Chapter-3

Process Optimization of Chemical Dose and Kinetically Studies of Chromium as a Model Pollutant
3.1. Introduction

The photochemical degradation of pollutants using semiconducting powders as catalysts is a subject of current interest. This photocatalytic method is based on the reactive properties of electron-hole pairs generated in the semiconductor particles under illumination by light of energy greater than the semiconductor band gap. These charge carriers can reach the particle surface and react with species in solution with suitable redox potentials [3.1]. The process has a potential of accomplishing two decontamination of simultaneously i.e. conversion of organics to water, carbon dioxide and dilute mineral acids and reducing the metals to their nontoxic forms [3.2]. This has been successfully applied to the degradation of organic or inorganic pollutants.

The photocatalytic degradation technology might be feasible for the treatment of wastewater containing hazardous contaminants at medium or low pollutant concentrations when biological treatment is impossible. The use of AOPs for wastewater treatment has been studied extensively, but generation of UV radiation by lamps. Therefore, research is focusing more and more on those AOPs, which can be driven by UV irradiation, i.e., light with a wavelength longer than 300 nm, heterogeneous, homogenous catalysis and photo-Fenton. Whenever different semiconductor or materials have been tested under comparable conditions for the degradation of the same compounds, TiO$_2$ has generally been demonstrated to be the most active [3.3].

Many studies concern only the catalytic activity of TiO$_2$ with single substrates. There are few papers concerning decontamination of complex systems, which, however, are the actual situation of the real environmental pollution. Many waste streams may contain mixtures of hazardous organic and inorganic species. Less attention has been paid to the catalytic elimination of inorganic compounds [3.1].

Metal ions have infinite lifetimes and build up their concentrations in food chains to toxic levels. As a result, in today's highly industrialized society, we are living in
an environment with a multitude of potentially harmful toxic metal ions [3.4]. Cr(VI) is a very toxic pollutant which is present in a great variety of industrial wastes [3.1]. The environmental importance of this process derives from the variety of sources which generate Cr(VI) in effluent streams: chrome plating, electronic, metallurgical, pigment, paint, timber and leather tanning industries. Chromium occurs in two common oxidation states in nature, Cr(III) and Cr(VI). Cr(VI) is toxic and carcinogenic. On the other hand, Cr(III) is readily precipitated or absorbed on a variety of inorganic and organic substrates at neutral or alkaline pH.

Precipitation, activated carbon adsorption, ion exchange and membrane separation are common methods currently adopted for the disposal or recovery of metal ions in wastewater. All these methods have their own advantages and disadvantages [3.4].

The catalytic photo-reduction of Cr(VI) to Cr(III) has been proved to be a practical and clean alternative. The catalytic materials usually used for Cr(VI) photoreduction are metal oxides and metal sulfates, including ZnO, TiO₂, WO₃ and CdS, etc. [3.5]. The spontaneous reactions among these two toxic species under environmental conditions are negligible. But important is that increase in the photocatalytic degradation when they are present at the same time [3.1].

Moreover, photo reduction of the Cr(VI) species is accompanied by oxidation of the electron donor, what creates a possibility of photodegradation by this way of many organic pollutants. The additional advantage is coming from sensitivity of the Cr(VI) photoreduction to the surface catalytic effects or to the presence of an additional electron donors and acceptors, then a synergistic effect was observed in two- or multi-component systems[3.6, 3.4].

A paper presents an interesting comparison study of two commercial TiO₂ for similar simultaneous photocatalytic redox reaction. In that case, they have used salicylic acid and Cr(VI) pollutant species. They have considered this binary system, since they are important industrial pollutant species and their mixture can be found in many waste streams [3.1].

The nature of the carboxylic acid used as the sacrificial agent seems to have a very important role in the photo reduction of Cr(VI). Citric acid leads to higher conversion rates without deactivation of the catalyst [3.7].
Schrank S.G. et al studied the adsorption and photocatalytic reactions using Luranzol S Kong (a dye extensively used in tannery industries) and Cr(VI) \((K_2Cr_2O_7)\) in both single and mixed systems. Isolated tests showed that both Cr(VI) and Luranzol S Kong are degraded in acidic pH, according to the L-H kinetic model. In neutral pH, the Cr(VI) was not reduced, but this might be explained by the fact that Cr(VI) was not adsorbed on TiO\(_2\) surface. In the simultaneous redox process, the reduction of Cr(VI) proceeds quicker than it does in the single process, showing synergism between the redox reactions [3.4].

The two spectra correspond to the solar UV spectra at ground level. The direct radiation spectrum \((UV_d)\) and the global radiation spectrum \((UV_g)\) cumulate 22 and 46 Wm\(^{-2}\), respectively, between 300 and 400 nm. These two values give an idea of the energy coming from the sun that is available for photocatalytic reactions with TiO\(_2\) that uses UV solar radiation just up to 387 nm. In any case, the UV radiation values vary from one location to another, and obviously, at different hours of the day and in different seasons, making necessary to know these data for any particular location in real time.

At present, there are not known reports of combined systems using TiO\(_2\) photo assisted reaction as pre-treatment process. There are many works based on supported TiO\(_2\) catalysts, in which a variety of supporting materials, coating methods and reactor arrangements have been investigated from both engineering and fundamental points of view [3.8].

Therefore, the purpose of this studied have emphasized on the capability of UV/TiO\(_2\)/H\(_2\)O\(_2\) process to meet the discharge standards for the disposal of spent reactive dye effluents into water courses [3.9]. The study focused on the identification of possible intermediate products and on the determination of inorganic ions formed during the process. Although many researched have been performed about use of photocatalysis processes in treatment of industrial wastewaters, this study should be regarded novel, because the efficiency of UV/TiO\(_2\)/H\(_2\)O\(_2\) process has been determined for the first time in simultaneous removal of phenol as an organic pollutant and heavy metals, inorganic pollutants under different conditions of treatment [3.10,3.11].

Among these AOPs, the combined systems UV/TiO\(_2\)/H\(_2\)O\(_2\) and UV/Fe\(^{3+}\)/H\(_2\)O\(_2\) are the most utilized for environmental applications since they use the UV component.
of UV light. A wide range of applications have been reported for different compounds using these systems i.e. direct UV, TiO$_2$/UV, TiO$_2$/(Citric Acid)/UV, H$_2$O$_2$/UV (Photo-Fenton) and TiO$_2$/UV/H$_2$O$_2$ process [3.8, 3.12-3.14]. Such as TiO$_2$ absorbs a photon of energy equal to or greater than its band gap width, an electron may be promoted from the valence band to the conduction band (e$_{cb}$) leaving behind an electron vacancy or “hole” in the valence band (h$^+_{vb}$). •OH radicals attack is not very selective, which is a useful attribute for use in pollution treatment. The versatility of AOPs is also enhanced by the fact that there are different •OH radical production possibilities, so they can be adapted to specific treatment requirements [3.3].

Many organic compounds have been reported added to aqueous solution to serve as hole scavengers and inhibit the recombination of electrons and holes. However, the information on the effect of these compounds on the photocatalytic reduction of metal ion was scarce [3.4].

The laboratory system will be the starting point for constructing a flow system with a new type of a photochemical reactor to further optimize the process by using TiO$_2$ and to check the possibility of integrating the photochemical process [3.12].

3.2. Objectives

This chapter describes the most important applications for chromium reduction. It outlines the decomposition of inorganic contaminants and the usefulness of optimization testing in addition to chemical dose. The use of optimize catalysts and additional oxidants to increase the process efficiency and reduces wastewater parameters mainly (pH, COD etc.) by trapping the photo-generated electrons and by producing extra oxidising species is discussed. Finally, an overview of the most common sophisticated optimization process is given below.

1. To determine the optimum dose of wastewater
2. The influence of catalyst concentration and find out the optimum catalyst mass in an experimental process.
3. To improve the reaction efficiency by using citric acid and H$_2$O$_2$ in an optimum dose for chromium concentration in wastewater.
4. The effects and thereby, reduce the number of variables affecting the tests.
5. Kinetically studied on the effect of process parameters.
3.3. Mechanism of Reaction

A brief outline of the redox process of photocatalytic reduction of dissolved metal ions is as follows: metal ions are reduced by capturing the photo-excited conduction band electrons and water is oxidized by the valence band holes. Figure 3.1 show a drawing which is frequently used to illustrate photocatalytic processes (described in chapter 1).

Figure 3.1. Energy band diagram and fate of electrons and holes in a semiconductor particle in the presence of water containing a pollutant [2.8]

Therefore, the following redox reaction cycle takes Catalyst Excitation [3.15]:

$$\text{TiO}_2 + \text{hv} \rightarrow \text{TiO}_2 (e_{\text{CB}}^\text{-} + h_{\text{VB}}^+)$$ ........................................ (3.1)

Either the $e^- h^+$ pair recombines or it participates in the chemical reactions on adsorbed species is called Recombination:

$$e_{\text{CB}}^- + h_{\text{VB}}^+ \rightarrow \text{heat}$$ ......................................................... (3.2)

Photocatalytic reduction of metal ions ($M$) in reaction (Eq. 3.3) may be limited by the conjugate electrochemical oxidation of water. If organics are absent, water will be oxidized by reaction (Eq. 3.4). This is a kinetically slow four-electron process and the competing recombination of the photogenerated holes and electrons plays an active inhibiting role [3.16].

$$M^{n+} + e^- \rightarrow M^{(n-1)+}$$ .................................................................. (3.3)
The oxygen radical may react with water to form $\text{H}_2\text{O}_2$.

$$\text{H}_2\text{O} + \text{O}_2 \rightarrow \text{H}_2\text{O}_2$$  \hspace{1cm} (3.7)

**Fate of $e^-$:**

In the studied system the electron acceptor can either be $\text{Cr}_2\text{O}_7^{2-}$ or the dissolved oxygen present in water:

$$\text{Cr}_2\text{O}_7^{2-} + 3e^- \rightarrow \text{Cr}^{3+}$$  \hspace{1cm} (3.5)

$$\text{O}_2 + e^- \rightarrow \text{O}_2$$  \hspace{1cm} (3.6)

**Fate of $h^+$:**

$$\text{OH}^- + \text{h}^+ \rightarrow \text{OH}^-$$  \hspace{1cm} (3.8)

$$\text{OH}^- + n\text{Citrate}^{3n-} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$$  \hspace{1cm} (3.9)

Or it could be directly oxidized with the help of hole.

$$n\text{Citrate}^{3n-} + \text{h}^+ \rightarrow \text{CO}_2 + \text{H}_2\text{O}$$  \hspace{1cm} (3.10)

Two different electron-donating processes occurred for different organic compounds (used as hole scavengers) during reaction, namely, direct and indirect donation of electron. In the former case, electrons from organics are directly filled to the valence band, thereby attenuating the electron-hole recombination and leaving more conduction band electrons available for reduction of metal ions. As a result, addition of these types of organics has much more pronounced effect on the reduction of metal ions. In the latter case, holes are filled only through the formation of $\cdot\text{OH}$ radicals and these radicals are subsequently consumed by the
oxidation of the added organics. Thus, organics in this class influence the reduction of metal ions indirectly, resulting in less promoting effect. Another possibility is that the initial oxidation of the organic additives by the photogenerated holes in TiO₂ (or by the •OH radicals) generates radical species with strong reducing power [3.18]. For example, the reduction potential of HCOO•/CO₂, formed due to oxidation of formic acid, is -1.7 V vs SHE [3.19], which is negative enough to reduce Cr(VI) [3.20]. This could also be a possible route for metal reduction in presence of organics.

Therefore, it could be expected that the addition of sacrificial electron donors such as suitable organic substrates may accelerate the photocatalytic reduction of metal ions. The organics would play an efficient role as an oxidation reaction counterpart of metal reduction. As a consequence, photocatalytic reduction on TiO₂ in metal-TiO₂-organics must be more efficient than that in metal-TiO₂ system resulting from the accelerating effect by the preferential photocatalytic oxidation of the organics.

In such metal-TiO₂-organics coexisted system, organic species accepts holes from valence band either directly or indirectly and subsequently was oxidized (Eqs. 3.8, 3.9 and 3.10) thereby suppressing the electron hole recombination and increasing the reduction efficiency.

The former applications of homogeneous photodegradation (single-phase system) to treat contaminated water concerned the use of H₂O₂/UV. The use of UV light for photodegradation of pollutants can be classified into two principal areas: (1) direct photodegradation, which proceeds following direct excitation of the pollutant by UV light and (2) photo-oxidation, where light drives oxidative processes principally initiated by •OH radicals. The latter process involves the use of an oxidant to generate radicals, which attack the organic pollutants to initiate oxidation. The most commonly accepted mechanism for the photolysis of H₂O₂ is the cleavage of the molecule into •OH radicals with a quantum yield of two •OH radicals formed per quantum of radiation absorbed (Eq.3.11). On the other hand, H₂O₂ is known to dismute producing •OH radicals (Eq.3.12) with maximum rate at the pH of its pKa value [3.8]. H₂O₂ may also be split photolytically to produce •OH radicals directly. It should be taken into consideration that photocatalytic oxidation will be inhibited via the reaction of excess H₂O₂ with OH radicals and hvB⁺ [3.21]:

\[
H₂O₂ + hv \rightarrow 2 \cdot OH \quad \text{........................................................................................................(3.11)}
\]
H₂O₂ + OH • → H₂O + HO₂ ................................................................. (3.12)

H₂O₂ + OH • → H₂O + O₂................................................................. (3.13)

H₂O₂ + 2h_vB → O₂ + 2H⁺................................................................. (3.14)

H₂O₂ reacts with electrons which are emitted from the valence band of the photocatalyst to generate •OH radicals and hydroxyl anions while inhibiting the e⁻/h_vB + recombination process [3.21]:

H₂O₂ + e_CB → OH⁻ + OH ................................................................. (3.15)

In both homogenous and heterogeneous processes, the •OH radicals are the main responsible for the organic pollutant oxidation. The addition of H₂O₂ to the TiO₂/UV-system enhances its photodegradation rate. The kapp for the abatement of p-NTS in the TiO₂/H₂O₂/UV-system is twice higher than that observed for the TiO₂/UV-system. For the TiO₂/UV-process, the •OH is generated by oxidation reaction involving electron donors (H₂O and -OH) and a less efficient electron acceptor than H₂O₂ such as O₂. The H₂O₂ is considered as an efficient electron scavenger, which reacts with electrons of the conduction band of the TiO₂ to generate additional •OH radical according to Eq.3.16.

TiO₂(e⁻) + H₂O₂ → TiO₂ + −OH + •OH......................................................... (3.16)

However, both homogeneous and heterogeneous photocatalysis can be considered as suitable methods to reach the complete degradation of pollutant. The efficiency photocatalytic treatment under UV light in different degradation systems: TiO₂/UV-system, H₂O₂/UV-system and TiO₂/H₂O₂/UV-system was studied and compared. The most efficient process, both homogeneous and heterogeneous photocatalysis can be considered as suitable methods to reach the complete mineralization of the solutions [3.8].

The mechanism of photocatalytic Cr(VI) reduction was not very clear but is fairly well described of photo-excited conduction band electrons followed by reduction, according to Eqs. (3.17), (3.18) and (3.19) depending on the pH [3.4, 3.17].

In acidic medium-

Cr₂O₇²⁻ + 14H⁺ + 6e⁻ → 2Cr³⁺ + 7H₂O \[ E^o = 0.98 \text{ Ev (SHE)} \] ........ (3.17)
Under neutral medium as follows:

\[
\text{Cr}_2\text{O}_4^{2-} + 8\text{H}^+ + 3e^- \rightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O} \quad E^0 = 0.56 \text{ Ev (SHE)} \quad (3.18)
\]

For alkaline solutions:

\[
\text{Cr}_2\text{O}_4^{2-} + 8\text{H}_2\text{O} + 3e^- \rightarrow \text{Cr(OH)}_3 + 5\text{OH}^- \quad E^0 = 0.24 \text{ Ev (SHE)} \quad (3.19)
\]

In the absence of reducing agents, \( \text{H}_2\text{O} \) accepts the valence band holes and the following photocatalytic redox cycle takes place (Eq. 3.20).

\[
2\text{H}_2\text{O} + 2h^+ \rightarrow \text{H}_2\text{O}_2 + 2\text{H}^+ \quad \text{................................................................................. (3.20)}
\]

**3.4. Experimental Plan**

The preliminary and primary study was used for optimisation of catalyst dose, to apply for industrial wastewater. This approach helped to identify the influence of individual factors, to arrive at the relationship between variables and operational conditions and finally, to establish the performance at the optimum levels, using a few well defined experimental sets. Studies on optimization of the photocatalytic redox reaction, the effect of such parameters as \( \text{TiO}_2 \) photocatalyst doses, chemical oxygen demand (COD), reaction time and lighting intensity were considered. The work was taken up with the following broad objectives.

1. Adsorption of total chromium in single or all combinations of the catalyst.
2. Reaction of total chromium in the adsorbed phase and desorption of reaction product.

In this chapter, study is emphasized on the kinetically interactions between reduction and oxidation processes for obtaining efficient detoxification of the model pollutant chromium in presence and absence of hole scavenger (citric acid), hydrogen peroxide (\( \text{H}_2\text{O}_2 \)) and the various factors affecting the photocatalytic reaction [3.22]. The basic considerations in the heterogeneous photocatalytic reaction are:

1. Direct UV,
2. \( \text{TiO}_2/\text{UV} \),
3. \( \text{H}_2\text{O}_2/\text{UV} \),
4. TiO$_2$/(Citric Acid)/UV,
5. TiO$_2$/H$_2$O$_2$/UV,
6. TiO$_2$/H$_2$O$_2$/(Citric Acid)/UV.

These aspects were considered during the experimental designing. Preliminary studies were performed for assessing process feasibility and selection of optimum dose of catalysts. Optimisation processes were used for catalyst dose applied for industrial wastewater. The TiO$_2$ catalyst dose was varied in the concentration of 0 to 5 g/l. The dose of citric acid was varied in the concentration of 0 to 140 mg/l and H$_2$O$_2$ varied in the concentration of 0 to 100 ml/l (Table 3.1). The experiments were carried out at natural pH for both adsorption and photocatalytic reduction. No attempt was made to adjust the pH of industrial wastewater. The results of this study facilitated the designing of further experiments.

In the primary study, experiments were carried out to obtain complete reduction total chromium by application of UV photocatalytic reaction. The industrial wastewater was studied in detail for the experimental validity for a concentration range of total chromium. H$_2$O$_2$ was used as a oxidant and citric acid as a hole scavenger for increasing the reaction rate. Besides its low cost and non-toxic nature, the choice of citric acid was made, as it does not form any harmful complexes, which could cause catalyst deactivation unlike aromatic compounds [3.23].

The experiments were carried out in two parts:

1) Varying Concentrations of oxidant and citric acid along with the TiO$_2$ on industrial wastewater.

2) Varying pH range from 2 to 10 for both adsorption and photocatalytic reduction in industrial wastewater in chapter 5.

The experimental processes were currently employed for this purpose the photocatalytic process performed to investigate any other reactions, like photolytic, among the wastewater constituents. Thereafter, dark adsorption photolytic and photocatalytic reduction was also investigated.
Table 3.1: Study of the experimental plan and variation dose

<table>
<thead>
<tr>
<th>Process Study</th>
<th>Objective of the Experiment</th>
<th>Applying on Source</th>
<th>Testing Variables</th>
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<tbody>
<tr>
<td>Preliminary Study</td>
<td>Assessing process to determine the most effective catalyst, feasibility for total chromium reduction and optimum catalyst loading concentration</td>
<td>Industrial wastewater</td>
<td>Catalyst : ( T )</td>
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<td>0 g/l,</td>
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<td>Preliminary Study</td>
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<tr>
<td>Primary Study</td>
<td>To determine the kinetic parameters total chromium reduction based on the L-H model by increasing the optimum dose of hole scavenger and oxidant used in single and with combinations.</td>
<td>Industrial wastewater</td>
<td>2g/l</td>
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<td>Primary Study</td>
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Where: \( T = TiO_2 \) Photocatalyst, \( CA = \) Citric Acid, \( HP = H_2O_2 \)
3.3. Results and Discussions

3.3.1. Preliminary Experiment

The preliminary experiments showed that the process was feasible for chromium reduction in presence of TiO₂ catalyst, citric acid and H₂O₂. The reduction was found to increase as well as increasing the concentration of TiO₂ catalyst, citric acid and H₂O₂ at optimal level.

The reduction of total chromium was studied by varying the amount of TiO₂ from 1 to 5g/l. Fig. 3.2(a) shows the variation of initial rate of chromium reduction as a function of catalyst dose. The initial reduction rate values indicate that increased with an increase in catalyst dose. Maximum reduction of total chromium was obtained 20.5% in 5g/l of TiO₂.

We have also studied the possible synergy effect of the simultaneous photo oxidation-reduction of both pollutants. However, complete reduction of total chromium was not obtained even at very minimum or maximum citric acid doses shown in Fig. 3.2(b). Maximum reduction of total chromium was 45.53% obtained from the concentration of 100mg/l. Since increasing the initial rate values of citric acid indicate that the reduction rate of total chromium increased with an increase in dose up to an optimum loading of 60mg/l. With the same procedure using H₂O₂ was obtained complete reduction of total chromium at very minimum to maximum level of doses up to 0 to 100ml/l. Maximum reduction 98.16% was observed by the dosing of 60ml/l of H₂O₂ depicted in Fig. 3.2(c).

3.3.2. Primary Experiment

The experiments for the advanced oxidation processes are usually conducted by optimizing the operating conditions and photo reactor characteristics since the efficiency of the AOPs is affected by various variables such as the concentration of initial compounds, residence time, citric acid, H₂O₂ dose, photocatalyst concentration, temperature and pH. The initial total chromium concentrations studies are for the Industrial wastewater.

From the different various tests carried out, the best conditions found for the TiO₂ catalyst process was 2g/l performing the photocatalytic reduction of total chromium. With the same procedure using citric acid and H₂O₂ concentration were
Figure 3.2(a): Photocatalytic reactions of percentage reduction of chromium concentration with time for different ratios:
TiO$_2$=Variable, H$_2$O$_2$=0ml/l, Citric Acid=0mg/l

Figure 3.2(b): Photocatalytic reactions of percentage reduction of chromium concentration with time for different ratios:
TiO$_2$=2g/l, H$_2$O$_2$=0ml/l, Citric Acid=Variable

Figure 3.2(c): Photocatalytic reactions of percentage reduction of chromium concentration with time for different ratios:
TiO$_2$=0g/l, H$_2$O$_2$=Variable, Citric Acid=0mg/l

y = 3.377x
R$^2$ = 0.958

y = 6.657x + 4.683
R$^2$ = 0.955

y = 20.33x - 4.042
R$^2$ = 0.774
varied which is mentioned in Fig. 3.3(a) & (b). The experimental results was carried out with 60mg/l dose of citric acid and 60ml/l dose of H2O2, react with of total chromium, given in Table 3.1. On the other hand, at citric acid in Fig. 3.4(a)-(h) and H2O2 concentration in Fig.3.5 (a)-(f) on the photocatalytic reaction was significantly accelerated. Finally the experimental process was carried from pH 2 to 10 with industrial wastewater in chapter 5.

3.3.2.1. Dark Adsorption

Study of chromium dark adsorption was performed in presence of TiO2 catalyst, citric acid and H2O2. This process was used for similar to all the experiments and before an initiation period of 1 hour (in dark, i.e. UV light irradiation was started after 1 hour). However, the time and experimental conditions of adsorption and photoreduction were identical. No more effect on this process but beneficial role of citric acid and H2O2 in photoreduction was found to be remarkable. For example, the amount of chromium initially adsorbed on TiO2 (in the dark) was affected as the citric acid and H2O2 concentration was added. This trend is given in Fig. 3.6(a) & (b).

The results showed that adsorption of total chromium on TiO2 surface in presence of citric acid was found to increase initially, but decreased after a particular concentration of citric acid. The experiment with H2O2 was same to citric acid reaction. It can be seen in Fig. 3.6(a) & (b) that the concentration at which maximum adsorption occurred on citric acid concentration of 40-60 mg/l and H2O2 on 60 ml/l. The adsorption therefore, clearly is not the single key to securing high photocatalytic conversion yields. In terms of mg/l of total chromium adsorbed, the adsorption was more for higher initial concentration of citric acid and H2O2. The adsorption was reduced due to decrease in pH at higher concentration of citric acid and H2O2.

3.3.2.2. Setup No.1 or Photolytic Interactions of chromium

In order to investigate any other reactions like, photolytic interactions among total chromium were carried out blank experiments in absence of photocatalyst, citric acid and H2O2.
Figure 3.3(a): Percentage reduction of chromium with time for different ratios of citric acid:
TiO2=2g/I, H2O2=60ml/I, Citric Acid=Variable

Figure 3.3(b): Percentage reduction of chromium with time for different ratios of H2O2:
TiO2=2g/I, Citric Acid=60mg/I, H2O2=Variable
Figure 3.4(a): Reduction trends of chromium with time for the different ratios of combinations and citric acid:
TiO2=2g/l, H2O2=60ml/l, Citric Acid=0mg/l

Figure 3.4(b): Reduction trends of chromium with time for the different ratios of combinations and citric acid;
TiO2=2g/l, H2O2=60ml/l, Citric Acid=20mg/l

Figure 3.4(c): Reduction trends of chromium with time for the different ratios of combinations and citric acid;
TiO2=2g/l, H2O2=60ml/l, Citric Acid=40mg/l

Figure 3.4(d): Reduction trends of chromium with time for the different ratios of combinations and citric acid;
TiO2=2g/l, H2O2=60ml/l, Citric Acid=60mg/l

Figure 3.4(e): Reduction trends of chromium with time for the different ratios of combinations and citric acid;
TiO2=2g/l, H2O2=60ml/l, Citric Acid=80mg/l

Figure 3.4(f): Reduction trends of chromium with time for the different ratios of combinations and citric acid;
TiO2=2g/l, H2O2=60ml/l, Citric Acid=100mg/l

Figure 3.4(g): Reduction trends of chromium with time for the different ratios of combinations and citric acid;
TiO2=2g/l, H2O2=60ml/l, Citric Acid=120mg/l

Figure 3.4(h): Reduction trends of chromium with time for the different ratios of combinations and citric acid;
TiO2=2g/l, H2O2=60ml/l, Citric Acid=140mg/l
Figure 3.5(a): Reduction trends of chromium with time for the different ratios of combinations and 
H2O2:
TiO2=2g/l, Citric Acid=60mg/l, H2O2=0ml/l

Figure 3.5(b): Reduction trends of chromium with time for the different ratios of combinations and 
H2O2:
TiO2=2g/l, Citric Acid=60mg/l, H2O2=20ml/l

Figure 3.5(c): Reduction trends of chromium with time for the different ratios of combinations and 
H2O2:
TiO2=2g/l, Citric Acid=60mg/l, H2O2=40ml/l

Figure 3.5(d): Reduction trends of chromium with time for the different ratios of combinations and 
H2O2:
TiO2=2g/l, Citric Acid=60mg/l, H2O2=60ml/l

Figure 3.5(e): Reduction trends of chromium with time for the different ratios of combinations and 
H2O2:
TiO2=2g/l, Citric Acid=60mg/l, H2O2=80ml/l

Figure 3.5(f): Reduction trends of chromium with time for the different ratios of combinations and 
H2O2:
TiO2=2g/l, Citric Acid=60mg/l, H2O2=100ml/l
Figure 3.6(a): Dark adsorption of chromium with different ratios of citric acid:
TiO$_2$=2g/l, H$_2$O$_2$=60ml/l, Citric Acid=Variable

Figure 3.6(b): Dark adsorption of chromium with different ratios of H$_2$O$_2$:
TiO$_2$=2g/l, Citric Acid=60mg/l, H$_2$O$_2$=Variable
The results for total chromium reduction for photolytic experiments in absence of citric acid and \( \text{H}_2\text{O}_2 \) are depicted in Figure 3.4(a) and 3.5(a). It can be observed that UV radiations reduces total chromium 5.82% and shows that reaction was found very slow on five hours without TiO\(_2\). In addition, pH remained unchanged during throughout the irradiation. It can be affirmatively said that the process was satisfactory results with photocatalytic and not photolytic.

### 3.3.2.3. Setup No.2 or TiO\(_2\)-UV system for reduction of chromium

After assuring that the process is truly photocatalytic experiment was performed for total chromium reduction on TiO\(_2\) surface. If organics are absent, water will be oxidized by reaction (Eq. 3.1). The experiments performed in the absence of citric acid supported that the electron hole recombination predominated with water as a reductant (Eq. 3.2, 3.3 and 3.4).

The results for total chromium reduction during experiments are depicted in Figure 3.3(a) & (b). In the absence of citric acid and presence of TiO\(_2\), total chromium was found to reduce 12.92% in UV exposure throughout the five hours. Although, the average UV irradiation in this experimental run was similar to other experiments yet the reaction rate was significantly enhanced with the addition of TiO\(_2\). The electron hole recombination acted as an active inhibitor in absence of a hole scavenger.

### 3.3.2.4. Setup No.3 or H\(_2\)O\(_2\)-UV system for reduction of chromium

Light absorbed by a molecule can result in electronic excitation, which increases the molecule's ability to lose or gain electrons. This makes the excited state more suitable as an oxidizing or reducing agent, that in turn makes it more likely and a highly reactive species such as the hydroxide radical (OH\(^•\)) can be produced from an electron transfer process between the excited state and contacting medium [3.24].

The results obtained by treating the sample with UV alone and in combination with \( \text{H}_2\text{O}_2/\text{UV} \) are reported. From Figure 3.3(a) & (b), it is possible to observe that the action of UV alone did not show any reduction capacity, although \( \text{H}_2\text{O}_2 \) can be a relatively powerful oxidant. The combination \( \text{H}_2\text{O}_2/\text{UV} \) was found to be effective in the reduction of total chromium in wastewater than UV alone.
The rate of photocatalytic reduction of total chromium was significantly improved by the addition of oxidant. Addition of citric acid reduces total chromium, 18.98% adding while of H$_2$O$_2$ concentration 20 to 100 ml/l reduces 9.52%, 12.19%, 33.44%, 41.84% and 47.50% respectively and it observed that reaction was found satisfactory on five hours of UV irradiation without TiO$_2$ dose. In addition, pH remained unchanged throughout the irradiation period.

3.3.2.5. Setup No.4 or TiO$_2$-Citric Acid-UV for reduction of chromium

Citric acid used in this study had a pronounced effect on reduction rate and probably attenuated the electron-hole recombination by donating electrons, which directly fill the valence band. The beneficial role of the organic additive was quite striking. With the addition of citric acid, the reduction rate was significantly enhanced. On increasing the citric acid concentration further, in the given as Table 3.1, the rate of reduction was also significantly enhanced. The faster degradation can be attributed to minimum electron-hole recombination due to sufficient concentration of hole scavenger. The reaction apparently followed partial order for low citric acid concentration and zero order for higher citric acid concentration indicating that the role of citric acid for lowering the solution pH, was more effective at higher concentrations thereby making the conditions favourable for total chromium reduction.

The results for total chromium reduction during experiments for the initial concentration, the percentage of increase was from 12.92% (without citric acid) to above concentration of 20-100 mg/l for 58.56%, 73.51%, 75.73%, 88.29% and 100% respectively, for the UV exposure throughout the five hours shown in Fig. 3.3(a). The citric acid concentration 100mg/l, showed complete reduction of total chromium was achieved, in five hours. There was a steep decrease in the total chromium concentration in the first 2-3 hours which contributed a maximum reduction to the UV, TiO$_2$/UV, H$_2$O$_2$/UV. Citric acid also decreases the solution pH, thereby favouring total chromium reduction. Almost complete reduction of Cr(VI) in presence of citric acid is also reported by Colon et al. [3.23].

The trends of reduction were similar but the quantity of citric acid required for complete reduction of total chromium was found to increase with increasing concentration. The total chromium concentration in the solution was obtained below permissible limit after photocatalytic reduction.
3.3.2.6. Setup No.5 or TiO₂-H₂O₂-UV system for reduction of chromium

In both homogeneous and heterogeneous processes, the •OH radicals are the main responsible for the redox reaction. This clearly indicates that photocatalysis can also be regarded as an applicable process for metals treatment. The efficiency of chromium reduction could be improved to a certain extent by addition of more \( \text{H}_2\text{O}_2 \) and \( \text{TiO}_2 \). Introducing \( \text{TiO}_2/\text{H}_2\text{O}_2/\text{UV} \) process improves mineralization rates, as \( \text{H}_2\text{O}_2 \) addition increases OH production. After 5 h, a 78% TOC removal is achieved [3.13].

The experimental studies with UV alone, \( \text{TiO}_2/\text{UV} \) and \( \text{H}_2\text{O}_2/\text{UV} \) in combination with \( \text{TiO}_2/\text{H}_2\text{O}_2/\text{UV} \) are reformed. The same trend was also considered for metals treatment and metals were removed much better when UV light was combined with \( \text{TiO}_2/\text{H}_2\text{O}_2 \).

The study, Fig. 3.3(a) & (b) reveal maximum treatment efficiency of total chromium reduction with citric acid, 24.84 % and as well as increasing \( \text{H}_2\text{O}_2 \) concentration upto 20-100 ml/l to reduces 15.12%, 32.64%, 40.57%, 58.70% and 61.03% respectively that is more efficient than the \( \text{H}_2\text{O}_2/\text{UV} \) process. Even when the \( \text{TiO}_2/\text{H}_2\text{O}_2/\text{UV} \) reaction happened to be the most efficient process, both homogeneous and heterogeneous photocatalysis can be considered as suitable methods to reach the complete mineralization of the solutions.

The efficiency of \( \text{TiO}_2/\text{H}_2\text{O}_2/\text{UV} \) systems for the removal of hazardous heavy metals is much greater using \( \text{H}_2\text{O}_2 \) as an oxidant. The removal of total chromium in the \( \text{TiO}_2/\text{H}_2\text{O}_2/\text{UV} \) process compared with the \( \text{TiO}_2/\text{UV} \) and \( \text{H}_2\text{O}_2/\text{UV} \) and \( \text{TiO}_2/\text{citric acid}/\text{UV} \) process, at the optimal conditions increased about 4.7, 1.8, and 2.3 times respectively. As shown in the equations, \( \text{H}_2\text{O}_2 \) reacts with conduction band electrons and with superoxide radicals produced between oxygen and electron to generate •OH radicals. Also, \( \text{H}_2\text{O}_2 \) produces •OH radicals directly by the photolytic split [3.22].

The same results were also obtained in previous works and it had been reported that photo catalytic oxidation of same organics as well as reduction of few metals is possible by coupling \( \text{TiO}_2 \) with UV light[3.10]. The performance of \( \text{TiO}_2/\text{UV} \) and \( \text{UV}/\text{TiO}_2/\text{chemical oxidant} \) processes for the removal of Cr(VI) in aqueous \( \text{TiO}_2 \) suspensions. The reaction rate of and hazardous heavy metals by \( \text{TiO}_2/\text{UV} \) was
higher than that of UV alone or TiO₂ alone, indication that the TiO₂/UV system was a more practical method than either UV illumination or TiO₂. In the TiO₂/UV system, the removal efficiency for Cr(VI) at acid or neutral pH was higher than that at basic pH. The addition of H₂O₂, in the TiO₂/UV system increased the degradation efficiency for the treatment of hazardous heavy metals. Finally, the degradation efficiency of the TiO₂/oxidant/UV systems was much greater when H₂O₂ was used as the oxidant [3.22].

3.3.2.7. Setup No. 6 or TiO₂-Citric Acid-H₂O₂-UV system for reduction of chromium

The efficiency of total chromium reduction by photocatalytic treatment under UV light in different degradation systems: UV, TiO₂/UV, H₂O₂/UV, TiO₂/citric acid/UV and TiO₂/H₂O₂/UV was studied and compared. Even when the TiO₂/Citric Acid/H₂O₂/UV reaction happened to be the most efficient process, both homogeneous and heterogeneous photocatalysis can be considered as suitable methods to reach the complete mineralization of the solutions.

In chromium reduction percentage was given in Fig. 3.3(a) & (b), the addition of citric acid to the TiO₂/H₂O₂/UV system enhances its photoreduction rate. This may be due to the production of a greater amount of OH radicals in the TiO₂/H₂O₂/citric acid/UV system compared with the production in other systems. The time in which complete reduction was obtained, decreased to two hours rather than five hours as in the earlier experimental runs. The faster degradation can be attributed to minimum electron-hole recombination due to sufficient concentration of hole-electron scavenger. Figure 3.3(a) & (b) shows, maximum treatment efficiency of total chromium reduction with increasing citric acid concentration from 20 to 80 ml/l reduces 62.00%, 76.70%, 77.91% and 100% respectively and as well as increasing H₂O₂ concentration from 20 to 100 ml/l for reduces 40.57%, 41.84%, 50.77%, 61.03% and 100% respectively that is more efficient than the H₂O₂/UV process.

3.3.2.8. Adsorption and Deposition of Total Chromium

As mentioned in Table 3.2 the results, the pH has a great influence on the reaction rate of reduction of total chromium. A decrease in the pH has two combined effects. On the one hand, the Nernst redox potential for chromate reduction increases.
Table 3.2. Percentage of total component concentration and species distribution of Chromium in presence/absence of TiO2, H2O2 and citric acid

<table>
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<tr>
<th>(1) Species name</th>
<th>%</th>
<th>(2) Species name</th>
<th>%</th>
<th>(3) Species name</th>
<th>%</th>
<th>(4) Species name</th>
<th>%</th>
<th>(5) Species name</th>
<th>%</th>
<th>(6) Species name</th>
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<td>CrO4-2</td>
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<td>Cr(OH)2+1</td>
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<td>HCrO4-</td>
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Where: T = TiO2 (2 g/l) Photocatalyst, CA = Citric Acid (60 mg/l), HP = H2O2 (60 ml/l)
On the other hand, the positive charge of titania particles increases. This fact could increase the adsorption of chromate by electrostatic attraction. Furthermore, the desorption of the product formed (Cr(III) species) could be favoured. At pH > 4.5, the catalyst surface is negatively charged.

Under these conditions the adsorption of anions, such as chromate, is more difficult which is due to the electrostatic repulsion. Otherwise, in these conditions the product formed (insoluble chromium hydroxide) could be adsorbed more easily on the titania surface, decreasing the active surface of the catalyst [3.25].

The total chromium present in the industrial was initially in the hexavalent form. However, after reduction and conversion to trivalent state, total chromium is used as a measure to assess chromium deposition. The Figure 3.7(a) & (b) was an overall decrease in total chromium concentration in the wastewater after treatment. The decreased concentration of total chromium is an indicative of Cr(III) hydroxide deposition on the catalyst surface found to occur at around pH 6.

A series of experiments were conducted at different combination systems (UV, TiO₂/UV, H₂O₂/UV, TiO₂/citric acid/UV, TiO₂/H₂O₂/UV and TiO₂/Citric Acid/H₂O₂/UV) and pH values ranging, containing total chromium in order to investigate photocatalytic reactions. Photolysis tests showed that no more reduction of total chromium was 1.68% observed either without catalyst, oxidant. The depositions for the TiO₂/UV, H₂O₂/UV, TiO₂/citric acid/UV, TiO₂/H₂O₂/UV and TiO₂/Citric Acid/H₂O₂/UV systems were 3.49%, 5.49%, 25.55%, 7.18% and 25.55% respectively for citric acid and 2.26%, 8.33%, 4.52%, 10.70% and 10.70% respectively with H₂O₂ concentrations. This close to the total percentage was 2-25% of total chromium reduced.

In presence of citric acid and H₂O₂, the deposition was higher for the experimental run in which more reduction was observed and final pH was closer to 6. Maximum deposition occurred in TiO₂/Citric Acid/H₂O₂/UV systems for concentrations (citric acid 88.29% and H₂O₂ 61.03% respectively) with final pH 7.24 and 8.06 respectively (Table 3.3). It can be observed that the deposition was also affected by initial pH. The deposition decreased with decreasing initial pH. At lower pH, Cr(III) hydroxide formation was expected to be less and Cr(III) remained in its cationic form thereby being repelled by the positive charged TiO₂ surface.
Figure 3.7(a): Milligrams of total chromium deposited per gram of TiO₂ for different ratios Citric Acid,
TiO₂=2g/l, H₂O₂=60ml/l, Citric Acid=Variable

Figure 3.7(b): Milligrams of total chromium deposited per gram of TiO₂ for different ratios H₂O₂,
TiO₂=2g/l, Citric Acid=60mg/l, H₂O₂=Variable
Table 3.3: The corresponding pH change in variation of Citric Acid and H₂O₂ concentration

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<th>(3)</th>
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<td>S+HP</td>
<td>S+T+CA</td>
<td>S+T+HP</td>
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Where: T = TiO₂ (g/1) Photocatalyst, CA = Citric Acid (mg/1), HP = H₂O₂ (ml/1)
3.3.3. Effect of Process Parameters

3.3.3.1. Effect of the pH on the Photocatalytic Reduction of Total Chromium

A series of experiments were performed by adding citric acid and H$_2$O$_2$ conducted at pH 7, containing chromium and catalysts (TiO$_2$) in order to investigate photocatalytic reactions. Under illumination with the UV lamp, the chromium solution gradually lost its original yellow color, while the originally white TiO$_2$ turned pale green.

The effect of pH 7 was studied for the reduction of total chromium in industrial effluent at a TiO$_2$ loading of 2g/l, with the variable of citric acid dosage of 60mg/l and H$_2$O$_2$ dosage of 60ml/l in Fig. 3.3(a) & (b). The results for pH change during the temporal profiles of total chromium reduction by UV, TiO$_2$/UV, H$_2$O$_2$/UV, TiO$_2$/citric acid/UV, TiO$_2$/H$_2$O$_2$/UV and TiO$_2$/Citric Acid/H$_2$O$_2$/UV reaction are depicted in Table 3.3. The initial pH 7.12, decreasing with increasing citric acid and increasing with increasing H$_2$O$_2$ dosing and at the end of reaction the pH was found to increase. Figure 3.3(a) & (b) shows the change of concentration for the photocatalytic reduction only (i.e., the results shown are obtained after it was ascertained that an adsorption equilibrium has been attained and the lamp was turned on) and indicates that reduction rates increase with acidic or alkaline pH [3.26].

Maximum pH change was found to occur during the first three hours of reaction which also corresponds to the maximum reduction of chromium. The pH increase was not significant in the UV alone runs in which chromium reduction was also minimum. There was an overall increase in about pH 8 units for maximum samples. The change in pH is due to formation of OH$^-$ ions. The samples, in which the pH was lower due to high citric acid concentration, showed higher reduction of chromium, which is expected as the reduction of chromium is favoured at acidic pH. The deposition of reduced chromium was lower at low pH due to repulsion of cationic Cr(III) species by TiO$_2$. No more adsorption was observed at pH 7.0. This result agrees with, no adsorption was detected at pH above 6.0, due to the negative charge on the photocatalyst surface at pH 7.0 repels the dichromate ion [3.4].
3.3.3.2. Determination of Chemical Oxygen Demand (COD)

The study of COD was also applied for the solutions, treated by $\text{H}_2\text{O}_2$ and citric acid combination with variation of concentration. Experimental results demonstrate that the COD removal efficiency is higher at initially increasing $\text{H}_2\text{O}_2$ and citric acid concentration. The citric acid and $\text{H}_2\text{O}_2$ oxidation is the counterpart reaction of chromium reduction. COD decrease was measured to trace the oxidation of citric acid and $\text{H}_2\text{O}_2$. The overall trend of COD reduction is depicted in Fig. 3.8(a)-(h) and 3.9(a)-(f). For citric acid and $\text{H}_2\text{O}_2$ in the reaction system was found to degrade completely as well as increasing concentration in about 5 hours of UV exposure. The exhaustion of citric acid ceased the reaction.

The results shows in Fig. 3.10(a) & (b) maximum COD reduction with $\text{H}_2\text{O}_2$/UV system with $\text{H}_2\text{O}_2$ increasing concentration 0 to 100 ml/l for increased with 6.66%, 30%, 44.44%, 57.77% 64.44% and 80% and $\text{H}_2\text{O}_2$/TiO$_2$/UV system 33.33%, 51.11%, 57.77%, 66.66% 82.22% and 92.22% respectively. The combination with TiO$_2$/Citric Acid/$\text{H}_2\text{O}_2$/UV system was 33.33%, 60%, 61.11%, 77.77% 94.44% and 98.88% respectively that is more efficient than the $\text{H}_2\text{O}_2$/UV and $\text{H}_2\text{O}_2$/TiO$_2$/UV process. Similar that maximum COD reduction with TiO$_2$/Citric Acid/UV was increasing citric acid concentration 20 to 140 ml/l for increased with 37.77%, 46.66%, 55.55%, 60%, 62.22%, 65.55% and 66.66% and $\text{H}_2\text{O}_2$/UV and $\text{H}_2\text{O}_2$/TiO$_2$/UV system 68.88%, 71.11% 77.77% and 83.33%, 86.66%, 85.55% 86.66% respectively that is more efficient than the TiO$_2$/Citric Acid/UV process. The combination was observed COD removal efficiency improvement in the treated solutions.

When the concentration of citric acid and $\text{H}_2\text{O}_2$ was increased further, complete reduction of total chromium was achieved. It is observed that, COD was reduced maximum in the time period in which total chromium reduction was more. This shows that there is a synergism in the redox reactions and the absence of any of the species leads to dominant electron hole recombination and show that the moles of citric acid/$\text{H}_2\text{O}_2$ consumed per mole of total chromium. As discussed earlier, the fast reduction of COD indicates that the oxidation of citric acid and $\text{H}_2\text{O}_2$ was by donating electrons, which directly fill the valence band, and not through an indirect pathway. Although, the COD reduction in percentage was different for all the samples due to initial concentrations of citric acid and $\text{H}_2\text{O}_2$ added.
Figure 3.8(a): COD values at different irradiation time with different combinations and citric acid: 
TiO₂=2g/l, H₂O₂=60mL/l, Citric Acid=0mg/l

Figure 3.8(b): COD values at different irradiation time with different combinations and citric acid: 
TiO₂=2g/l, H₂O₂=60mL/l, Citric Acid=20mg/l

Figure 3.8(c): COD values at different irradiation time with different combinations and citric acid: 
TiO₂=2g/l, H₂O₂=60mL/l, Citric Acid=40mg/l

Figure 3.8(d): COD values at different irradiation time with different combinations and citric acid: 
TiO₂=2g/l, H₂O₂=60mL/l, Citric Acid=60mg/l

Figure 3.8(e): COD values at different irradiation time with different combinations and citric acid: 
TiO₂=2g/l, H₂O₂=60mL/l, Citric Acid=80mg/l

Figure 3.8(f): COD values at different irradiation time with different combinations and citric acid: 
TiO₂=2g/l, H₂O₂=60mL/l, Citric Acid=100mg/l

Figure 3.8(g): COD values at different irradiation time with different combinations and citric acid: 
TiO₂=2g/l, H₂O₂=60mL/l, Citric Acid=120mg/l

Figure 3.8(h): COD values at different irradiation time with different combinations and citric acid: 
TiO₂=2g/l, H₂O₂=60mL/l, Citric Acid=140mg/l
Figure 3.9(e): Reduction trends of COD with time for the different ratios of combinations and H₂O₂:
TiO₂ = 2 g/L, Citric Acid = 60 mg/L, H₂O₂ = 40 mL/L

Figure 3.9(d): Reduction trends of COD with time for the different ratios of combinations and H₂O₂:
1.2 TiO₂ = 2 g/L, Citric Acid = 60 mg/L, H₂O₂ = 60 mL/L

Figure 3.9(c): Reduction trends of COD with time for the different ratios of combinations and H₂O₂:
1.2 TiO₂ = 2 g/L, Citric Acid = 60 mg/L, H₂O₂ = 100 mL/L

Figure 3.9(b): Reduction trends of COD with time for the different ratios of combinations and H₂O₂:
1.2 TiO₂ = 2 g/L, Citric Acid = 60 mg/L, H₂O₂ = 20 mL/L

Figure 3.9(a): Reduction trends of COD with time for the different ratios of combinations and H₂O₂:
1.2 TiO₂ = 2 g/L, Citric Acid = 60 mg/L, H₂O₂ = 80 mL/L

Figure 3.9(f): Reduction trends of COD with time for the different ratios of combinations and H₂O₂:
1.2 TiO₂ = 2 g/L, Citric Acid = 60 mg/L, H₂O₂ = 60 mL/L

Figure 3.9(g): Reduction trends of COD with time for the different ratios of combinations and H₂O₂:
1.2 TiO₂ = 2 g/L, Citric Acid = 60 mg/L, H₂O₂ = 20 mL/L

Figure 3.9(h): Reduction trends of COD with time for the different ratios of combinations and H₂O₂:
1.2 TiO₂ = 2 g/L, Citric Acid = 60 mg/L, H₂O₂ = 80 mL/L

Figure 3.9(i): Reduction trends of COD with time for the different ratios of combinations and H₂O₂:
1.2 TiO₂ = 2 g/L, Citric Acid = 60 mg/L, H₂O₂ = 100 mL/L

Figure 3.9(j): Reduction trends of COD with time for the different ratios of combinations and H₂O₂:
1.2 TiO₂ = 2 g/L, Citric Acid = 60 mg/L, H₂O₂ = 60 mL/L
Figure 3.10(a): Reduction trends of COD with time for the different ratios of combinations and H2O2:
TiO2=2g/l, Citric Acid=60mg/l, H2O2=Variable

Figure 3.10(b): Percentage of the COD values at different irradiation time with different combinations and citric acid:
TiO2=2g/l, H2O2=600ml/l, Citric Acid=Variable
3.3.3.3. Statistical Correlation

To find the optimum conditions for degradation of industrial wastewater in a batch type reactor, the surface response as a function of the selected main factors has to be determined. TiO$_2$, citric acid and H$_2$O$_2$ concentration were chosen as the major factors to be considered. The correlation obtained in the reduction of total chromium and oxidation of citric acid and H$_2$O$_2$ were quite significant. The correlation coefficients obtained are mentioned in Table 3.4. The values clearly indicate that the oxidation and reduction process was intrinsically related and complementary to each other.

Table 3.4: Statistical correlation for photocatalytic reduction of Chromium with Citric Acid and H$_2$O$_2$ oxidation for different concentration

<table>
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<th>Industrial Wastewater</th>
<th>Setup No.</th>
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<th>(2)</th>
<th>(3)</th>
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<td>S+HP</td>
<td>S+T+CA</td>
<td>S+T+HP</td>
<td>S+T+CA+HP</td>
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<table>
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<th>S+T+CA</th>
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Where: S=Industrial Wastewater Sample, T= TiO$_2$ (g/l) Photocatalyst, CA= Citric Acid (mg/l), HP= H$_2$O$_2$ (ml/l)
3.3.3.4. Effect of the Photocatalyst Loading

The oxidation rates, after equilibration in irradiation time for TiO₂ loadings from up to 1-5g/l are shown in Fig. 3.2(a). It can be seen that the amount of total chromium adsorbed on the catalyst surface generally increases when increasing the TiO₂ loading at optimum level. It is also evident from Fig. 3.2(a) that as the TiO₂ loading increases reduction of chromium reaction becomes faster, especially up to 2g/l. The use of bigger photocatalyst doses was not recommended mainly for economic reasons and because of the degree of photocatalyst utilization when the process was carried out in slurry [3.12].

It is observed that irradiation time required for degradation of effluent decreases with increasing catalyst concentration, until 2g/l. Further increase in catalyst concentration decreases the degradation rate. As seen in this Fig. 3.3(a) & (b), the addition of TiO₂ increases the initial reaction rate constant for the TiO₂/UV and TiO₂/H₂O₂/UV process and reaches an apparent at about 2g/l of photocatalyst. For comparison, the initial reaction rate constant for TiO₂/citric acid/H₂O₂/UV is also given in this Fig. 3.3(a) & (b). The TiO₂/citric acid/H₂O₂/UV system has a higher initial reaction rate constant at all levels of catalyst loading by 6-20%, depending on the TiO₂ concentration. Moreover, in the absence of citric acid and H₂O₂, no optimum value of photocatalyst is observed, instead the reaction rate increases continuously with TiO₂ addition.

3.3.3.5. Effect of H₂O₂ concentration

Reduction rates increase with H₂O₂ concentration which is explained by the effect of the additionally produced •OH radicals. However, above a certain H₂O₂ concentration, the reaction rate levels off and sometimes is negatively affected by the progressive increase of the H₂O₂. This may be due to auto-decomposition of H₂O₂ to oxygen and water and recombination of •OH radicals (Eq. 3.12). Therefore, H₂O₂ should be added at an optimal concentration to achieve the best degradation. This optimal H₂O₂ concentration depends on the nature and concentration of the compound to treat [3.8].
It can be concluded that the reduction rate of the dark reaction is far lower than that of the photocatalytic reaction. The results showed that the homogeneous photochemical reaction of total chromium after 5 h irradiation is so small to be negligible, which is in agreement with a previous report [3.27].

The effect of H₂O₂ concentration was varied systematically in the reaction solutions. This phenomenon indicates that competing mechanisms are present in this system. In fact, according to the available literatures, H₂O₂ and citric acid in the TiO₂/UV system could act as: (a) the electron acceptor; (b) the scavenger of positive holes; (c) the scavenger of *OH radicals; or (d) the producer of *OH radicals.

In the presence of UV and TiO₂, the degradation rate increased by adding H₂O₂. The degradation rates, however, were lower in the presence of H₂O₂ but in the absence of TiO₂. As shown in Fig. 3.11(a), (b) & (c), a significant enhancement of degradation efficiency is demonstrated when H₂O₂ concentrations are increased from 0 to 100ml/l. Above this concentration, the rate of COD reduction is negatively affected by the progressive increase of H₂O₂.

3.3.3.6. Effect of Initial Concentration of Total Chromium

The absorption of light by the solution increases with the chromium concentration and the expected reaction rate decreases, since less radiation reaches to the catalyst because chromates absorb light in the range of 300-400 nm. Therefore the amount of light reaching the photocatalyst depends on the amount of chromate in solution. This could be a possible reason for low reduction rates of total chromium obtained.

Another effect of initial concentration of chromium in the lower concentration was that the quantity of citric acid and H₂O₂ required for complete reduction. The trend of Fig. 3.12(a) & (b) shown as well as increase concentration of CA: H₂O₂, which gave corresponding reduction rates were quite similar. Citric acid and H₂O₂ was 60mg/l and 60ml/l the optimum with variable for each other for the reduction of total chromium.

3.3.7. Kinetically Analysis of Photocatalytic Reduction of Total Chromium

The photocatalytic oxidation of total chromium in aqueous solutions has been successfully modelled using Langmuir-Hinshelwood kinetics. According to the L-H
Figure 3.11(a): Reduction trends of chromium with time for the different ratios of combinations and citric acid:
- TiO₂=2g/l, Citric Acid=0mg/l, H₂O₂=Variable

Figure 3.11(b): Reduction trends of chromium with time for the different ratios of combinations and H₂O₂:
- TiO₂=2g/l, Citric Acid=0mg/l, H₂O₂=Variable

Figure 3.11(c): Reduction trends of chromium with time for the different ratios of combinations and H₂O₂:
- TiO₂=2g/l, Citric Acid=0mg/l, H₂O₂=Variable

Figure 3.12(a): Reduction trends of chromium with time for the different ratios of combinations and citric acid:
- TiO₂=2g/l, H₂O₂=Variable, Citric Acid=Variable

Figure 3.12(b): Reduction trends of chromium with time for the different ratios of combinations and citric acid:
- TiO₂=2g/l, H₂O₂=Variable, Citric Acid=Variable
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model confirming the heterogeneous catalytic character of the system with the rate ‘r’ varying proportionally with the surface coverage θ as [3.28]:

\[ r = kθ = \frac{k(KC)}{1+KC} \]  

Where ‘r’ is the rate of reaction, ‘K’ is the Adsorption constant, ‘k’ is the rate constant and ‘C’ is the concentration of the species.

The degradation rate constant (k) is determined and evaluated at different citric acid and H₂O₂ concentrations to find out the values at which maximum efficiency (k_max) is obtained. In all the following experiments is described assuming a pseudo-first order reaction. Then, an approximation of L-H expression can be used [3.8]:

\[ -\frac{d(C)}{dt} = k(C) \]  

Where, k is the pseudo-first order reaction rate constant. Integration of Equation 3.23 leads to:

\[ \frac{ln(C)}{C_0} = -kt \]  

From where the slope of the plot ln (C)/Co vs. t (time of irradiation) renders the reaction rate constant (k).

The reaction apparently followed partial order for low citric acid concentration and zero order for higher citric acid concentration indicating that the role of citric acid for lowering the solution pH, was more pronounced at higher concentrations thereby making the conditions more favourable for total chromium reduction. The zero order kinetics could also be interpreted by assuming a saturation of surface sites by all the organic molecules. However, it was not possible to determine the rate constant due to varying reaction conditions throughout the day. Therefore, the initial rates of reaction were determined for the first two hours of reaction for all the experimental runs given in Fig. 3.13(a) & (b).

Since the rate of reduction was found to varied with the initial concentration of citric acid and H₂O₂, the initial rate (in first 2 hours) determined for total chromium reduction are compared with the increasing concentration. The L-H plots the values of slope (R²) and equation for the trend line with respect to increase in citric acid and H₂O₂ concentrations. A straight line was obtained on plotting the 1/rate versus
Figure 3.13(a): Initial rate of chromium reduction for different ratios of Citric Acid
TiO₂=2g/l, H₂O₂=60ml/l, Citric Acid=Variable

Figure 3.13(b): Initial rate of chromium reduction for different ratios of Citric Acid
TiO₂=2g/l, Citric Acid=60mg/l, H₂O₂=Variable
1/concentration of TiO₂ and citric acid separately, the trend line are depicted on the Fig. 3.14(a). It can be observed that the L-H mechanism was followed with respect to increasing citric acid and H₂O₂ concentrations in the wastewater shown in Fig. 3.14(a)-(f) linearized higher value of correlation coefficient (r² = 0.935, 0.977, 0.785, 0.972 and 0.902 respectively).

3.3.3.8. Effect of UV Irradiance

A comparison of total chromium reduction % under UV light Fig. 3.3(a) & (b) shows that complete total chromium reduction was achieved in 5 hours under 30W/m² UV irradiation, whereas, under UV light, total chromium was reduction completely in 3 hours only depicted in Table 3.5.

Table 3.5: Hourly attained maximum temperature (°C) and UV Irradiance (W/m²) during various experiments

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<table>
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<tr>
<th>UV Irradiance (W/m²)</th>
<th>H₂O₂ Concentration</th>
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</table>
Figure 3.14(a): Langmuir-Hinshelwood plot of chromium reduction at the different ratios of combinations and citric acid:

- $\text{TiO}_2=2\text{g/l}, \text{H}_2\text{O}_2=0\text{ml/l}, \text{Citric Acid}=20\text{mg/l}$

- $y = 3.12x + 2829$
- $R^2 = 0.98$

Figure 3.14(b): Langmuir-Hinshelwood plot of chromium reduction at the different ratios of combinations and citric acid:

- $\text{TiO}_2=2\text{g/l}, \text{H}_2\text{O}_2=0\text{ml/l}, \text{Citric Acid}=\text{Variable}$

- $y = 1779x + 1578$
- $R^2 = 0.955$

Figure 3.14(c): Langmuir-Hinshelwood plot of chromium reduction at the different ratios of combinations and citric acid:

- $\text{TiO}_2=2\text{g/l}, \text{H}_2\text{O}_2=60\text{ml/l}, \text{Citric Acid}=\text{Variable}$

- $y = 1659x + 140.1$
- $R^2 = 0.977$

Figure 3.14(d): Langmuir-Hinshelwood plot of chromium reduction at the different ratios of combinations and $\text{H}_2\text{O}_2$:

- $\text{TiO}_2=0\text{g/l}, \text{Citric Acid}=0\text{mg/l}, \text{H}_2\text{O}_2=\text{Variable}$

- $y = 47470x + 73.18$
- $R^2 = 0.785$

Figure 3.14(e): Langmuir-Hinshelwood plot of chromium reduction at the different ratios of combinations and $\text{H}_2\text{O}_2$:

- $\text{TiO}_2=2\text{g/l}, \text{Citric Acid}=0\text{mg/l}, \text{H}_2\text{O}_2=\text{Variable}$

- $y = 34415x - 92.28$
- $R^2 = 0.972$

Figure 3.14(f): Langmuir-Hinshelwood plot of chromium reduction at the different ratios of combinations and $\text{H}_2\text{O}_2$:

- $\text{TiO}_2=2\text{g/l}, \text{Citric Acid}=60\text{mg/l}, \text{H}_2\text{O}_2=\text{Variable}$

- $y = 8477x + 312.1$
- $R^2 = 0.902$
It has been reported that degradation rate is proportional to light intensity, which confirms the photo-induced nature of the catalytic process activation, with the participation of photo induced electrical charges (electrons and holes) in the reaction mechanism. The optimal light power utilization corresponds to the domain where the degradation rate is proportional to light intensity [3.8].

The corresponding ultraviolet light intensity of $4.488 \times 10^{-6}$ W/cm$^2$ was thereby found to be adequate for the catalyst activation and reduction of Cr(VI). Ku and Jung [3.29], reported similar light intensity to be sufficient for reduction of similar concentrations of total chromium. Another reason for faster reduction could be the availability of more active sites during the initial reaction time, which were occupied later by the deposition of reaction products.

It is reported [3.28] that above a certain value (estimated to be 25W/m$^2$ of UV in laboratory experiments), the reaction rate becomes proportional to the square root of UV intensity. The optimal light power utilization corresponds to the domain where rate is directly proportional to UV intensity. Therefore, the average solar irradiation during winter months with a maximum of about 900 W/m$^2$ in the study area, corresponding to 27 W/m$^2$ of UV, (assuming to be 3% of the total radiation) would also be sufficient for photoreaction.

3.3.3.9. Temperature Change

Most of photoreactions are not sensitive to small variations in temperature. Very few cases have shown Arrhenius dependence during detoxification. The pH of the aqueous solution significantly affects the particle size, the surface charge, and the band edge positions of the TiO$_2$ due to its amphoteric character. The Zero Point Charge (pH$_{zpc}$) or pH at which the surface of an oxide is uncharged, for TiO$_2$ is around 7. Above and below this value, the catalyst is negatively or positively charged according to Eqs.3.24 and 3.25. In consequence the photocatalytic degradation of organic compounds is affected by the pH [3.8].

\[
\text{TiOH}^+ \leftrightarrow \text{TiOH} + H^+ \tag{3.24}
\]

\[
\text{TiOH} \leftrightarrow \text{TiO}^- + H^+ \tag{3.25}
\]
However, at very low temperatures (-40 °C to 0 °C), the activity decreases and Ea becomes positive. This behaviour can be easily explained within the framework of the L-H mechanism, which is the suggested mechanism for photocatalytic reaction. The decrease in temperature favors adsorption, which is a spontaneous exothermic phenomenon. Additionally, the lowering temperature also favours adsorption of final reaction products. Consequently the optimum temperature is generally between 20 and 80 °C [3.28]. The temperature measured in this study was found to vary from 28 °C to as high as 64 °C (Table 3.5) during the first four hours of reaction. This lies in the optimum temperature range of 20 and 80 °C as suggested earlier. So, this system did not require any extra expenditure of a cooling device. Instead, the photocatalytically treated water at high temperature could be used for some thermal applications in the industry.

3.4. Conclusions

The synergism effect described in the work gave an enlightenment to optimize both half reactions of photocatalysis in order to get an efficient pollution treatment and indicated that photocatalytic decontamination can be successfully applied directly to wastewater containing both toxic metal ions and hazardous organic species. It also revealed the possibility of efficient photocatalytic decontamination using UV radiation. The results presented in this study not only described the photo-behavior of multi component complex pollution systems, which were more similar to real environmental situations.

The major conclusions of the study are as follows:

- Of the metals tested for which photocatalytic reduction occurs, all but chromium are deposited in the metallic state onto the photocatalyst. Cr(VI) is only reduced to Cr(III).
- The dark adsorption of total chromium is differ significantly from the reduction trends showing that the adsorption is not the only key factor to secure high photocatalytic reductions.
- The total chromium reduction rates increase in the TiO₂/UV process with the increase of TiO₂ loading, especially up to about 2g/l.
- The deposition of total chromium mg/l for TiO₂ g/l increases with increase reduction is maximum at optimum concentration. The deposition with final pH at the range of 7-8.
• Total chromium reduction results in \( \text{H}_2\text{O}_2/\text{UV} \) process faster than \( \text{TiO}_2/\text{UV} \) process.

• The \( \text{TiO}_2/\text{H}_2\text{O}_2/\text{UV} \) process results in the fastest total chromium reduction. Finally, the degradation efficiency of the \( \text{TiO}_2/\text{oxidant}/\text{UV} \) systems was much greater when \( \text{H}_2\text{O}_2 \) was used as the oxidant.

• Citric acid is not proper chromium reduction with photolytic so the reaction is photocatalytic in nature. The rate of reduction absence of citric acid is very less and is significantly enhanced on addition of citric acid. Citric Acid is an efficient hole scavenger and reduces \( \text{Cr}^{7+} \) completely, in the initial and higher concentration of citric acid is given experimental conditions. A high correlation coefficient (above 0.9) for total chromium and citric acid oxidation is obtained for all experimental runs.

• Finally the combination of \( \text{TiO}_2/\text{Citric Acid}/\text{H}_2\text{O}_2/\text{UV} \) result is observed more efficient than the \( \text{TiO}_2/\text{Citric Acid} \) and \( \text{TiO}_2/\text{H}_2\text{O}_2/\text{UV} \) process in the solutions.

• The L-H plots of total chromium reduction with respect to citric acid shows that linearity increased with increasing concentration (\( R^2 = 0.935 \) and 0.977 for \( \text{TiO}_2/\text{Citric Acid}/\text{UV} \) and \( \text{TiO}_2/\text{Citric Acid}/\text{H}_2\text{O}_2/\text{UV} \) systems).

• The \( \text{H}_2\text{O}_2 \) reaction apparently followed partial order for low concentration and zero order for higher concentration. The L-H plots of chromium reduction with respect to \( \text{H}_2\text{O}_2 \) concentration shows a linear fit (\( R^2 = 0.785, 0.972 \) and 0.902 for \( \text{H}_2\text{O}_2/\text{UV}, \text{TiO}_2/\text{H}_2\text{O}_2/\text{UV} \) and \( \text{TiO}_2/\text{Citric Acid}/\text{H}_2\text{O}_2/\text{UV} \) systems).

• UV Irradiance in the range of 30W/m\(^2\) efficiently reduced total chromium. In the tropical climate like India, the photocatalytic treatment process can therefore be used for 250 to 300 days a year. Additionally, the time of the photocatalytic treatment could be as low as 2 to 4 hours UV exposure.
References


