA its much more significant (the significant results, one can notice in case of titania pillared ZrP). This is mainly due to the strong chelating effect of EDTA which forms a stable complex with Cr(VI) in solution. From Fig. 8(a) and (b) it was clearly observed that the initial rate of photo-reduction in case of 2 wt.% titania pillared ZrP increased from 0.065 to 0.074 ppm/min by addition of EDTA where as for 4-nitrophenol the increase was from 0.065 to 0.068 ppm/min (Fig. 8(a)). One can see for each wt.% variation the addition of EDTA showed the significant results. Similar observations were found in case of titania loaded TiP (Fig. 8(b)). The initial rate of photo-reduction was increased from 0.076 to 0.082 ppm/min for EDTA and for 4-nitrophenol the increase was from 0.076 to 0.077 ppm/min in case of 4 wt.% titania loaded TiP. Prairie et al. [32] proposed that two different electron donating process occurred for different organic substrates during reaction, i.e. direct and indirect donation of electron. In the former case, electrons from organics are directly transferred to the valence band, thereby attenuating the electron–hole recombination process and leaving more conduction band electrons available for the reduction of metal ions. As a consequence, addition of these types of organics to the system has a significant effect on the photo-reduction of Cr(VI). In case of indirect donation, holes are transferred only through the formation of hydroxyl radicals and these radicals are subsequently consumed by the oxidation of added organics. So organics in this class influence the photo-reduction process indirectly, hence it shows less

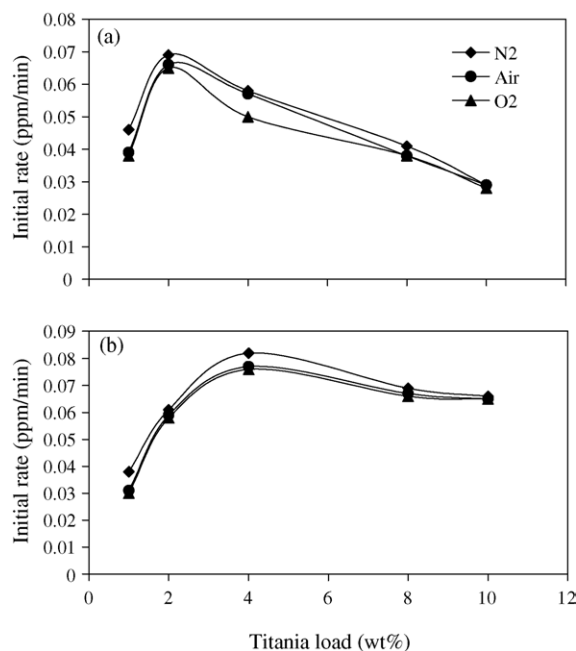


Fig. 9. Effect of N₂, air and O₂ on the initial rate of Cr(VI) photo-reduction: (a) 2 wt.% titania pillared ZrP; (b) 4 wt.% titania pillared TiP; catalyst dose = 0.6 g/L; [Cr(VI)] = 20 mg/L; pH 2.0; time = 240 min.

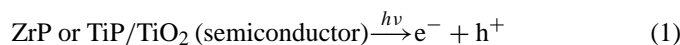
significant effect. This could be the reason that 4-nitrophenol plays a less significant role towards the photo-reduction of Cr(VI).

3.2.8. Effect of dissolved oxygen

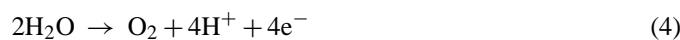
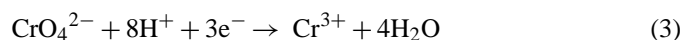
Experiments were carried out by varying the atmosphere of the photo-reduction process by bubbling N₂, O₂ and air. This can be observed that oxygen has got the minimum effect on the photo-reduction of Cr(VI) (Fig. 9). In case of 2 wt.% titania loaded ZrP the initial rate of Cr(VI) photo-reduction was increased to 0.069 ppm/min in case of N₂ bubbling, 0.066 ppm/min in case of air bubbling and in case of O₂ bubbling the initial rate remains almost the same, i.e. 0.065 ppm/min (Fig. 9(a)). The similar type of trend was observed for different wt.% of titania loaded ZrP. In case of 4 wt.% titania loaded TiP, the initial rate of Cr(VI) photo-reduction was increased to 0.082 ppm/min in case of N₂ bubbling, 0.077 ppm/min in case of air bubbling and the value remains unchanged in case of O₂ bubbling (Fig. 9(b)). This is due to the reason that the presence of oxygen molecule dissolved in aqueous solutions is assumed to be the electron scavenger which compete with Cr(VI) for electrons. From Fig. 9, it was observed that N₂ has got the maximum promoting ability than air and oxygen for both the catalysts. Some controversial results are obtained by different authors; some authors found the negative effect [33] and no effect of oxygen [34]. The result of this work agrees with Khalil et al. [29]. This may be due to varying conditions under which the experiments were carried out.

From all these observations it was found that the photo-reduction takes place when the catalyst was illuminated with light having photon energy greater than the band gap energy

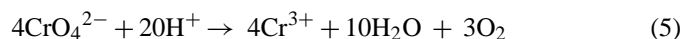
of the semiconductor itself. During this photo-catalysis first adsorption takes place which is a reversible process and also takes place even in absence of light illumination. During the light illumination electron–hole pairs are produced inside the semiconductor catalyst. The species migrate to the surface of the catalyst out of which electron reduces Cr(VI) to Cr(III) and holes oxidize water:



Since all the experiments were carried out at pH 2.0, only CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ species can exist [35]. Irrespective of the species involved and expressing the species simply as CrO_4^{2-} , the net photocatalytic reaction is a three electron-reduction of Cr(VI) to Cr(III) with oxidation of water to oxygen:



The net reaction is as follows:



Assuming that one electron step is occurring in the reduction of Cr(VI) some Cr(V) species are formed in the first stage:



Successive one electron reductive steps will form some species of Cr(IV) and then Cr(III). This mechanism agrees with Munoz et al. [26].

4. Conclusions

- (1) Photo-reduction of Cr(VI) takes place in acidic medium.
- (2) The initial rate of photo-reduction of Cr(VI) increases with increasing the catalyst dose up to 0.6 g/L and there after it remains constant.
- (3) The photo-reduction of Cr(VI) was studied in the wide range of chromium concentration from 2 to 50 mg/L. It was observed that the initial rate of photo-reduction is high in case of 20 mg/L of Cr(VI), for higher concentration the rate decreases.
- (4) The photo-reduction of Cr(VI) over titania pillared ZrP and TiP follow pseudo first-order kinetics.
- (5) The apparent rate constant values (k) were found to decrease with increase in the initial concentration of Cr(VI).
- (6) Comparing the effects of sacrificial electron donors like EDTA and 4-nitrophenol, a significant effect was observed for EDTA in case of 2 wt.% titania pillared ZrP.
- (7) Among N_2 , O_2 and air, the N_2 has got more and significant effect on the photo-reduction of Cr(VI) over titania pillared ZrP and TiP. The dissolved oxygen has got almost no effect or very negligible effect on this photo-reduction process.

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References

- [1] H.J. Gibb, P.S. Leacs, P.F. Pinsky, B.C. Rooney, *Am. J. Ind. Med.* 38 (2) (2000) 115.
- [2] M. Costa, *Crit. Rev. Toxicol.* 27 (5) (1997) 431.
- [3] M.E. Losi, C. Amrhein, W.T. Frankenberger Jr., *Rev. Environ. Contam. Toxicol.* 136 (1994) 91.
- [4] Y. Zhang, J. Crittenden, *D.W. Hand, Chem. Ind.* 19 (1994) 714.
- [5] J. Galvez, S.W. Rodriguez, *Proceedings of the International Conference on Comparative Assessments of Solar Power Technologies*, 14–18 February, Jerusalem, 1994, p. 1.
- [6] D.W. Chen, M. Sivakumar, A.K. Ray, *Dev. Chem. Eng. Miner. Process.* 8 (5/6) (2000) 505.
- [7] M. Gratzel, *Energy Resources through Photochemistry and Catalysis*, Academic Press, New York, 1983.
- [8] M. Schiavello, *Photochemistry, Photocatalysis and Photoreactor. Fundamentals and Developments*, Nato Asi Series, Series C: Mathematical and Physical Sciences, vol. 146, Reidel, Dordrecht, 1985.
- [9] M. Schiavello, *Photocatalysis and Environment. Trends and Applications*, Nato Asi Series, Series C: Mathematical and Physical Sciences, vol. 237, Kluwer Academic Publishers, Dordrecht, 1988.
- [10] N. Serpone, E. Borgarello, E. Pelizzetti, in: M. Schiavello (Ed.), *Photocatalysis and Environment. Trends and Applications*, Nato Asi Series, Series C: Mathematical and Physical Sciences, vol. 237, Kluwer Academic Publishers, Dordrecht, 1988, pp. 527–565.
- [11] N. Serpone, E. Pelizzetti, *Photocatalysis, Fundamentals and Applications*, Wiley, New York, 1989.
- [12] J. Domenech, J. Munoz, *J. Chem. Res. Synopses* (1987) 106.
- [13] S. Wang, Z. Wang, Q. Zhong, *Appl. Catal. B: Environ.* 1 (1992) 257.
- [14] H. Yoneyama, Y. Yamashita, H. Tamura, *Nature (London)* 282 (1979) 817.
- [15] C.-M. Zhang, Y.-S. Jiang, W. Liu, H.-M. Yang, T.-J. Li, L.-Z. Xiao, *Acta Energiae Solaris Sinica* 12 (1991) 176.
- [16] J. Domenech, J. Munoz, *Electrochim. Acta* 32 (1987) 1383.
- [17] S. Zheng, Z. Xu, Y. Wang, Z. Wei, B. Wang, *J. Photochem. Photobiol. A: Chem.* 137 (2000) 185.
- [18] S. Zheng, L. Gao, Q. Zhang, W. Zhang, J. Guo, *J. Mater. Chem.* 11 (2001) 578.
- [19] P. Mohapatra, S.K. Samantaray, K.M. Parida, *J. Photochem. Photobiol. A: Chem.* 170 (2005) 189.
- [20] H. Yoneyama, S. Haga, S. Yamanaka, *J. Phys. Chem.* 93 (1989) 4833.
- [21] C. Wei, S. German, S. Basak, K. Rajeswar, *J. Electrochem. Soc.* 140 (1993) L60.
- [22] K.M. Parida, D.P. Das, *J. Photochem. Photobiol. A: Chem.* 163 (2004) 561.
- [23] Y. Xu, X. Chen, *Chem. Ind.* (1990) 497.
- [24] M.A. Malati, L. Attubato, K. Beaney, *Sol. Energy Sol. Cells* 40 (1996) 1.
- [25] W.-Y. Lin, C. Wei, K. Rajeswar, *J. Electrochem. Soc.* 140 (1993) 2477.
- [26] J. Munoz, X. Domenech, *J. Appl. Electrochem.* 20 (1990) 518.
- [27] S. Zheng, D. Yin, W. Miao, G.K. Anderson, *J. Photochem. Photobiol. A: Chem.* 117 (1998) 105.

- [28] J. Gimenez, M.A. Aguado, S. Cervera-March, *J. Mol. Catal. A: Chem.* 105 (1996) 67.
- [29] L.B. Khalil, W.E. Mourad, M.W. Rophael, *Appl. Catal. B: Environ.* 17 (1998) 267.
- [30] D. Chen, A.K. Ray, *Chem. Eng. Sci.* 56 (2001) 1561.
- [31] J.A. Navio, G. Colon, M. Trillas, J. Peral, X. Domenech, J.J. Testa, J. Padron, D. Rodriguez, M.I. Litter, *Appl. Catal. B: Environ.* 16 (1998) 267.
- [32] M.R. Prairie, L.R. Evans, B.M. Stange, S.L. Martinez, *Environ. Sci. Tech.* 27 (1993) 1776.
- [33] Y. Guo, J. Qi, S. Yang, K. Yu, Z. Wang, H. Xu, *Mater. Chem. Phys.* 78 (2002) 132.
- [34] M.A. Aguda, J. Gimenez, M. Cervera, *Chem. Eng. Commun.* 104 (1991) 71.
- [35] F.H. Westheimer, *Chem. Rev.* 45 (1949) 419.