

# Photocatalytic reduction of metals in presence of combustion synthesized nano-TiO<sub>2</sub>

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## Abstract

The photocatalytic reduction of the metal ions, Cu(II) and Cr(VI), was investigated in presence of solution combustion synthesized (CS) nano-TiO<sub>2</sub>. The efficiency of this catalyst was compared with that of commercial titania, Degussa P-25. For the reduction of Cu<sup>2+</sup>, the first-order rate constants were 0.003 and 0.018 min<sup>-1</sup> in presence of Degussa P-25 and CS TiO<sub>2</sub>, respectively. For the reduction of Cr<sup>6+</sup>, the initial rate constants were 0.007 and 0.247 min<sup>-1</sup> in presence of Degussa P-25 and CS TiO<sub>2</sub>, respectively. Thus, the rate of reduction of Cu(II) and Cr(VI) is higher in CS TiO<sub>2</sub> compared to Degussa P-25 TiO<sub>2</sub>. The effect of pH and the effect of initial concentration on the photocatalytic reduction of Cu(II) and Cr(VI) in presence of solution combustion synthesized TiO<sub>2</sub> and Degussa P-25 catalyst were investigated. The variation of the photoreduction rate of Cu(II) and Cr(VI) with respect to pH correlates with the variation of the driving force, which is the difference between the standard reduction potential of the metal ion and the energy level of the electrons in the conduction band. The other metal ions like Zn(II), Cd(II), Pb(II) and Mn(II) could not be reduced in both the catalytic systems and this is attributed to the thermodynamic infeasibility of their reduction by photo generated electrons.

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## 1. Introduction

Photocatalysis is an advanced oxidation process, utilized for the oxidation of organics and the reduction of metal ions. Most of the heavy metal ions are non-degradable and toxic in specific valence states. Hg(II), Pb(II), Cd(II), Ag(I), Ni(II) and Cr(VI) are toxic [1]. Photocatalysis can be used to change the hazardous ionic states of the metal ions. Chromium contamination of water is caused by disposal of industrial waste, particularly from the metal plating, tanning and textile industries. When aqueous solutions of the semiconductor particles (photocatalyst) are illuminated by UV light, positive holes and electrons are generated in the catalyst particles. The reduction of the metal ions by semiconductor photocatalysis technology is based

on the reduction of the metals by the generated electrons in the system. The photocatalytic reduction of the metal ions by the electron can occur only if the standard reduction potential is positive of the conduction band edge. Among all metals, the photocatalytic reduction of Cr(VI) in presence of Degussa P-25 is well reported [2–7]. The simultaneous photoreduction of Cr(VI) and photooxidation of organics by catalysts like Degussa P-25, ZnO and Hombikat UV 100 has also been reported [8,9]. The photoreduction of Cu(II) in presence of Degussa P-25 is not significant and thus it has been studied using ZnO [10] and in presence of different sacrificial donors [11]. Combustion synthesized titania (CS TiO<sub>2</sub>) has proved [12,13] to be a superior catalyst for the degradation of various dyes and organics compared to that of the commercial catalyst, Degussa P-25. The present study aims at exploring the photocatalytic activity of combustion synthesized TiO<sub>2</sub> for the photoreduction of Cu(II) and Cr(VI) and compare its efficiency with that of Degussa P-25.

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## 2. Experimental

### 2.1. Materials

Titanium isopropoxide (Lancaster Chemicals, UK), and glycine (Merck, India) were used in the preparation of catalyst. Double-distilled water was filtered through a Millipore membrane filter before use. Sodium diethyldithiocarbamate was purchased from Sigma–Aldrich, USA. Diphenyl carbazide was obtained from Merck, India. The reagent 4-(2-pyridylazo)-resorcinol and the salts, cupric sulphate, cadmium sulphate, lead nitrate, zinc nitrate and potassium dichromate were purchased from SD Fine Ltd., India.

### 2.2. Catalyst preparation

The solution combustion method [12,13] was used to prepare nano-sized anatase  $\text{TiO}_2$ . The precursor titanyl nitrate [ $\text{TiO}(\text{NO}_3)_2$ ] and the fuel glycine ( $\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$ ) were used in this method. The precursor titanyl nitrate was synthesized as follows: Titanyl hydroxide [ $\text{TiO}(\text{OH})_2$ ] was obtained by the hydrolysis of titanium isopropoxide [ $\text{Ti}(i\text{-OPr})_4$ ]. Titanyl nitrate was obtained by the reaction of titanyl hydroxide with nitric acid. In a typical combustion synthesis, a Pyrex dish (with a volume of  $300\text{ cm}^3$ ) containing an aqueous redox mixture of stoichiometric amounts of titanyl nitrate and glycine was introduced into a preheated muffle furnace. A spark appears at one corner, which spreads throughout the mass, finally yielding anatase titania.

### 2.3. Catalyst characterization

The catalyst has been characterized by various techniques such as XRD, TEM, BET, TG-DTA, XPS, IR and UV spectroscopy. The X-ray diffraction (XRD) patterns of catalysts indexed to pure anatase phase of  $\text{TiO}_2$ . The crystallite size was determined from XRD pattern and the mean crystallite size is estimated to be  $10 \pm 2\text{ nm}$ . Transmission electron microscopy (TEM) also showed the crystallites of  $\text{TiO}_2$  are homogeneous with the mean size of  $8 \pm 2\text{ nm}$ . The surface area of the catalyst was  $240\text{ m}^2/\text{g}$  and is higher than the surface area of Degussa P-25 ( $50\text{ m}^2/\text{g}$ ). Fourier transform infrared (FTIR) studies showed higher surface hydroxyl content for the combustion synthesized and Degussa  $\text{TiO}_2$  powders were obtained. The combustion synthesized  $\text{TiO}_2$  shows two optical absorption thresholds at 570 and 467 nm that corresponds to the band gap energy of 2.18 and 2.65 eV, respectively (compared to the band gap energy of 3.1 eV for Degussa P-25). The decrease in the band gap can be due to carbide ion substitution for oxide ion in the  $\text{TiO}_2$ . C(1s) spectra of combustion synthesized  $\text{TiO}_2$  shows a peak at 285.5 and 284.3 eV that can be assigned to graphitic carbon and carbidic species. Ti(2p) core level spectra showed peaks at 459.0 and 464.8 eV indi-

cating that Ti is in 4+ state. Therefore, the combustion synthesized  $\text{TiO}_2$  indeed shows substitution of carbon in the form of  $\text{TiO}_{2-2x}\text{C}_x$ . Further details are presented elsewhere [12,13].

### 2.4. Photochemical reactor

The photochemical reactor employed in this study was comprised of a jacketed quartz tube of 3.4 cm i.d., 4 cm o.d., and 21 cm length and an outer Pyrex glass reactor of 5.7 cm i.d. and 16 cm length. The UV light was provided by a 125 W high pressure mercury vapor lamp (Philips, India) where the lamp radiated predominantly at 365 nm, corresponding to energy of 3.4 eV. Water was circulated through the annulus of the quartz tube to avoid heating of the solution due to dissipative loss of UV energy. The solution was taken in the outer reactor and continuously stirred using a magnetic stirrer to ensure that the suspension of the catalyst was uniform during the course of the reaction. Further details of the experimental setup can be found elsewhere [12,13].

### 2.5. Reduction experiments

During the reduction of each metal ion, a known mass of the salt was dissolved in Millipore-filtered double-distilled water and subjected to UV irradiation in the photochemical reactor described above with a catalyst loading of 1 g/L. The reactions were carried out at  $40\text{ }^\circ\text{C}$ , which was maintained by circulating water in the annulus of the jacketed quartz reactor. Samples were collected at regular intervals, filtered through Millipore membrane filters, and centrifuged to remove the catalyst particles prior to analysis.

### 2.6. Sample analysis

The concentration of all the metal ions was estimated photometrically. 2 ml of the solution was used for the analysis.  $\text{Cu}^{2+}$  was estimated photometrically using the reagent sodium diethyl dithiocarbamate that formed a colored complex with  $\text{Cu}^{2+}$  whose  $\lambda_{\text{max}}$  is 436 nm [14,15].  $\text{Cr}^{6+}$  was also estimated photometrically using the reagent diphenyl carbazide [7], which formed a colored complex with  $\text{Cr}^{6+}$  whose  $\lambda_{\text{max}}$  is 547 nm. The metal ions  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Mn}^{2+}$  were estimated by forming a colored complex with the reagent 4-(2-pyridylazo)-resorcinol, giving a colored complex whose  $\lambda_{\text{max}}$  is 495 nm, 495 nm, 512 nm and 496 nm, at pH 10, 8, 10 and 10, respectively.

## 3. Results and discussion

The photocatalytic reduction of the metal ions was investigated in the absence of the catalyst and in the presence of catalysts, Degussa P-25 titania and CS  $\text{TiO}_2$ . There is no appreciable change in the absorbance when the metal ions were reduced in the absence of any of these two cata-

lysts. The concentration of the catalyst was maintained as 1 g/L throughout all the experiments. After the addition of the catalyst, the solution was stirred for 30 min in dark to ensure that the equilibrium adsorption/desorption of the metal ion on the catalyst was attained. The corresponding concentration of the metal ion (as measured by UV spectrophotometer and the concentration evaluated using Beer–Lambert's law), was taken as the initial concentration of the metal ion for all the catalyzed reactions.

Among the metal ions studied ( $\text{Cr}^{6+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Mn}^{2+}$ ), except for  $\text{Cr}^{6+}$  and  $\text{Cu}^{2+}$ , the rest of the metal ions did not show any appreciable photocatalytic reduction in both the catalytic systems—CS  $\text{TiO}_2$  and Degussa P-25. This is attributed to that the thermodynamic infeasibility of the reduction of metal ions such as  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Mn}^{2+}$ . This can be explained as follows.

The following steps occur during the photocatalytic reduction of the metals.



Eq. (1a) denotes the generation of electrons in conduction band and holes in valence band, when an energy  $h\nu$  greater than the band gap of the semiconductor photocatalyst ( $\text{TiO}_2$ ) is given to an aqueous dispersion of the catalyst. Eq. (1b) denotes the possible recombination of the generated electrons and the holes generating heat, which is an unfavorable reaction. Eq. (2) denotes the reduction of any metal ion of valence state  $n+$ ,  $\text{M}^{n+}$  which gets reduced by the photo generated electron in the system. The oxidation of water is denoted by Eq. (3).

For a metal ion to be reduced by photocatalysis, the conduction band of the semiconductor must be more negative compared to the reduction potential of the metal ion involved in the system [1]. The energy level of the conduction band (ECB) depends on the pH of the system and variation of this energy level is linear with respect to pH [1]. For example, the valence band of anatase titania varies from 3.1 V to 2.7 V from a pH 1–7 while the conduction band changes from  $-0.11$  V to  $-0.46$  V as pH increases from 1 to 7.

In case of metal ions such as  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Mn}^{2+}$ , the standard reduction potentials are  $-0.37$  V,  $-0.76$  V,  $-0.12$  V and  $-0.13$  V, respectively, and is invariant with respect to pH. The difference between the reduction potential of  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Mn}^{2+}$  and the conduction band energy level is 0.09 V, 0.3 V, 0.34 V and 0.33 V, respectively at pH 7. Thus the photocatalytic reduction of these metal ions is either infeasible or very small to be measured quantitatively. Therefore, no reduction of these metal ions was observed experimentally in presence of either of the catalysts. In case of  $\text{Cr}^{6+}$ , the reduction of  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$  is thermodynamically favorable. In case

of  $\text{Cu}^{2+}$ , the reduction potential of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  is constant at 0.16 V and thermodynamically favorable. Thus in this study, the effect of initial concentration of metal ions at neutral pH and the influence of pH on the photocatalytic reduction of  $\text{Cu}^{2+}$  and  $\text{Cr}^{6+}$  for both the catalytic systems (CS  $\text{TiO}_2$  and Degussa P-25) is investigated.

The reduction in the metal ion concentration is first measured after adsorption by stirring the solution in dark and this is followed by photocatalytic experiments. In case of  $\text{Cu}^{2+}$ , for both the catalysts (CS  $\text{TiO}_2$  and Degussa P-25), the adsorption of  $\text{Cu}^{2+}$  on the catalyst increases with increase in pH. At pH 10.8, for an initial concentration of 145  $\mu\text{M}$  of  $\text{Cu}^{2+}$ , the percentage of  $\text{Cu}^{2+}$  removed by adsorption was found to be 100% and 36.7% in presence of CS  $\text{TiO}_2$  and Degussa P-25, respectively. At pH 7, the percentage of  $\text{Cu}^{2+}$  removed by adsorption was found to be 11% and 15% in presence of CS  $\text{TiO}_2$  and Degussa P-25, respectively, indicating that the extent of removal is similar in both the systems. At pH 1.8, there was no reduction in the  $\text{Cu}^{2+}$  concentration indicating no adsorption. After adsorption, the photocatalytic experiments were conducted and the concentration of  $\text{Cu}^{2+}$  was measured at regular intervals.

Fig. 1a shows the variation of the concentration of  $\text{Cu}^{2+}$  as a function of reaction time. At a pH 1.8, no significant reduction of  $\text{Cu}^{2+}$  was observed in presence of either CS  $\text{TiO}_2$  or Degussa P-25 and the trends of reduction rate with both these catalysts were similar. The reason for this observation could be attributed to the photoreduction of protons or water that are prevalent in this pH regime ( $\text{pH} < 1.84$ ), which prevents the reduction of  $\text{Cu}^{2+}$  ions [16,17]. The lower rates of photoreduction at acidic pH are because that the protons begin to successfully compete with  $\text{Cu}^{2+}$  ions for the conduction band electrons [17]. A higher level of  $\text{Cu}^{2+}$  reduction in CS  $\text{TiO}_2$  system is observed compared to that of observed in the presence of Degussa P-25 at pH 7. At basic pH 10.8,  $\text{Cu}^{2+}$  exists in its hydroxide form ( $\text{Cu}(\text{OH})_2$ ) and 100% adsorption of the metal ion is observed in presence of CS  $\text{TiO}_2$ . Thus, the photocatalytic reduction of  $\text{Cu}^{2+}$  in presence of CS  $\text{TiO}_2$  at pH 10.8 is not shown in Fig. 1(a). The photocatalytic reduction of  $\text{Cu}^{2+}$  in presence of Degussa P-25 at pH 10.8 is shown in Fig. 1a. The figure also shows that the photocatalytic reduction rate increases with increasing pH. The reduction potential of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  is 0.16 V and independent of pH. However, the energy level of the conduction band (ECB) becomes more negative as pH increases. Therefore, the driving force, which is the difference between the reduction potential of the metal ion and the energy level of the conduction band, increases with an increase in pH. Thus the photocatalytic reduction rate of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  increases with increase in pH.

We next investigate the adsorption and photoreduction of chromium ion. In case of  $\text{Cr}^{6+}$ , at an initial concentration of 215  $\mu\text{M}$ , the percentage removal of  $\text{Cr}^{6+}$  by adsorption was 63%, 32% and 11% in presence of CS  $\text{TiO}_2$  at pH 7, 2.4 and 1.8, respectively, indicating that adsorption

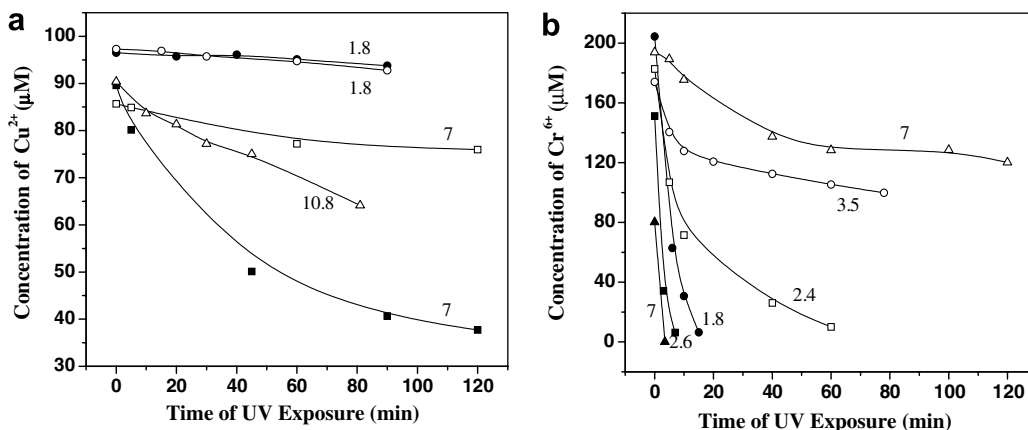


Fig. 1. Effect of pH on the photocatalytic reduction of (a)  $\text{Cu}^{2+}$  and (b)  $\text{Cr}^{6+}$  in presence of CS  $\text{TiO}_2$  and Degussa P-25. Filled and unfilled points correspond to CS  $\text{TiO}_2$  and Degussa P-25, respectively, while the numbers correspond to the pH value.

decreases with decreasing pH. At  $\text{pH} < 2$ ,  $\text{Cr}^{6+}$  exists as neutral chromic acid molecule ( $\text{H}_2\text{CrO}_4$ ), while at  $2 < \text{pH} < 6$ ,  $\text{Cr}^{6+}$  exists [5] as negatively charged  $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$ . Thus at  $\text{pH} 1.8$ ,  $\text{H}_2\text{CrO}_4$  shows less affinity to the positive anatase  $\text{TiO}_2$  surface and hence lower adsorption. At intermediate pH, the negatively charged forms of  $\text{Cr}^{6+}$  are adsorbed due to the balance with the positive surface charge of  $\text{TiO}_2$ . Near the  $\text{pH}_{zpc}$  of 6–7 for anatase  $\text{TiO}_2$ , maximum levels of adsorption are observed for  $\text{pH} 7$  as shown in Fig. 1b. In case of Degussa P-25, the percentage removal of  $\text{Cr}^{6+}$  by adsorption was 15%, 17% and 19% at  $\text{pH} 7$ , 2.4 and 1.8, respectively, i.e., almost invariant with respect to pH. The lower levels of adsorption observed in presence of Degussa P-25 compared to that observed in presence of CS  $\text{TiO}_2$  can be attributed to the higher surface of CS  $\text{TiO}_2$ . Fig. 1b shows the photocatalytic reduction of  $\text{Cr}^{6+}$  in both the catalytic systems. The effect of pH on the reduction of  $\text{Cr}^{6+}$  in the presence of CS  $\text{TiO}_2$  system cannot be concluded from the experiments owing to the different initial concentration at different pH after adsorption, though it appears that the rate of reduction slightly decreases with increasing pH but

is considerably higher than the reduction observed in presence of Degussa P-25. In case of reduction in presence of Degussa P-25, however, it is clear that the rate of reduction decreases with increasing pH. The reduction potential of  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$  decreases [5] with pH. Thus the difference between its reduction potential and the conduction band energy level is higher at lower pH and this difference decreases with increase in pH. For example, the standard reduction potential of  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$  varies from 1.32 V at  $\text{pH} 0$  to 0.38 V at  $\text{pH} 7$ . The energy level of the conduction band of anatase  $\text{TiO}_2$  varies from  $-0.11$  at  $\text{pH} 1$  to  $-0.46$  at  $\text{pH} 7$ . Thus the difference decreases from 1.43 V to 0.84 V as pH increases from 1 to 7. Thus in case of reduction of  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$ , the adsorption increases with increase in pH but the photocatalytic reduction rate increases with decrease in pH.

Fig. 2a and b shows the effect of the initial concentration of  $\text{Cu}^{2+}$  and  $\text{Cr}^{6+}$  on their photoreduction rate, respectively in both CS  $\text{TiO}_2$  and Degussa P-25 systems at neutral pH. The reduction rate is higher at higher concentrations. The rate expression for this system is  $r = kc/(1 + Kc)$  (where  $r$ ,  $k$ ,  $K$  and  $c$  denote the initial reduction rate, reac-

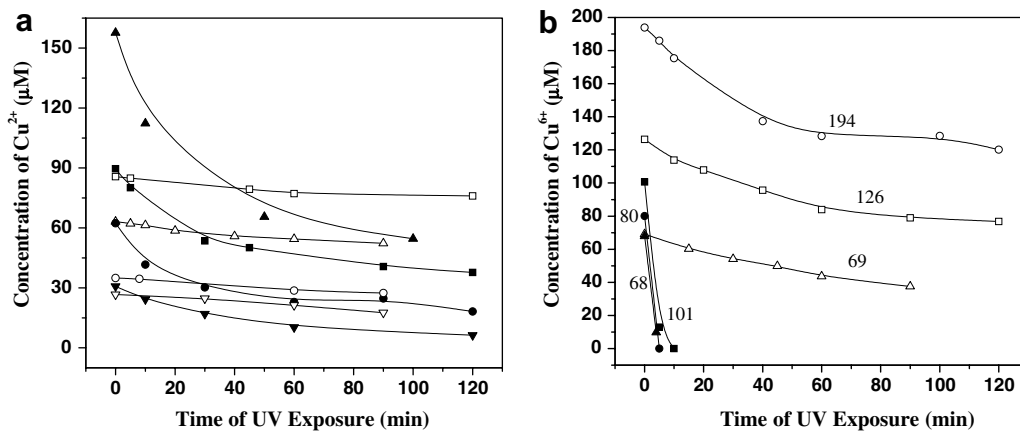


Fig. 2. Concentration profiles of photocatalytic reduction of (a)  $\text{Cu}^{2+}$  and (b)  $\text{Cr}^{6+}$  in presence of CS  $\text{TiO}_2$  and Degussa P-25. Filled and unfilled points correspond to CS  $\text{TiO}_2$  and Degussa P-25, respectively, while the numbers correspond to the concentration.

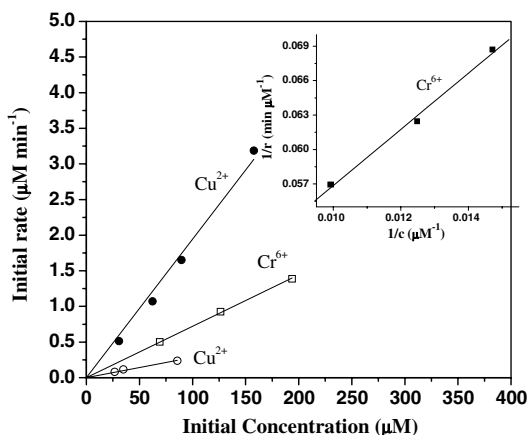


Fig. 3. Variation of the inverse of the rate of the photocatalytic reduction of  $\text{Cu}^{2+}$  and  $\text{Cr}^{6+}$  in presence of CS  $\text{TiO}_2$  and Degussa P-25. See Fig. 1 for legends.

tion rate constant, the equilibrium adsorption coefficient and the initial concentration, respectively) obtained from Langmuir–Hinshelwood kinetics was used to fit the experimental data at various concentrations and obtain the constants  $k$  and  $K$ . These kinetic constants can be obtained from the linear regression of the inverse of rate with the inverse of concentration, as shown in Fig. 3.

For the reduction of  $\text{Cu}^{2+}$ , the first-order rate constant is 0.003 and 0.018  $\text{min}^{-1}$  in presence of Degussa P-25 and CS  $\text{TiO}_2$ , respectively. For the reduction of  $\text{Cr}^{6+}$ , only Degussa P-25 follows the first-order kinetics and the value of rate constant is 0.007  $\text{min}^{-1}$ . The inset of Fig. 3 shows the variation of the inverse of the initial rate with the inverse of the initial concentration of  $\text{Cr}^{6+}$  in CS  $\text{TiO}_2$  catalytic system. For the reduction of  $\text{Cr}^{6+}$  in presence of CS  $\text{TiO}_2$ , the values of constants  $k$  and  $K$  are 0.409  $\text{min}^{-1}$  and 0.013  $\mu\text{M}^{-1}$ , respectively. Thus the rate constants for the reduction obtained in presence of CS  $\text{TiO}_2$  are higher than that obtained in presence of Degussa P-25. This could be attributed to the lower band gap value and the higher rate of generation of electrons and holes in CS  $\text{TiO}_2$  compared to that of Degussa P-25  $\text{TiO}_2$ .

#### 4. Conclusions

The photoreduction of  $\text{Cu}^{2+}$  and  $\text{Cr}^{6+}$  was investigated with solution combustion synthesized nano- $\text{TiO}_2$  and the commercial catalyst Degussa P-25. The dependence of the photocatalytic reduction rate of  $\text{Cu}^{2+}$  and  $\text{Cr}^{6+}$  on the pH and the initial concentration was discussed based on the reduction potential of the metal ion and the Langmuir–Hinshelwood kinetics. It was concluded that

CS  $\text{TiO}_2$  was more beneficial compared to Degussa P-25 for converting the hazardous metal ions such as  $\text{Cu}^{2+}$  and  $\text{Cr}^{6+}$  to non-hazardous states by photocatalytic reduction.

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