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Photocatalytic reduction of hexavalent chromium in aqueous solution over sulphate modified titania

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Abstract

Samples of different crystal forms and sizes of unmodified and sulphate modified TiO_2 were prepared by varying pH, source and concentration of sulphate ion and by activating at different temperatures. Samples prepared at lower pH exhibit more surface area than that of higher pH. The percentage of photocatalytic reduction of Cr(VI) under solar radiation is higher at low pH and decreases with rise in pH of suspension. Presence of sacrificial electron donor such as EDTA enhances the photocatalytic reduction whereas presence of oxygen reduces it. Photocatalytic reduction of hexavalent chromium depends on surface area, the crystal form and particle size of TiO_2. Samples containing mixtures of anatase and rutile phases exhibit highest activity for reduction of hexavalent chromium than that of single phases.

Keywords: Hexavalent chromium; Sulphated TiO_2; pH; Photocatalytic reduction; Adsorption

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1. Introduction

The presence of heavy metals in aquatic bodies has been known to cause pollution problems. The major source of heavy metals is the improper discharge of various industrial wastewater [1]. Among them the potential sources of chromium include leather tanning, paints, dyes, photographic materials, steel alloy cement industries, mining, etc. [2].

Chromium exhibits variable valencies of which tri and hexavalent forms are common. The behaviour of Cr-species depends strongly on its oxidation state. Cr(VI) is mobile and highly toxic where as Cr(III) is mostly immobile and environment friendly [3]. 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 [4]. 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 as well as present a toxic hazard to livestock and wildlife. Also as the hexavalent form is more stable than trivalent, it can easily penetrate through the cell membrane in case of animals and subsequently retains inside the cell forming stable complexes. Hexavalent form of chromium is 100 times toxic than trivalent [4]. Therefore, increasing in the concentration of chromium and consequent increase in intake manifest in a variety of metabolic diseases such as dermatitis, perforation of nasal septum and abortion, DNA lesim and finally leads to cancer.

The methods employed for the removal of hexavalent chromium are chemical precipitation, reverse osmosis, ion exchange, foam flotation, electrolysis, photocatalytic reduction, adsorption, etc. However, most of these methods require either high energy or large quantities of chemicals whereas the photocatalytic process is found to be superior to all.

Photocatalytic process in aqueous suspension of semiconductor has received considerable attention in view of

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solar energy conversion [5,6]. This photocatalytic process was achieved for rapid efficient destruction of environmental pollutants. Upon illumination of semiconductor–electrolyte interface with light energy greater than the semiconductor band gap, electron–hole pairs (e^-–h^+) are formed in the conduction and the valence band of the semiconductor, respectively [7]. These charge carriers, which migrate to the semiconductor surface, are capable of reducing or oxidizing species in solution having suitable redox potential. Reduction of Cr(VI) to Cr(III) leads to drastic decrease in bioavailabilty and toxicity of this element. The photocatalytic reduction of Cr(VI) with semiconductor such as CdS [8], ZnS, WO_3, ZnO [9] and TiO_2 [10] in UV light has been reported in literature. Among them TiO_2 is found to be suitable photocatalyst owing to its low cost of production and high activity.

So in the present work, we have studied the activity of unmodified and sulphate modified TiO_2 towards photocatalytic reduction of hexavalent chromium under solar radiation and also made a comparison between photocatalytic and adsorption process.

2. Experimental

2.1. Sample preparation

Hydrated titania was prepared at pH 3, 5, 7 and 9 by adding dilute ammonia to the stirred aqueous solution of titanium tetrachloride (Spectrochem, Bombay). Obtained gel was filtered and washed repeatedly to remove Cl^- (negative $AgNO_3$ test), dried at 383 K for 10 h, powdered to 45–75 μm mesh size and kept for anion impregnation.

One series of sulphated titania samples with varying the weight percentage of SO_4^{2-} was prepared using $(NH_4)_2SO_4$ as the source of sulphate ions by solid-solid kneading method and the other series of samples was prepared by aqueous wetness impregnation method using dilute H_2SO_4 (strength = 1.0 M). The suspended mass was evaporated to dryness on a hot plate while stirring. The samples were then dried in an air oven at 383 K and subsequent activation (by calcination) at 573, 673, 773, 873, 973 and 1073 K at the heating rate of 283 K/min in a muffle furnace for 3 h.

2.2. Characterisation

The XRD patterns of pure and modified TiO_2 samples were recorded on a Philips X-ray diffractometer. The FT-IR spectra of the samples were recorded with a Perkin-Elmer (model: Paragon 500) FT-IR spectrometer in the range of 4000–400 cm^{-1} on KBr (spectrophotometric grade). The morphologies of the samples were examined using a Hitachi H-600 transmission electron microscope (TEM). Surface area (BET) was determined by the N_2 adsorption–desorption method at liquid nitrogen temperature using Quantasorb (Quantachrome, USA).

2.3. Photocatalytic reduction and adsorption

The photocatalytic reduction of hexavalent chromium was performed taking 25 ml of 20 ppm Cr(VI) solution ($K_2Cr_2O_7$, BDH) in 100 ml pyrex flask and 0.6 g/L of catalyst. The pH of the dispersion was adjusted by addition of sulfuric acid (BDH). The solutions were exposed to sunlight at room temperature (no extra cooling) and agitated with magnetic stirrer so that no appreciable amount of the catalyst remained on the bottom of the reaction vessel. All the experiments were performed in triplicate during the second half of March 2003 (sunny days), from 10.00 a.m. to 14.00 p.m. The reduction in hexavalent chromium concentration due to adsorption is measured by carrying out similar experiment in dark. Blank experiment was carried out taking dichromate solution without photocatalyst to know the extent of reduction of hexavalent chromium concentration due to solar radiation. After irradiation and also adsorption the suspension was filtered and the Cr(VI) content was analysed quantitatively by measuring the absorption band at 348 nm using Cary-1E (Varian, Australia) spectrophotometer [11].

3. Results and discussion

3.1. Sample characterisation

From the TEM images it is found that TiO_2 sample prepared at pH 3 possesses uniform, finely distributed TiO_2 particles of size ≅12 nm and with sulphate loading the particle size sharply decreases to 2–3 nm. The XRD patterns revealed that the samples prepared at pH 3 possess mixture of anatase and rutile phases whereas at pH 5, 7 and 9 possess only anatase phases. It is also found that sulphate ion stabilises the anatase phase of TiO_2 up to 973 K activation temperature. From surface area measurement, it is found that the presence of low amount of sulphate ion is responsible for the formation of porous network. The details of the sample characterisation results are published elsewhere [12].

3.2. Photocatalytic reduction and adsorption

From the experiments carried out without the presence of catalyst under solar radiation we found that the percentage of hexavalent chromium reduction is very negligible. It is seen Fig. 1 that with increase in reaction time up to 3 h, the percentage of reduction and as well as adsorption increases and then it remains almost constant. While 80% of Cr(VI) reduction take place during photocatalysis only 23% of adsorption take place under similar conditions. From this it can be concluded that equilibrium is achieved only after 3 h of illumination.

Fig. 2 shows the effect of catalyst concentration on the percentage of reduction of hexavalent chromium. It is observed that as we increase the catalyst concentration up to 0.8 g/L the

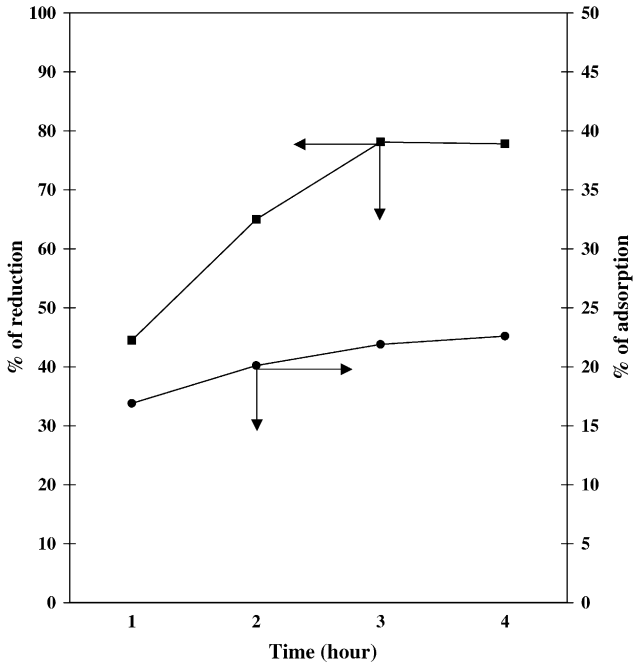

Fig. 1. Effect of time on photocatalytic reduction and adsorption of Cr(VI). [Cr(VI)] = 20 ppm, catalyst: 2.5 wt.% SO_4^{2-}/TiO_2 (0.6 g/L).

percentage of reduction increases and there after it remains constant. This may be due to that with increase in catalyst concentration the number of photons absorbed by TiO_2 particles and numbers of reacting molecules adsorbed on TiO_2 surface are increased. But after certain concentration there is no further reacting molecules are 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.

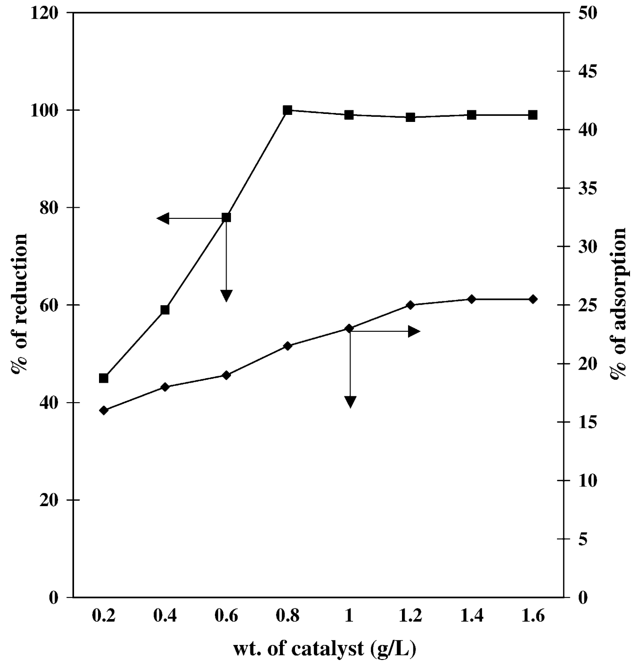

Fig. 2. Effect of catalyst concentration on the photocatalytic reduction and adsorption of Cr(VI). [Cr(VI)] = 20 ppm, catalyst: 2.5 wt.% SO_4^{2-}/TiO_2, time = 3 h.

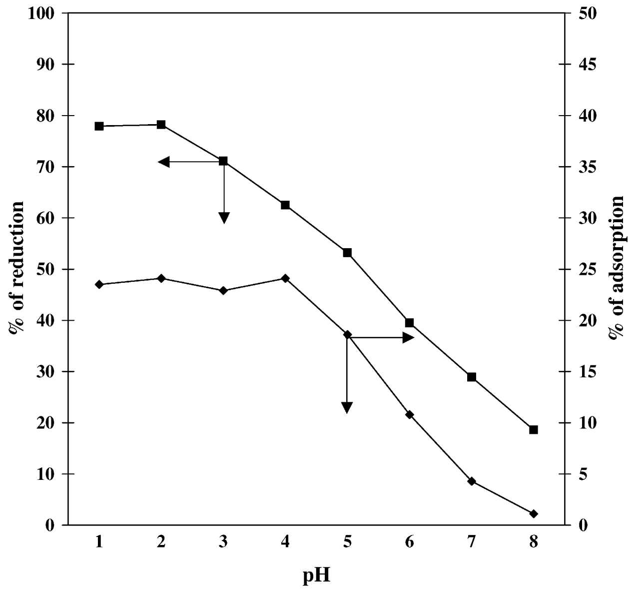

Fig. 3. Effect of pH of the solution on the photocatalytic reduction and adsorption of Cr(VI). [Cr(VI)] = 20 ppm, catalyst: 2.5 wt.% SO_4^{2-}/TiO_2 (0.6 g/L), time = 3 h.

pH is one of the most important controlling parameter in the adsorption and photocatalytic reduction of metal ion taking place on semiconductor metal oxides [15,13]. Fig. 3 represents the effect of pH (adjusted by H_2SO_4) of the solution on the adsorption and photocatalytic reduction of hexavalent chromium. With increasing pH of the solution up to 2, the percentage of reduction remains almost constant and thereafter it decreases gradually. The same trend is also observed for hexavalent chromium adsorption. The highest reduction rate was obtained at the lower pH. At pH above 7 neither adsorption nor reduction takes place; this type of observation is also reported by other researchers [16,14]. The reason probably may be due to the dominant form of Cr(VI) at pH 2 is $HCrO_4^-$, increasing the pH will shift the concentration of $HCrO_4^-$ to form CrO_4^- and $Cr_2O_7^{2-}$. At pH above 7 the photocatalyst surface becomes negative and repels dichromate ion [14,15]. The pH affects the surface charge on the photocatalyst and also the state of ionization of the substrate and hence its adsorption. Similar observations were also made by others by taking different materials such as rice husk carbon [16], activated red mode [2], hydrotalcite [17]. The specific adsorption of H^+ ions favours the approach of Cr(VI) species to the semiconductor surface, whereas for higher pH excess of absorbed

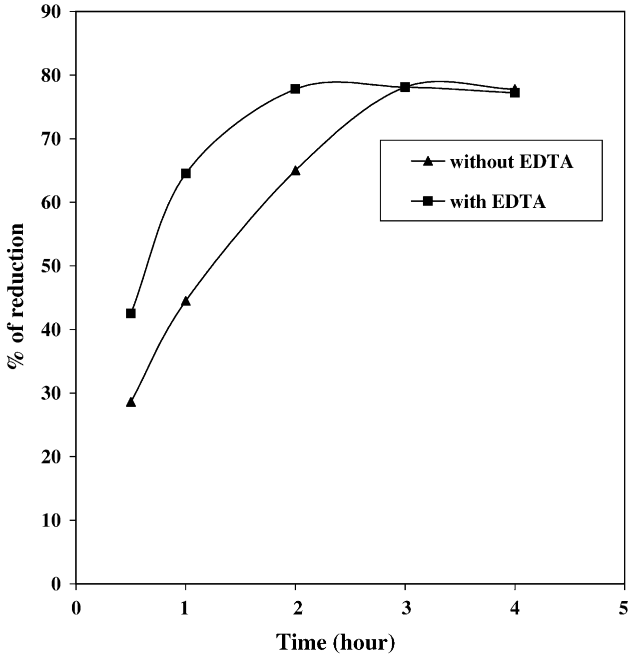

Fig. 4. Effect of EDTA on the photocatalytic reduction of Cr(VI). [Cr(VI)] = 20 ppm, catalyst: 2.5 wt.% SO_4^{2-}/TiO_2 (0.6 g/L).

OH^- ions has the opposite effect, leading to low levels of Cr(VI) adsorption.

The presence of sacrificial electron donor such as organic species may accelerate the photocatalytic reduction of metal ions [13]. In order to investigate the role of organic species we have carried out the experiments in the presence of methanol, ethanol and EDTA (Fig. 4). It was observed that EDTA has the significant effect on the photocatalytic reduction than that of others. This may be due to the strong chelating action of EDTA that forms stable complex with Cr(VI). This can enhance the adsorption of Cr(VI) and hence the photocatalytic reduction of hexavalent chromium.

The role of oxygen in the photocatalytic reduction of hexavalent chromium is controversial. We have carried out the reduction by bubbling the suspension with oxygen, air and nitrogen. Fig. 5 shows that the rate of reduction is higher for suspension bubbled with nitrogen. Oxygen competes with photogenerated electron on the surface of photocatalyst, which results in decrease in the percentage of reduction. There are controversial results found by different authors; some authors found the negative effect [14] and no effect of oxygen is also reported [18]. Our results agreed with the results obtained earlier [19]. The discrepancies in the result may be due to varying conditions under which experiments were performed.

Fig. 6 represents the effect of TiO_2 samples prepared at different pH on the photocatalytic reduction of hexavalent chromium. The percentage of reduction decreases with the increase in pH of precipitation. This may be due to the high surface area, lower porosity, crystallite size, and more number of hydroxyl groups present on the TiO_2 sample prepared at

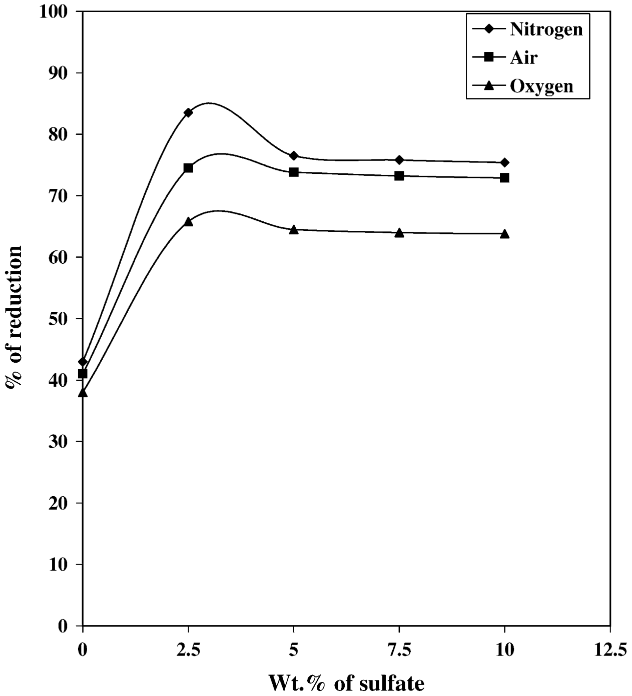

Fig. 5. Effect of nitrogen, oxygen and air on the photocatalytic reduction of Cr(VI). [Cr(VI)] = 20 ppm, catalyst: different wt.% of sulphate impregnated TiO_2 prepared at pH 3 (0.6 g/L), time = 3 h.

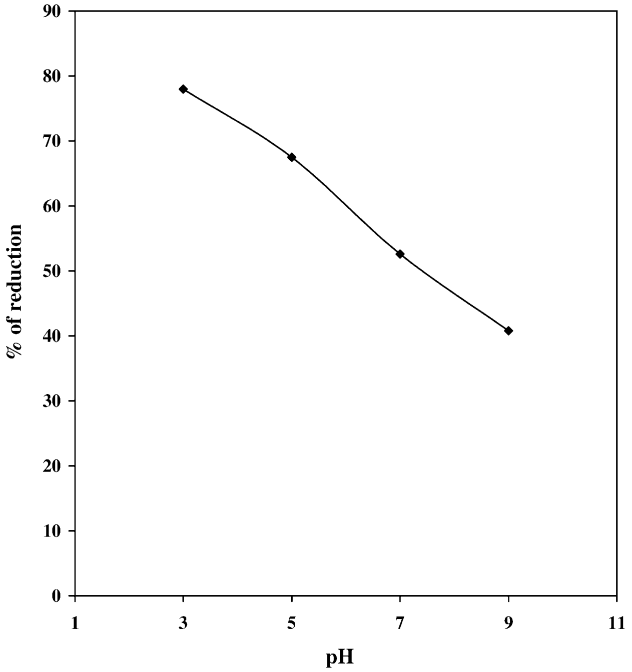

Fig. 6. Effect of pH of precipitation on the photocatalytic reduction of Cr(VI). [Cr(VI)] = 20 ppm, catalyst: 2.5 wt.% SO_4^{2-}/TiO_2 prepared at different pH (0.6 g/L), time = 3 h.

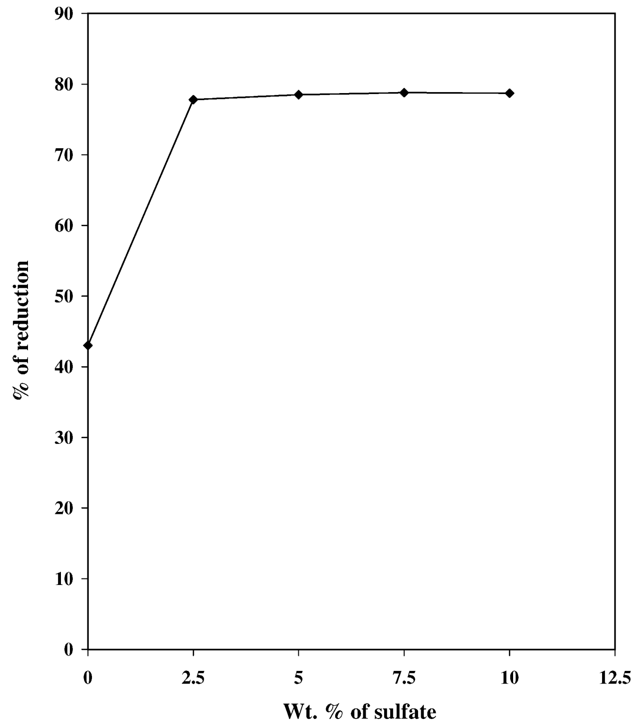

Fig. 7. Effect of wt.% of sulphate on the photocatalytic reduction of Cr(VI). [Cr(VI)] = 20 ppm, catalyst: different wt.% of sulphate impregnated TiO_2 prepared at pH 3 (0.6 g/L), time = 3 h.

low pH [12]. As reported earlier [20] the surface hydroxyl groups bound to titanium atoms constitute the active sites for adsorption. The large amount of hydroxyl groups on the surface of titania might have trap the holes in the valence band and enhanced the reduction in the conduction band. Sample prepared at pH 3 contains a mixture of anatase and rutile phase and shows higher surface area. This may be responsible for higher rate of reduction by effective adsorption of the substrate.

Fig. 7 shows the effect of wt.% of sulphate loading in TiO_2 on the photocatalytic reduction of hexavalent chromium. Sample loaded with 2.5 wt.% of sulphate shows higher percentage of reduction. However, further addition of higher sulphate content does not affect more to the percentage of reduction. This may be due to the addition of a small amount of sulphate that decreases the crystallite size of titania [12], which facilitates higher percentage of reduction. The reason may be due to the so-called particle size quantization effect. A blue shift in absorption spectra is usually observed when the size of semiconductor particles becomes small [21]. However, further increasing the wt.% of sulphate on TiO_2 does not affect the crystallite size resulting almost same percentage of reduction. So, crystallite size is an important factor for reduction of hexavalent chromium.

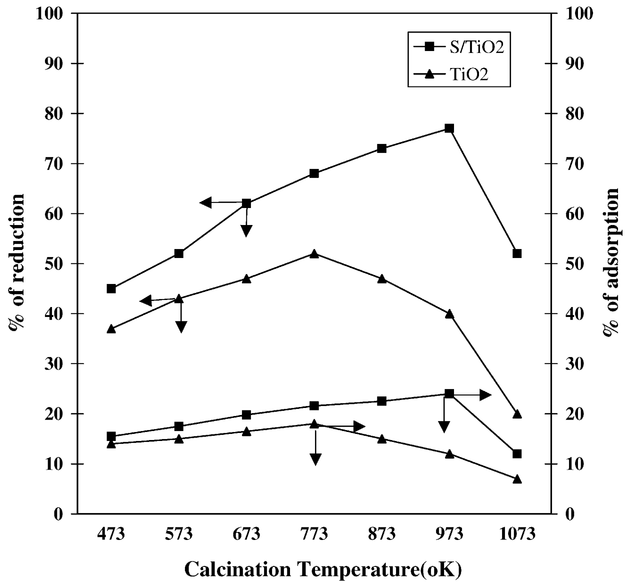

Fig. 8. Effect of calcination temperature on the photocatalytic reduction and adsorption of Cr(VI). [Cr(VI)] = 20 ppm, catalyst: 2.5 wt.% SO_4^{2-}/TiO_2 and TiO_2 prepared at pH 3 calcined at different temperatures (0.6 g/L), time = 3 h.

Fig. 8 represents the effect of activation temperature of unmodified and sulphate modified TiO_2 on the photocatalytic reduction of Cr(VI). It is observed that the percentage of reduction gradually increases with increase in activation temperature up to 773 K and thereafter decreases for unmodified TiO_2. But the percentage of reduction increases with increase in activation temperature up to 973 K and thereafter decreases for sulphate modified TiO_2. This is due to the presence of mixture of anatase and rutile phase of TiO_2. The percentage of reduction of Cr(VI) in case of sulphate modified TiO_2 is higher than that of unmodified TiO_2 at all activation temperature. Similar trend is also observed in case of both the series of sample for adsorption. The decrease in photocatalytic activity at higher activation temperature is perhaps due to loss of porous structure of nano-particles, formation of denser particles due to sintering as well as transformation into rutile from anatase phase.

From the above studies it is observed that photocatalytic reduction of Cr(VI) to Cr(III) takes place when Cr(VI) solution containing TiO_2 is illuminated in light having photon energy greater than the band gap energy of the semiconductor. During photocatalysis, adsorption occurred first when TiO_2 was dispersed in the aqueous solution containing metal ions [13]. This process is reversible and even takes place in absence of light illumination. The reduction of Cr(VI) to Cr(III) occurs because under illumination electron–hole pairs are created inside the semiconductor particles. After migration of these species to the surface of the particle, the photogenerated electrons reduce Cr(VI) to Cr(III) and holes oxidize water. The possible mechanism of the photocatalytic reduction of hexavalent chromium is as follows:

$$TiO_2 \rightarrow TiO_2(h^+ + e^-)$$

$$Cr_2O_7^{2-} + H^+ + e^- \rightarrow Cr^{3+} + H_2O$$

$$H_2O + h^+ \rightarrow O_2 + H^+$$

Which is also supported by Munoz and Domenech [15].

4. Conclusion

1. Complete reduction of hexavalent chromium (20 ppm) in aqueous solution takes place using 0.8 g/L (2.5 wt.%) sulphated TiO_2 prepared at pH 3 in 3 h.
2. Photocatalytic reduction of hexavalent chromium depends on surface area, phase, composition and crystallite size of titania.
3. sulphated TiO_2 can be effectively used for reduction of hexavalent chromium under solar radiation.
4. The photocatalytic reduction of hexavalent chromium can be enhanced in the presence of complexing agent such as EDTA.
5. Adsorption and photocatalytic reduction proceeds side by side; photocatalytic process increases with increase in adsorption.

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