Photo-reduction of Hexavalent Chromium in Aqueous Solution in the Presence of TiO$_2$ as Semiconductor Catalyst

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Abstract. The objective of this work is to determine the optimal conditions for the reduction of the hexavalent chromium in water using the photocatalytic system TiO2/ UV. The results show that the effectiveness of this system was significantly higher compared to direct photolysis. The influence of parameters such as photocatalyst loading and initial concentration of the substrate was studied. The study of the influence of pH shows that the reduction rates are grater for acid solutions. Furthermore the experimental results show that the presence of H2O2 at small concentration (10-6M) accelerates the reduction. However at higher concentration (10-4M) H2O2 inhibits the reduction. The presence of inorganic ions such as Cl- and SO42- does not seem to have any significant influence on the reduction rate of Cr (VI).

**Key words:** Hexavalent chromium, reduction, TiO2, UV, pollution

Introduction

The presence of heavy metals in aquatic bodies is known to cause pollution problems. The major source of heavy metals is the improper discharge of various industrial wastewaters. Among these the potential sources of chromium include leather tanning, paints, dyes, photographic materials, steel alloy, cement industries, mining, etc.. Chromium exhibits variable valences of which tri- and hexa-valent forms are common. The behavior of Cr species depends strongly on its oxidation state. Chromioum(VI) is mobile and highly toxic whereas Cr(III) is mostly immobile and environment friendly. Chromium is necessary for life, a dose of 0.1–0.3 mg/day is required for normal development and the amount comes from various foods and drinks. Trivalent form of chromium plays an essential role in plant and animal metabolism, while hexavalent chromium is directly toxic to man, animals and plants. In the environment Cr(VI) salts do not readily precipitate or become bound to components of soil, therefore Cr(VI) can move throughout aquifers to contaminate ground water and other sources of drinking water. It also presents a toxic hazard to livestock and wildlife.

Conventional methods used for the removal of Cr(VI) ions from wastewater include reduction following hydroxide precipitation, ion exchange, adsorption, electrochemical precipitation, foam separation, membrane separation, solvent extraction, bacterial reduction etc. All of these methods have their own advantages and disadvantages. The source of the wastewater and the concentration of the contaminants are the two main factors that influence the efficiencies of these methods. Recently, a new technology known as the advanced oxidation processes (AOP) based on the photocatalytic reduction of Cr(VI) ions in aqueous suspensions or film of semiconductors Sun *et al*. (2005) has received increasing attention due to cost effectiveness, high reduction efficiency and so on. Numerous semiconductors, such as ZnO, ZrO$_2$, CdS, WO3, BiVO$_4$, various types of TiO$_2$, TiO$_2$-supported layered compounds and titania-modified mesoporous silicate, have been used as photocatalysts. However, apart from TiO$_2$ these catalysts have poor stability in rigorous conditions such as strong acidic medium. The photocatalytic method is based on the reactive properties of an electron–hole pair generated in the semiconductor when irradiated by UV 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. The objective of the present work is to explore the 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 TiO_2, the influence of pH, the presence of H_2O_2 and inorganic ions. The photocatalytic reduction of Cr(VI) to Cr(III) takes place when a Cr(VI) solution containing TiO_2 is illuminated in light having a photon energy greater than the band gap energy of the semiconductor. During photocatalysis, adsorption occurs first when TiO_2 is dispersed in the aqueous solution containing metal ions. The reduction of Cr(VI) to Cr(III) occurs because, under illumination, electron–hole pairs are created inside the semiconductor particles (Eq 1):

$$TiO_2 + h\upsilon \rightarrow TiO_2(e^- + h^+) \quad (1)$$
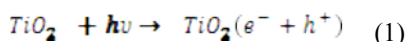
After the migration of these species to the surface of the particles, the photogenerated electrons reduce Cr(VI) to Cr(III) and the holes oxidize water and the sacrificial electron donor. The possible mechanism of the photocatalytic reduction of hexavalent chromium is as follows Rodenas *et al.* (2000):

In acidic medium, Cr (VI) is reduced to Cr(III) according to the following reaction :

$$Cr_2O_7^{-2} + 6e^- (BC) + 14 H^+ \leftrightarrow 2Cr^{+3} + 7H_2O \quad (2)$$
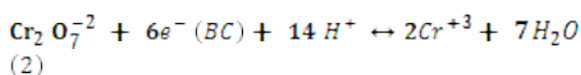
In the absence of reducing agents, H_2O accepts the valence band holes, and the following photocatalytic redox cycle takes place (Eq 3):

$$H_2O + h^+ \rightarrow OH^\circ \quad (3)$$
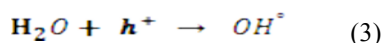
Materials and Methods

The photocatalyst used was TiO_2 (PC 500) (Millennium inorganic chemicals), it mainly consists of anatase form ($\geq 99\%$), the mean particle size was 10 nm and the BET surface area was 250 m^2/g. The potassium dichromate solutions were prepared in bidistilled water, adjusting the pH with hydrochloric acid or sodium hydroxide and monitoring by pH-meter HANNA HI 9812-5.

The irradiation experiments were performed in a beaker covered by a cylindrical metal enclosure, a UV lamp TLD whose emission maximum is located at 365 nm was placed in the vertical direction of the beaker, the mixture (dichromate solution + photocatalyst) was kept under magnetic stirring at 400 rev/min. The catalyst was suspended in the dark for 20 min in order to reach the adsorption equilibrium prior to the photoreduction. During the irradiation, samples were collected at selected time intervals. The catalyst powders were removed by filtration (filter Millipore; 0.45μm) and the residual concentration of Cr(VI) was determined at 350nm using UV–vis spectrophotometer (JENWAY 6405).

The rate of reduction was calculated according to the following equation:

$$T(\%) = \frac{C_0 - C}{C_0}$$

Where C_0 and C represent the concentrations of the $K_2Cr_2O_7$ solution before and after irradiation respectively.

Results and Discussion

In order to show the possible photocatalytic reduction of dichromate, we conducted a preliminary study to see if the dichromate would not undergo a reduction in direct irradiation in the absence of TiO_2. The results (Fig. 1) show that the reduction of hexavalent chromium is negligible during 60 minutes of irradiation (T%=2.4).
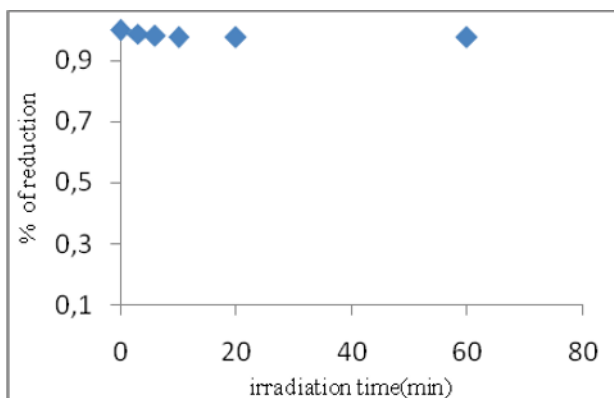

Fig. 1. The rate of reduction of Cr (VI) by direct photolysis. $C_0 = 2.10^{-4}M$, pH natural.

The major parameters that influence the rate and conversion of Cr(VI) to Cr(III) are the loading of the semiconductor catalyst, the initial concentration of the substrate, the influence of pH, the effects of presence of H_2O_2 and inorganic ions namely Cl^- and SO_4^{2-}. The effects of the parameters were studied over reasonable concentration ranges.

Figure 2 shows the effect of catalyst concentration on the percentage of reduction of hexavalent chromium. It is observed that as the catalyst concentration is increased the percentage of reduction increases and there after remains constant. This may be due to the fact that with increase in catalyst concentration the number of photons absorbed by TiO_2 particles and numbers of reacting molecules adsorbed on the TiO_2 surface are increased. But after certain concentration (8 g/L) there is no further reacting molecules available for adsorption hence additional catalyst are not involved in the catalytic activity.

From this observation it can also be presumed that with increase in catalyst loading there is an increase in the surface area of the catalyst available for adsorption and hence photoreduction, however further increase in the catalyst loading increases the solution opacity leading to decrease in the penetration of the photon flux thereby affecting the percentage of reduction Chakrabarti *et al.* (2009). For economic reasons and for subsequent reactions the load of 5 g/ L was chosen. The extent of photo-reduction decreases with increase in the initial concentration of the substrate Fig 3. Since the absorbance of the solution increases with the $K_2Cr_2O_7$ concentration,
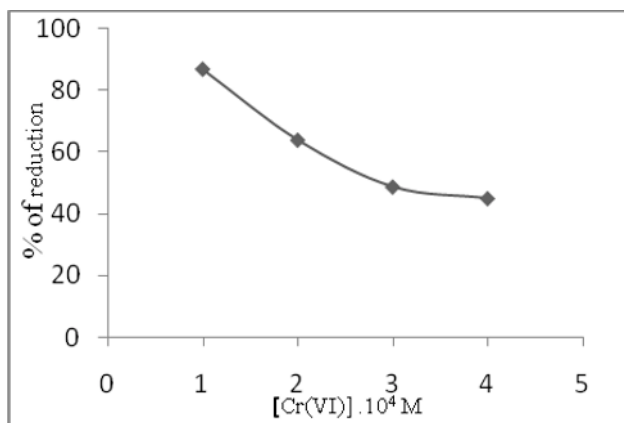
Fig. 2. Effect of catalyst concentration on the photocatalytic reduction of Cr(VI). pH = 5.3, [Cr(VI)] = 2.10^{-4}M, time 60 min.
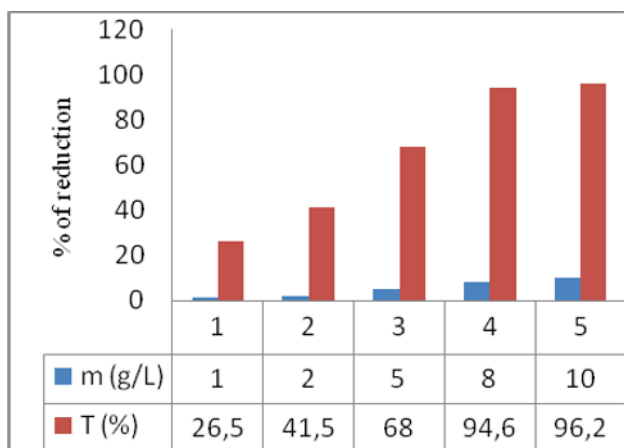

Fig. 3. Photocatalytic reduction of Cr(VI) on TiO_2 with different Cr(VI) initial concentrations under UV irradiation at pH = 5.3, [TiO2] = 5 g/l. time : 60 min.
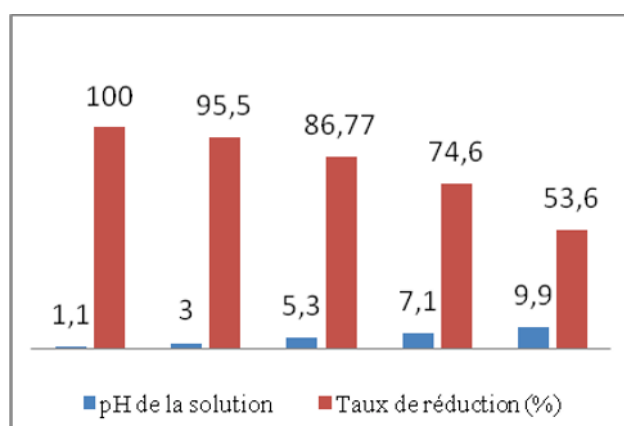

Fig. 4. Effect of pH on the photocatalytic reduction of Cr(VI). [Cr(VI)] = 10^{-4}M, [TiO2] = 5 g/l. time : 60 min.

a higher fraction of the UV radiation is intercepted before it reaches the surface of the photocatalyst thereby decreasing the conversion Ku and Jung (2001).
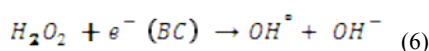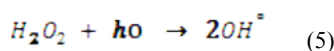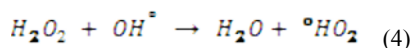
The pH of solution is one of the most important controlling parameter in the adsorption and photocatalytic reduction of metal ion taking place on semiconductor.We conducted a few experiments for 60 min at different pH values. Figure 4 represents the effect of pH of the solution on the photocatalytic reduction of hexavalent chromium. The highest reduction rate was obtained at the lower pH. It appears that the conversion is maximum (100%) at pH 1.1, but decreases rapidly with increasing pH. It is known that heterogeneous reaction in an aqueous TiO2 suspension is also dependent on the adsorption rate on the catalyst surface. On the surface of TiO2, ''Titanol'' (Ti–OH) is present. This species is amphoteric and exists in an acid–base equilibrium, as indicated by the following equation.
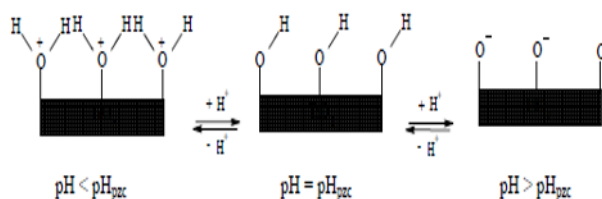
Therefore, the adsorption properties of catalysts can vary greatly with the pH. In an acidic environment, H^+ ions are adsorbed onto the surface of TiO_2, which has been reported to have a large surface proton exchange capacity. The photogenerated electrons can be captured by the adsorbed H^+ to form H_{ads}, which is able to reduce Cr(VI).

At high pH, the surface of the catalyst has a net negative charge due to the significant fraction of total surface sites present as TiO^- and repels dichromate ion. Moreover, the morphology and size of coated metals are also crucial factors in determining the catalytic activity, at pH 2 the species is $HCrO_4^-$, increasing the pH will shift the concentration of $HCrO_4^-$ to form CrO_4^{2-} and $Cr_2O_7^{2-}$. Redox potential of Cr(VI) species is different at different pH medium with higher potential of $HCrO_4^-$ than that of $Cr_2O_7^{2-}$ Kota´s and. Stasicka (2000).

Furthermore, the experimental results showed that the presence of H_2O_2 at small concentration (10^{-6}M) accelerates the reduction. However at higher concentration (10^{-4}M) H_2O_2 inhibits the reduction Table 1. The possible mechanism of the photocatalytic reduction of hexavalent chromium in the presence of H_2O_2 is as follows:

$$H_2O_2 + OH^\circ \rightarrow H_2O + {}^\circ HO_2 \quad (4)$$

$$H_2O_2 + h\mathbf{o} \rightarrow 2OH^\circ \quad (5)$$

$$H_2O_2 + e^- (BC) \rightarrow OH^\circ + OH^- \quad (6)$$

And it is possible that homogeneous reduction of Cr(VI) in solution occurs by H_2O_2 as shown in Eq. (7). Khalil *et al.* (1998) Suggested homogeneous reduction of hexavalent chromium by H_2O_2 responsible for supply of electron to the hexavalent chromium in solution.

Table 1. Effect of H_2O_2 on the photocatalytic reduction of Cr(VI), $C_0= 10^{-4}$M, TiO_2 5g/l and pH 5.3, time 60 min :

$[H_2O_2]$ (M)	0	10^{-6}	10^{-4}
Reduction (%)	86.77	98.8	92.96

The presence of other ions coexisting with Cr(VI) ions is inevitable in industrial wastewater. Therefore, it is necessary to investigate how these coexisting ions influence the photocatalytic activity of TiO_2. The effect of salts in the solution on the photocatalytic activity is summarized in Table 2.

From Table 2, it can be seen that the reduction efficiency of Cr(VI) ions remain almost unchanged when the salts except for NaCl and Na_2SO_4 are introduced into the photocatalytic reaction system.

Table 2. Effect of salts in the solution on the photocatalytic reduction $C_0= 10^{-4}$M, TiO_2 5g/l, pH 5.3 and $[H_2O_2] = 10^{-6}$ M, time 60 min.

Salt	C.(M).10^{-3}	Reduction (%)
None	0	98.80
NaCl	0.5	100
NaCl	1	100
NaCl	3	98.77
Na_2SO_4	0.5	100
Na_2SO_4	1	99.87
Na_2SO_4	3	99.77

Conclusion

Hexavalent chromium in aqueous solutions can be effectively reduced to the trivalent state using TiO_2 as the semiconductor photocatalyst under UV radiation.

- The extent of reduction as well as its initial rate increased with the loading of the photocatalyst and decreases with increasing initial concentration of the substrate.
- The highest reduction rate was obtained at the lower pH, it appears that the conversion is maximum (100%) at a pH 1.1.
- The presence of H_2O_2 at small concentration accelerates the reduction, but at higher concentration it inhibits the reduction.
- The presence of inorganic ions such as Cl^- and SO_4^{2-} do not seem to have any significant influence on the reduction rate of Cr (VI)

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