Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.944222

56 (2015) 1335–1363
October

Taylor & Francis
Taylor & Francis Group

Influence of pH on photocatalytic reduction, adsorption, and deposition of metal ions: speciation modeling

Rajendra Singh Thakur, Rubina Chaudhary*, Chandan Singh

School of Energy and Environmental Studies, Devi Ahilya University, Takshashila Campus, Khandwa Road, Indore, 452001 MP, India, Tel. +91 731 2460309; Fax: +91 731 2467378; emails: rsthakur.sees@gmail.com (R.S. Thakur), rubina_chaudhary@yahoo.com (R. Chaudhary), csingh07_sees@yahoo.com (C. Singh)

Received 4 February 2014; Accepted 8 July 2014

ABSTRACT

The present study is targeted on photocatalytic removal of metal ions from wastewater. Photoreduction, deposition, and dark adsorption of Cr^{6+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} metal ions have been investigated using TiO_2 with UV-irradiated. Also investigated that citric acid as a hole scavenger and hydrogen peroxide as a oxidant at pH values 2, 4, 6–8, and 10. The modeling of metal species has been performed and speciation is used as a tool for discussing the photoreduction and deposition trends. The modeling of metal species at different pH values has been performed. It was observed that the photocatalytic process was effective in removing most of the metal ions in specific reaction circumstances. The maximum reduction and deposition of Cr and Cu^{2+} were found to be favorable at acidic pH 2–4, while Ni^{2+} and Zn^{2+} reductions were found to be most suitable at neutral to alkaline pH 10. The photocatalytic reduction and deposition trend of the metal ions prove the theoretical thermodynamic predictions about a reaction time period (5 h).

Keyword: Photocatalysis; Citric acid; Hydrogen peroxide; Metal ions; PH; Modeling; Speciation; Adsorption; Reduction; Deposition

1. Introduction

There is a great interest in photocatalytic oxidation of contaminants using advanced oxidation processes (AOP) based on photocatalytic oxidation in recent years [1]. AOP like photocatalysis is a potential method among heterogeneous photocatalysis employing semiconductor solids has been applied with success for the oxidation of a variety of organic compounds as well as for the reduction of toxic metals from aqueous solutions contaminants against the problem of environmental pollution [2]. Research work and applications based on AOP in treatment of water have increased considerably during last 25 years. The photocatalytic bleaching was found to be the most promising and efficient process in controlling the environmental pollution, waste water treatment, etc., in which semiconductor particles act as photocatalyst or short-circuited microelectrodes on excitation [3]. To date, the most efficient procedure for the treatment of contaminated water consists of UV light irradiation of suspensions of a semiconductor (TiO_2) in solutions containing the organic and inorganic substrate to be reduced [4].

In the photocatalytic treatment process, the pH is an important parameter for adsorption of metal ions

---

*Corresponding author.

from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent, and the degree of ionization [5]. It not only influences the surface charge properties of TiO_2, but also pollutant adsorbed on the photocatalyst surface, affecting their photoreduction and deposition trends. It is even more relevant as the speciation of some of the metals and metal complexes are changed at different pH values, which thereby change their toxicity. The amount of sludge generated in the wastewater treatment facility is also dependent on pH value. Additionally, the final discharge pH of treated wastewater is regulatory requirement (discharge limit of pH range 6.5–8.5), thereby making it an important parameter for wastewater treatment.

1.1. Photocatalyst at different pH

The pH is a crucial factor for designing a photocatalytic wastewater treatment facility. It not only influences the surface change properties of the photocatalyst used like TiO_2 in the study, but also pollution absorption on the photocatalyst surface. 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, value for TiO_2 is around 7. Above and below this value, the catalyst is negatively or positively charged according to Eqs. (1) and (2). In consequence, the photocatalytic degradation of organic compounds is affected by the pH [6–8].

$$\mathrm{TiOH} \leftrightarrow \mathrm{TiO^-} + \mathrm{H^+} \tag{1}$$

$$\mathrm{TiOH_2} \leftrightarrow \mathrm{TiOH} + \mathrm{H^+} \tag{2}$$

The amphoteric character of TiO_2 is due to the formation of hydroxyl surface groups after the chemisorptions and dissociation of water molecules on the oxide surface [8,9]. Under these conditions, the photocatalytic degradation of the organic and inorganic compounds is affected by it. But the variations are further dependent on the thermodynamic driving force and chemical speciation of these compounds at different pH range. These differences have been observed in the present study, which lead to variations in reduction trends. Another aspect of pH dependence of TiO_2/wastewater interface surface charge is that, it is the determining parameter in the colloidal stability of oxide particle suspensions. This is exemplified in Fig. 1 for TiO_2 Degussa P-25 [6,10]. The zero surface charge yields zero electrostatic surface potentials that cannot produce the interactive rejection necessary to separate the particles within the liquid. This induces a phenomenon of aggregation and TiO_2 clusters become larger.

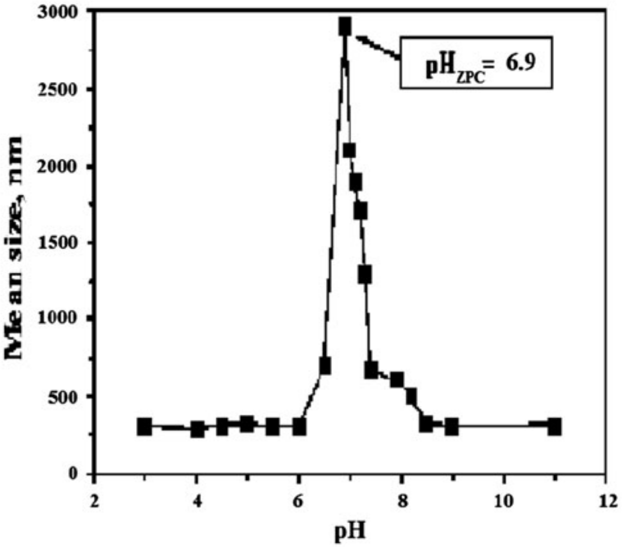


Fig. 1. Mean particle size of TiO_2 (P-25) suspended in water versus pH, (TiO_2 = 0.2 g/L) [6].

1.2. Effect of pH on metal speciation and toxicity

The Cr^{6+} are soluble in water and highly toxic. Under toxic conditions, chromium can exist as bichromate ($HCrO_4^-$) or chromate (CrO_4^{2-}), depending on the pH of the aqueous system. These oxy-anions are readily reduced to trivalent forms when the electron donors (reducing reagents) exist in aqueous solution. The reduction rate increases as the pH decreases. Trivalent chromium (Cr^{3+}) species are very stable with respect to the oxidation reduction potential. They can react with particulates and form metal salts as $Cr(OH)_3$ that are less soluble in water when the pH is 8–10 or higher [11]. Toxicity depends both on the oxidation state and form of a metal and its tendency to form complexes with ligands.

Thermodynamically, the reduction of chromium is favored in the acidic pH range whereas that of Ni^{2+}, Cu^{2+}, and Zn^{2+} are favored in the alkaline pH range. However, another consideration of the treatment efficiency is high in the weakly acidic region, about pH 4–5 reported by a number of authors [12–15]. Therefore, the anionic species of metal ions will be deposited well in the acidic pH range, whereas the cationic species in the alkaline pH range. Additionally, the charge of the photoreduction product formed, would decide whether it remains deposited on the catalyst surface or is desorbed. Chromium reaches its least theoretical chromium solubility of 0.08 at pH of 7.5. If both chromium and nickel are present, a pH value that precipitates both ions must be chosen. It is common to utilize a pH of 9.0–9.5 to precipitate both metals [14,15].

The major objective studied and discussed to ascertain the optimum values that enhance the yields at different pH values of toxic metal species of chromium involve the photocatalytic reduction. The geochemical modeling by the metal speciation at different pH values with the following objectives:

- To determine optimum pH value for dark adsorption, photolytic, and photocatalytic reduction of chromium, copper, nickel, and zinc.
- To determine the speciation of these metals at different pH values.
- To obtain an optimum pH value at minimum catalyst dose and hydrogen peroxide.

2. Experiment

2.1. Materials and methods

The samples were collected from the collection tank of chrome plating industry before entering the treatment cycle. The major wastewater pollutant was chromium. Titanium dioxide (Merck) was used as a photocatalyst. The reduction and oxidation processes for obtaining efficient detoxification of the chromium in the presence and in the absence of a hole scavenger, hydrogen peroxide (H_2O_2), and factors affecting the photocatalytic reaction were studied [16]. H_2O_2 was used as an oxidant and citric acid (Merck) as a hole scavenger for increasing the reaction rate. Besides its low cost and non-toxic nature, the choice of citric acid was made, because it does not form any harmful complexes, which could cause catalyst deactivation unlike aromatic compounds [14,17].

Experiment was carried out at different pH and catalyst dose (2 g/L), which could give complete reduction at optimum pH value. However, this study could only be performed for the metals in which complete reduction was obtained. Therefore, citric acid (60 mg/L) and H_2O_2 (60 mL/L) were used for the work to obtain a minimum catalyst dose at the optimum pH value. NaOH and HCl were used to change the pH of the wastewater.

These aspects were considered during the experimental designing. Fig. 2 shows a schematic diagram of the setup consists of a UV-lamp-box-type reactor made up of wood insulated by thermo-coal sheet having dimensions of 3ft × 3ft × 3ft consisting of two UV lamps inside. Input power of each lamp was 15 W (F15T8/GL/WS, Philips) of wavelength ($k < 380$ nm), fitted in parallel on the back side wall and top of the box. In order to reveal the photocatalytic degradation behavior, the photo-degradation reaction was conducted under ambient condition in a lamp-housing box. The photoreactor and the UV lamps were enclosed in a box to ensure safe operation and to prevent the entrance of extraneous light. Measurement of UV light intensity was done by digital lux meter (DLM2). The measured intensity was approximately 30 W/m^2.

Dark adsorption, photolytic, and photocatalytic reduction experiments were performed at pH values 2, 4, 6–8, and 10. The experimental details are summarized in Table 1.

2.2. Analysis

Batch-type reactor was carried out in six 500-ml capacity conical flasks. The experiments were performed in daytime. Constant stirring of solution had been carried out continuously by using simple magnetic stirrers for proper mixing. Temperature and pH levels were measured using a digital temperature indicator and pH meter (digital pH-systronics model-335). The metal concentration was analyzed using Atomic Absorption Spectrophotometer (Shimadzu AA 6300). To get the deposited chromium on the TiO_2 surface, the final value of total chromium was subtracted from the initial one:

$$\text{Deposition} = \text{TCr}_\text{i}(\text{s}) - \text{TCr}_\text{f}(\text{s}) \tag{3}$$

where $\text{TCr}_\text{i}(\text{s})$ = initial value of total metal, $\text{TCr}_\text{f}(\text{s})$ = final value of total metal.

The photocatalytic reduction percentage and trend were calculated from below equation.

$$\text{Reduction percentage}\,(\%) = \frac{(C_0 - C)}{C_0} \times 100 \tag{4}$$

$$\text{Reduction trend} = \frac{C}{C_0} \tag{5}$$

where C_0 = initial concentration, C = final concentration.

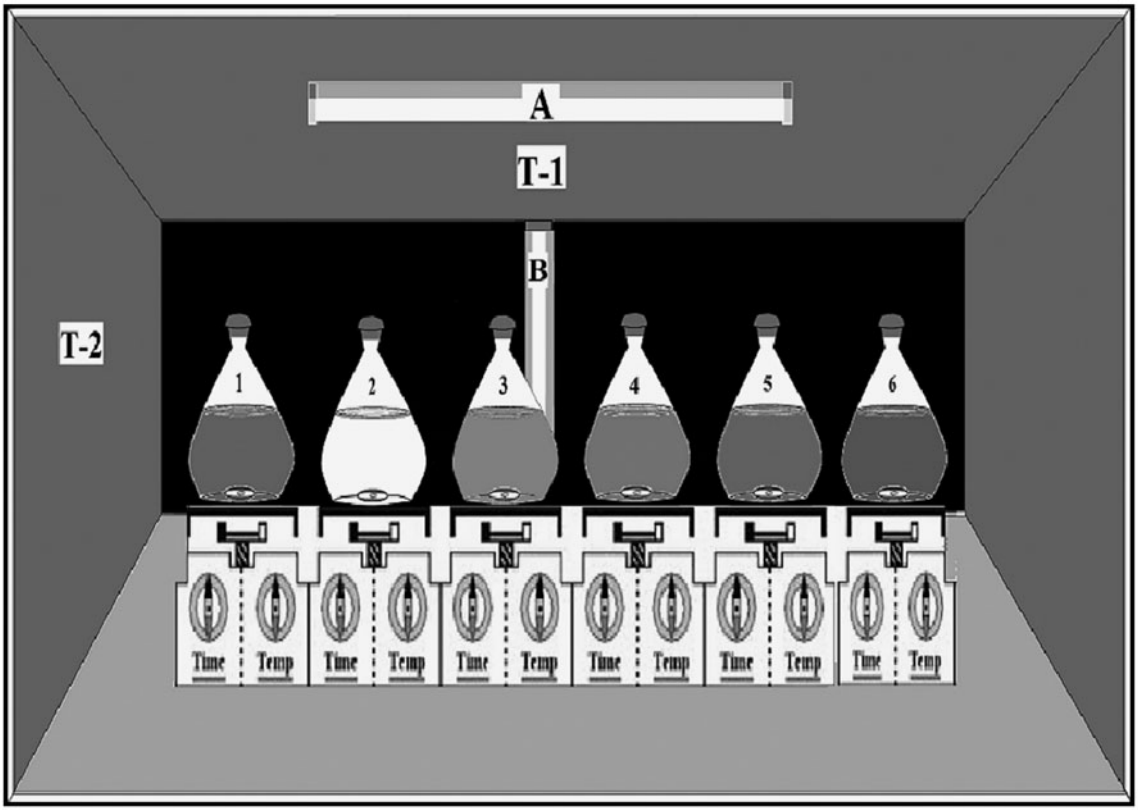


Fig. 2. The apparatus of UV light irradiation. (1) Wastewater without any catalyst, (2) Wastewater with TiO_2 catalyst, (3) Wastewater with H_2O_2 oxidant, (4) Wastewater with TiO_2 catalyst and Citric Acid as hole scavengers, (5) Wastewater with TiO_2 catalyst and H_2O_2 oxidant, and (6) Wastewater with TiO_2 catalyst, H_2O_2 oxidant and Citric Acid as hole scavengers. T-1.Thermometer (settled in center side), T-2. Thermometer (settled in right side). (A) 15 W UV Lamp (settled in centre side on roof in horizontal direction) and (B) 15 W UV Lamp (settled in back side in vertical direction).

Table 1
Details of experiments carried out for various compositions of wastewater constituents and respective metal: catalyst, hole scavenger, oxidant, and different pH values

Experimental study		Testing variables			
	Process	Catalyst: T	Hole scavenger: CA	Oxidant: HP	Variable: pH
Chromium, Copper, Nickel, and Zinc metal ions	Obtain maximum reduction with catalyst and citric acid in absence of H_2O_2 at optimum pH	2 g/L	60 mg/L,	–	2, 4, 6, 7, 8, 10
	Obtain maximum reduction with catalyst and H_2O_2 in absence of citric acid at optimum pH	2 g/L	–	60 mL/L	2, 4, 6, 7, 8, 10
	Obtain maximum reduction with catalyst, citric acid, and H_2O_2 at optimum pH	2 g/L	60 mg/L,	60 mL/L	2, 4, 6, 7, 8, 10

Note: Where T = TiO_2 (Photocatalyst), CA = citric acid (hole scavenger), HP = H_2O_2 (hydrogen peroxide).

2.3. Modeling

Geochemical modeling of metal species was carried out by Visual MINTEQ model to obtain the predominance of various metal species and their percentage of components at different pH values. The modeling results were compared to the experimental results to check the model validity. In the model, the original concentration of metal ions, citric acid and H_2O_2 were incorporated as input values and pH values were fixed to the 2, 4, 6–8, and 10 (pH values at which experiments were performed) separately and the species were determined.

3. Results and discussion

Metal species at different pH values 2, 4, 6–8, and 10 were carried out to observe the influence of pH on reduction in the presence of H_2O_2 and citric acid.

3.1. Influence of pH on chromium speciation

The photocatalytic reduction of chromium is affected by a number of factors: pH of the waste stream is most crucial, due to change in speciation of chromium and nature of photocatalytic surface at different pH values. Different reaction mechanisms under acidic and alkaline conditions for photocatalytic reduction are proposed [18]. The mechanism of photocatalytic chromium reduction was not very clear, but is fairly well described by the capture of photo-excited conduction band electrons followed by reduction, according to Eqs. (6)–(8) depending on the pH [19,20].

In acidic medium,

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \quad E^{\text{o}} = 0.98\,\text{Ev (SHE)} \tag{6}$$

Under neutral medium as follows,

$$Cr_2O_4^{2-} + 8H^+ + 3e^- \longrightarrow Cr^{3+} + 4H_2O \quad E^{\text{o}} = 0.56\,\text{Ev (SHE)} \tag{7}$$

For alkaline solutions,

$$Cr_2O_4^{2-} + 8H_2O + 3e^- \longrightarrow Cr(OH)_3 + 5OH^- \quad E^{\text{o}} = 0.24\,\text{Ev (SHE)} \tag{8}$$

In the absence of reducing agents, H_2O accepts the valence band holes and the following photocatalytic reduction-oxidation cycle takes place (Eq. 9).

$$2H_2O + 2h^+ \longrightarrow H_2O_2 + 2H^+ \tag{9}$$

The most dominant species of chromium below pH 2 is neutral chromic acid molecule H_2CrO_4 and the species $HCrO_4^-$, CrO_4^{2-}, and $Cr_2O_7^{2-}$ are present above pH 2 [21].

It can also be observed from the speciation graph in Fig. 3(a)-(f) obtained by Visual MINTEQ model shows that different species of chromium, H_2O_2, and citric acid. The neutral chromic acid molecule has less affinity for TiO_2 surface, whereas the other anionic species have a strong affinity for TiO_2 surface below pzc, whereas, above the pzc, these species have a lesser affinity for the TiO_2 surface and were not adsorbed.

3.2. Dark adsorption for reduction of chromium

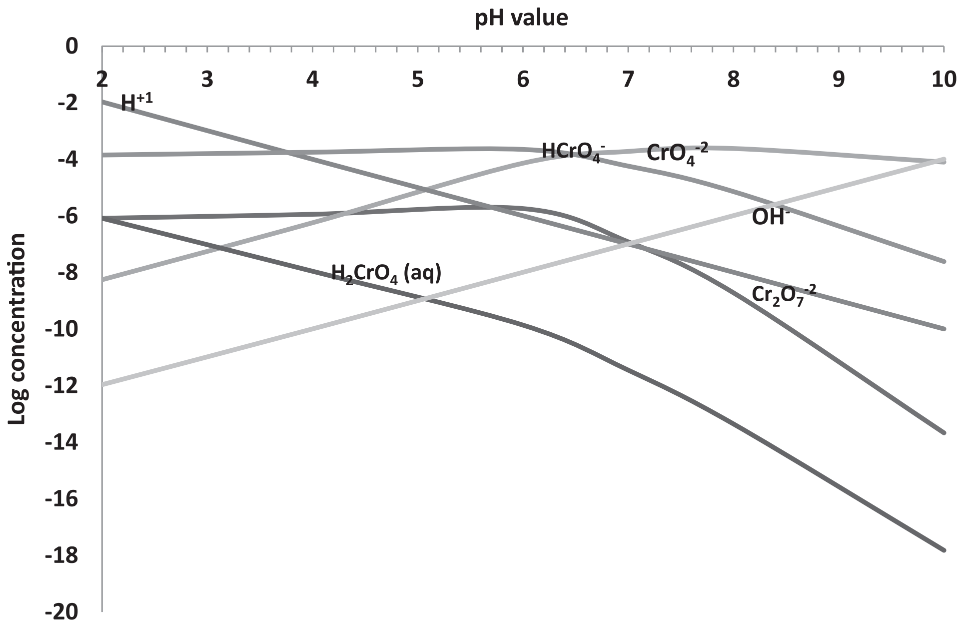
Study of chromium in dark adsorption was performed in the presence of TiO_2 catalyst, citric acid, and H_2O_2. Similarly, this process was used to all the experiments and before an initiation period of 1 h (in dark, i.e. UV light irradiation was started after 1 h). However, the time and experimental conditions of adsorption and photoreduction were identical. The adsorption of chromium in dark was decreased with the increasing in pH (Fig. 4).

The results showed that chromium adsorption decreased on TiO_2 surface in the presence of citric acid and H_2O_2 [14]. TiO_2/UV, H_2O_2/UV, TiO_2/citric acid/UV, TiO_2/H_2O_2/UV, and TiO_2/H_2O_2/citric acid/UV processes were occurred maximum adsorption 69.87, 64.24, 70.84, 67.44, and 68.34%, respectively, at pH 2. At alkaline pH values, a reduction in the solubility of metals may contribute to lower uptake rates [22,23] and reported similar trends of more adsorption at lower pH [24].

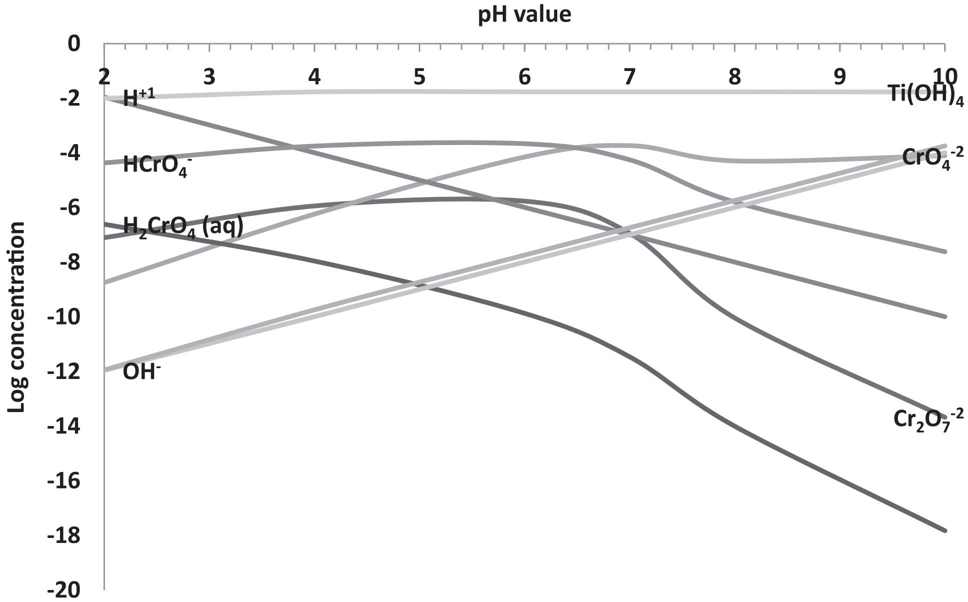
3.2.1. Photolytic interactions of chromium

Photolytic interactions among chromium were carried out in the absence of photocatalyst, citric acid, and H_2O_2. The time dependent behavior of the photolytic reaction when using different filters with irradiation of UV light on the chromium solution under continuous stirring without TiO_2 was carried out in the reactor. In acidic solution, it has a very high positive reduction-oxidation potential, therefore strongly oxidizes and remains unstable in the presence of e-donors.

At pH value 2, 4, and 6, higher concentration of $HCrO_4^-$ species shows 98.29, 98.43, and 74.46% respectively, depicted in Fig. 3(a). At pH value 7, $HCrO_4^-$ with minimum concentration of 23.16% and at pH value 8, 10 were observed to less than 2% concentration. At the lower pH, dominant species of Cr ions in solution have very less concentration of H_2CrO_4 (aq) CrO_4^{2-} and $Cr_2O_7^{2-}$ i.e. Cr^{6+}. These anions would be expected to interact more strongly with the ligands



(a): TiO_2 = 0 g/L, Citric Acid = 0 mg/L, H_2O_2 = 0 mL/L

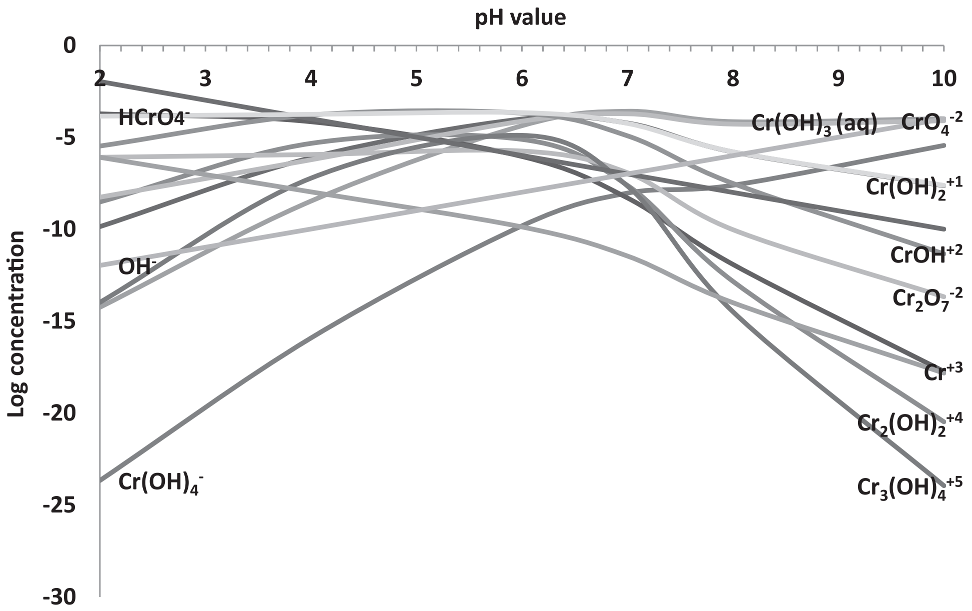


(b): TiO_2 = 2 g/L, Citric Acid = 0 mg/L, H_2O_2 = 0 mL/L

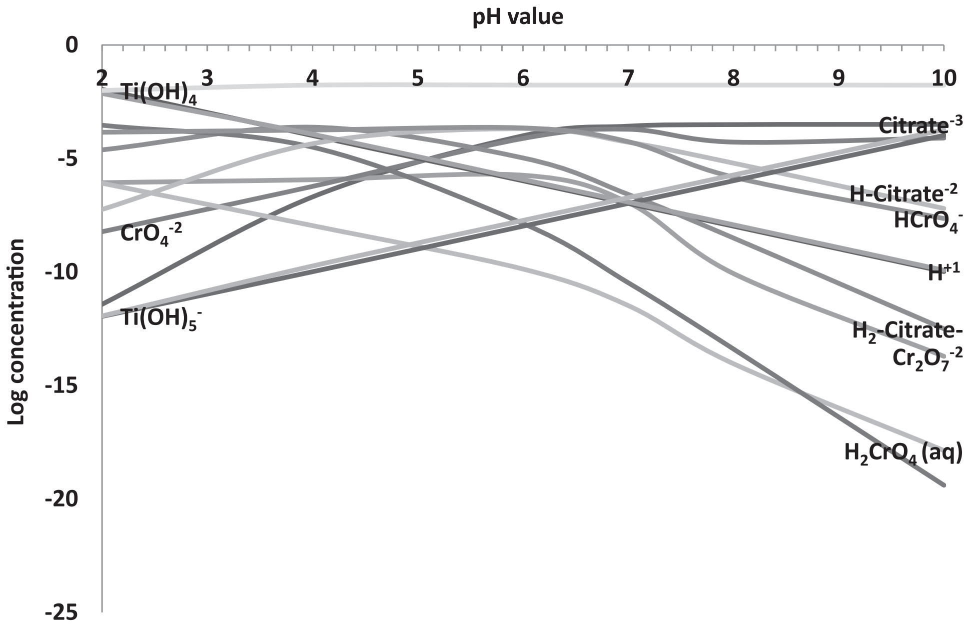
Fig. 3. Speciation of chromium at different pH level determined by "Visual MINTEQ Model": (a) without TiO_2, (b) with TiO_2, (c) with H_2O_2, (d) TiO_2 and citric acid, (e) TiO_2 and H_2O_2, and (f) TiO_2, citric acid, and H_2O_2.

carrying positive charges. Further as well as increase the pH up to 6, 7, 8, 10, the percentage of adsorption were decreased but increases the species concentration of CrO_4^{2-} that were observed 24.34%, 76.75%, 97.08%, 99.96% respectively and $Cr_2O_7^{2-}$ observed 1.20% to less. Because OH^- ions increased the hindrance of diffusion, some of the divalent cations may react with OH^- ion and precipitated and thereby decreased the free metal ions available in the solution. At lower pH, there may be competition between H^+ and Cr^{3+} ions and thus decreased the adsorption capacity for the metal ion [5,14].

The results for chromium reduction for photolytic experiments of chromium with absence of citric acid and H_2O_2 are depicted in Figs. 5 and 6(a). It can be observed that UV reduced maximum 16.4–18.5% at



(c): TiO_2 = 0 g/L, Citric Acid = 0 mg/L, H_2O_2 = 60 mL/L



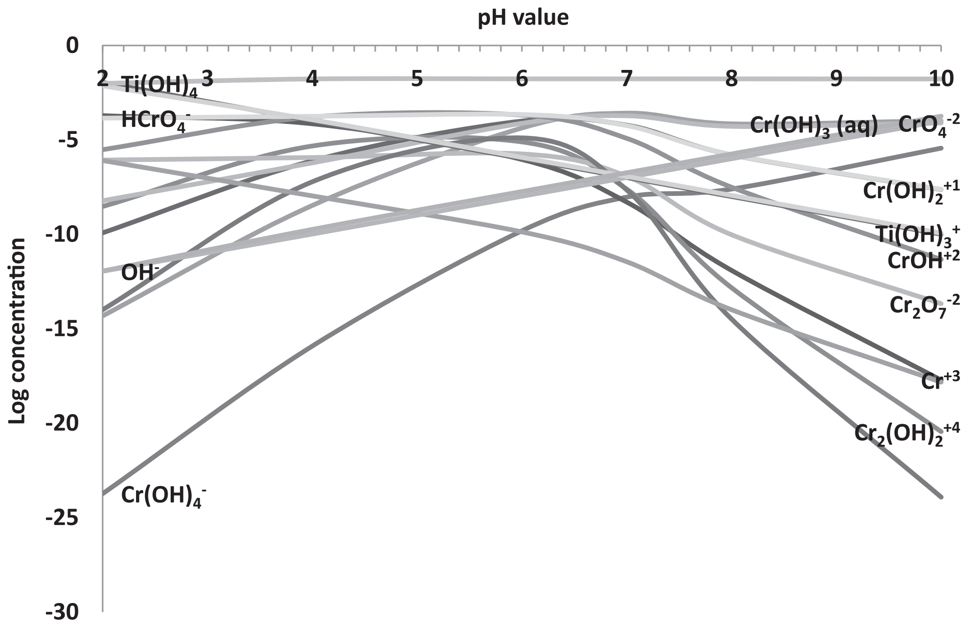
(d): TiO_2 = 2 g/L, Citric Acid = 60 mg/L, H_2O_2 = 0 mL/L

Fig. 3. (*Continued*)

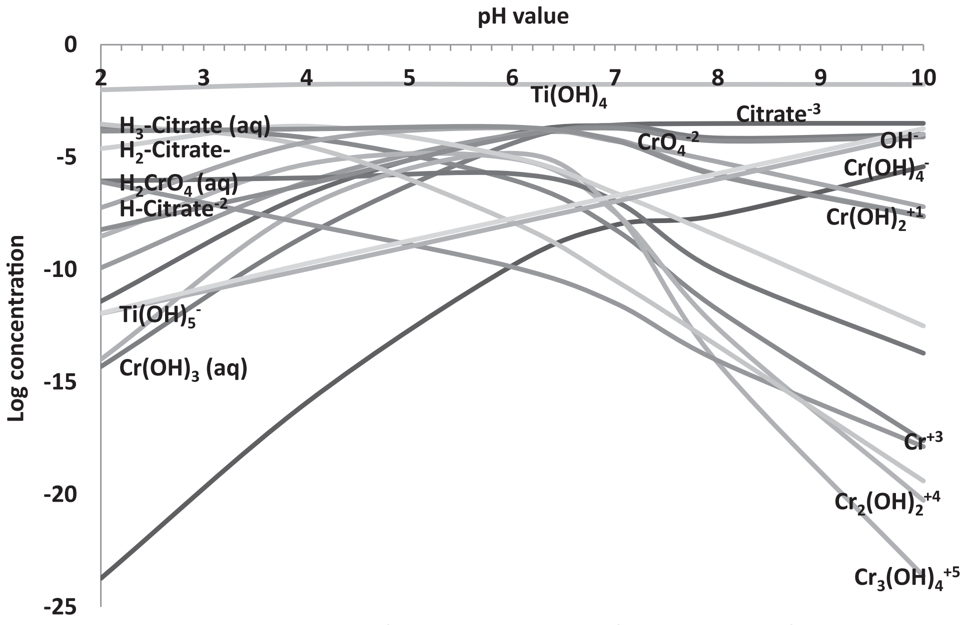
pH 4 and 10. It shows that reaction was found to decline, because less species present in the reaction to occur. In terms of mg/L, chromium deposition was 2.2–3.4% at pH 2 and 4 (Fig. 7).

3.2.2. TiO_2–UV process for reduction of chromium

A decrease in pH has two combined effects and then Ernst reduction-oxidation potential for chromate reduction increases and the positive charge on Titania increases, favoring the adsorption of negatively charged chromate ions by electrostatic attraction. Furthermore, desorption of the product formed (Cr^{3+} species) could be favored by electrostatic repulsion [22]. The surface of TiO_2 has a point of zero charge (pzc) value of 6.2 as reported by a number of authors [6,14,25]. Below this pH, the surface of TiO_2 has a net positive charge, and above this pH, it has a negative



(e): TiO_2 = 2 g/L, Citric Acid = 0 mg/L, H_2O_2 = 60 mL/L



(f): TiO_2 = 2 g/L, Citric Acid = 60 mg/L, H_2O_2 = 60 mL/L

Fig. 3. (*Continued*)

charge. The neutral chromic acid molecule has less affinity for TiO_2 surface, whereas the other species being negatively charged have a strong affinity for TiO_2 surface. Above the pzc, these species have a lesser affinity for the TiO_2 surface and are not adsorbed [24].

The speciation shows $HCrO_4^-$ at pH value 2, 4, and 6 observed higher concentration of 99.06, 98.42, and 74.50%, respectively, depicted in Fig. 3(b). At pH 7, $HCrO_4^-$ with minimum concentration of 23.18% was observed, and at pH 8 and 10 very less 3.02% concentration was observed. The $Ti(OH)_4$ species at pH value 4, 6, 7, 8, and 10 were observed in all the above 99% and at pH 2 57.63%. The $Ti(OH)_{3+}$ species at pH value 2 observed 42.38% and negligible in other pH values. The CrO_4^{-2} species at pH value 7, 8, and 10 observed

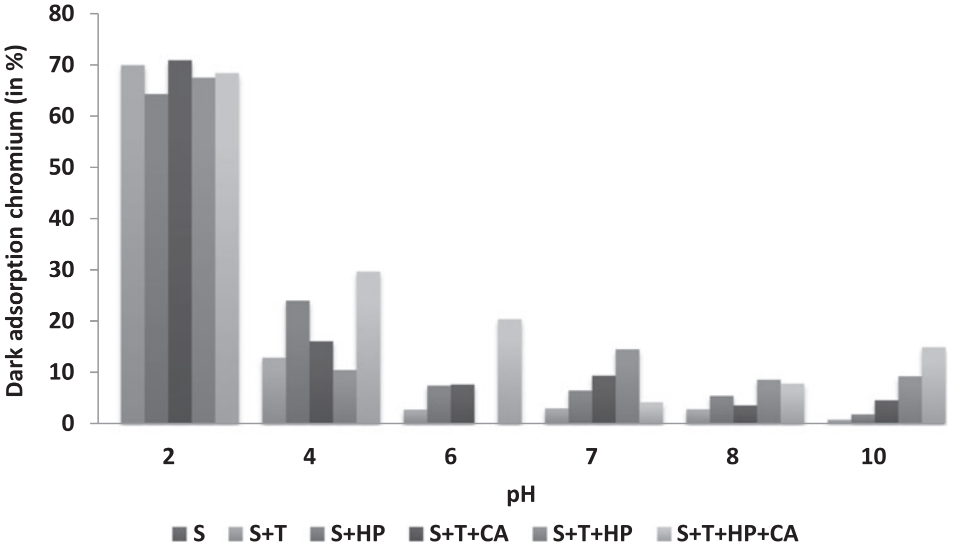


Fig. 4. Dark adsorption of chromium at different pH level ($TiO_2 = 2$ g/L, $H_2O_2 = 60$ mL/L, citric acid = 60 mg/L).

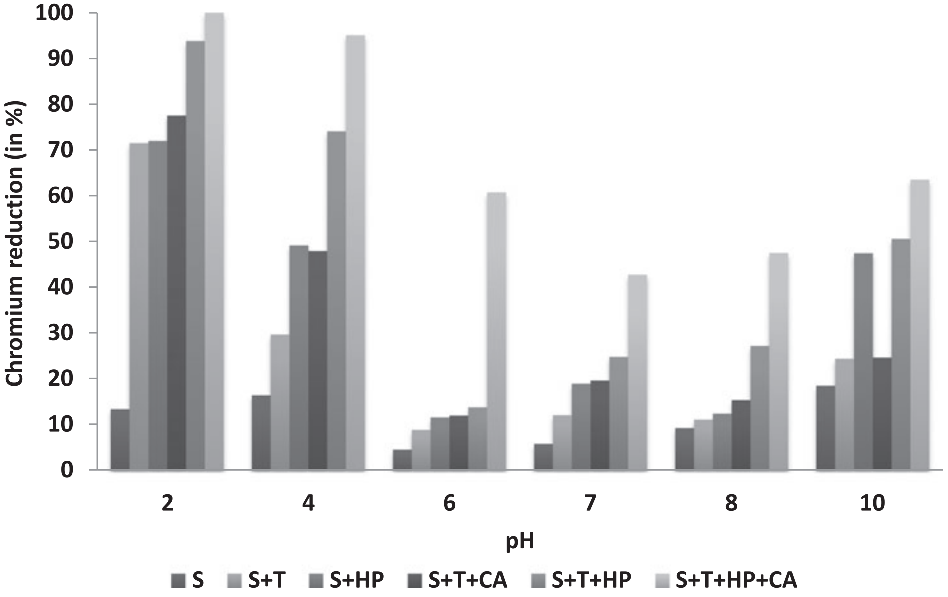
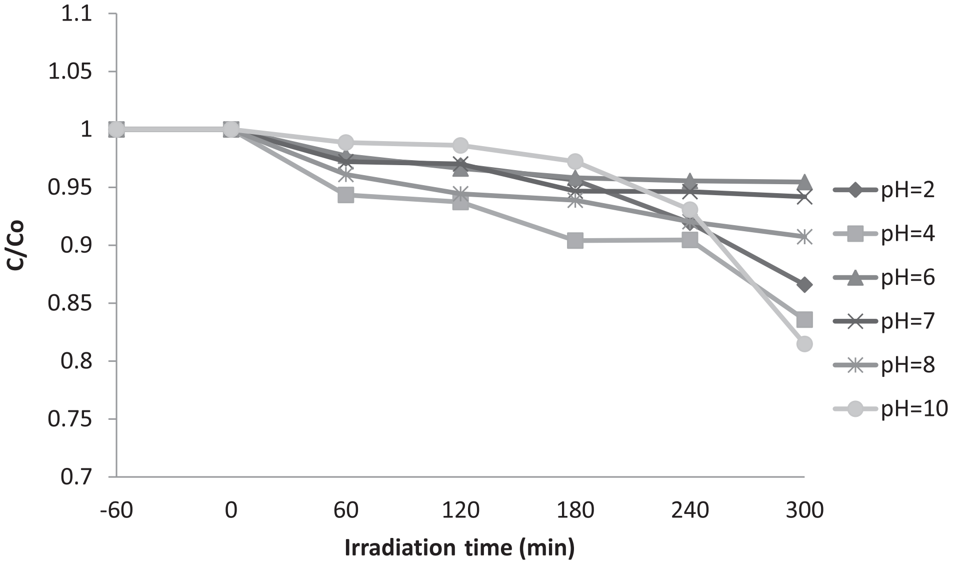


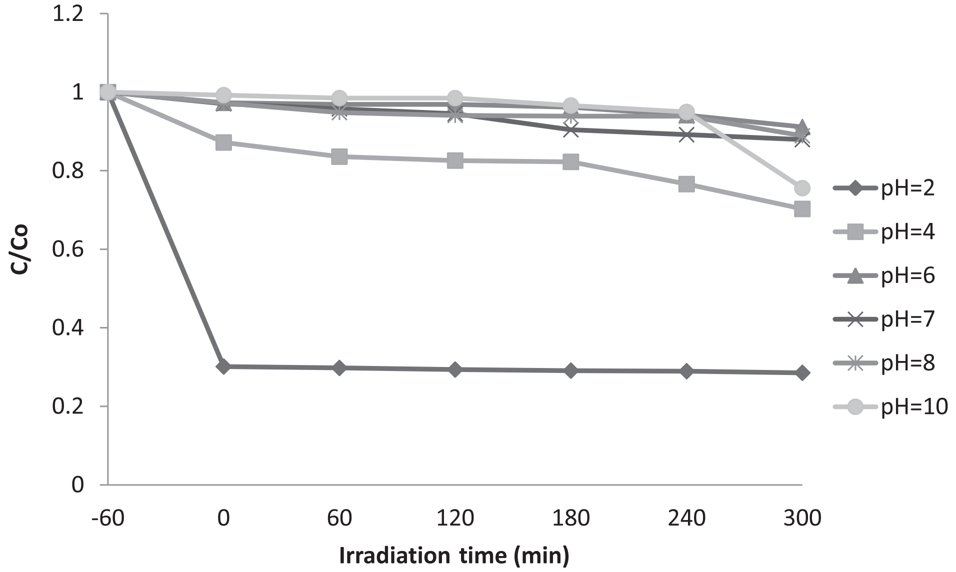
Fig. 5. Percentage reduction of chromium with time at different pH level ($TiO_2 = 2$ g/L, $H_2O_2 = 60$ mL/L, citric acid = 60 mg/L).

76.72, 96.98, and 99.97%, respectively, maximum concentration increases with increasing pH value.

The chromium reduction results during experiments are depicted in Figs. 5 and 6(b). In the presence of TiO_2 at pH 2, 4, and 10, chromium was reduced to 71.4, 29.73, and 24.43%, respectively, due to the presence of $HCrO_4^-$ species. The reaction rate was significantly enhanced after addition of TiO_2. In terms of mg/L chromium, the maximum deposition was 12.0, 6.2, 3.4, and 3.0%, respectively, at pH 2, 4, 7, and 6 (Fig. 7). At pH 7, again half of the reduced chromium was found to be deposited on the TiO_2 surface. However, minimal deposition was seen at pH 8 and 10, showing a prominence of unreduced negatively charged chromium species which were repelled by the negative surface charge, hindering reduction and deposition, even in the presence of significant quantity of reducing agent. It has been observed that the pH of the solution plays an important role in this reaction. An acidic medium is favorable for chromium



(a): TiO_2 = 0 g/L, Citric Acid = 0 mg/L, H_2O_2 = 0 mL/L



(b): TiO_2 = 2 g/L, Citric Acid = 0 mg/L, H_2O_2 = 0 mL/L

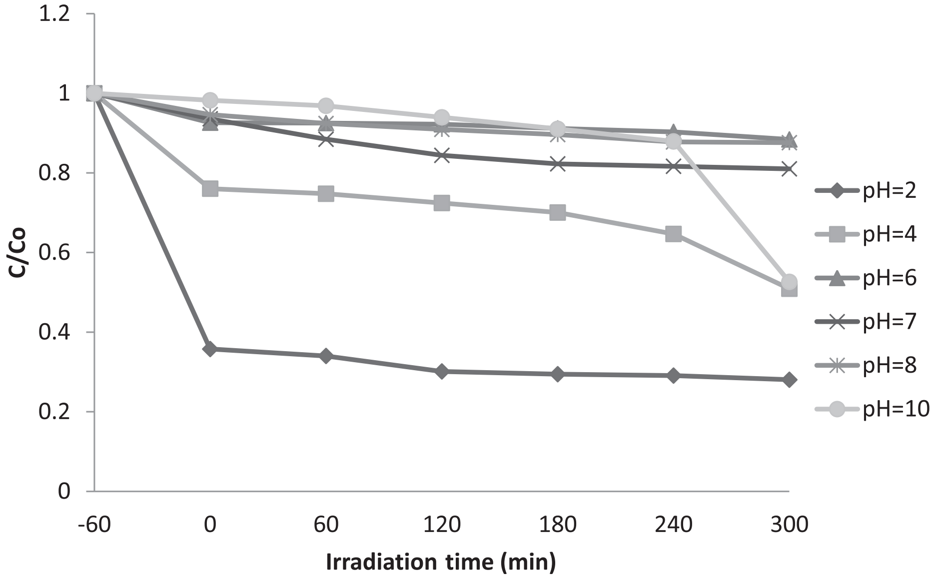
Fig. 6. Reduction trends of chromium with time at different pH level: (a) without TiO_2, (b) with TiO_2, (c) with H_2O_2, (d) TiO_2 and citric acid, (e) TiO_2 and H_2O_2, and (f) TiO_2, citric acid, and H_2O_2.

photocatalytic reduction, where 94% of chromium was photoreduced within 1 h at pH 3 when 2 g/L of TiO_2 was used as the slurry [14,26].

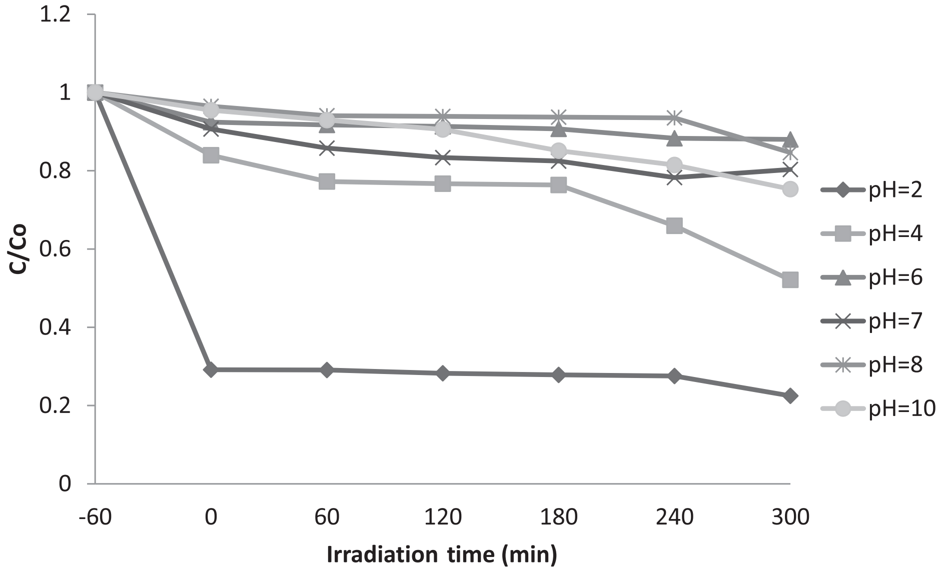
3.2.3. H_2O_2–UV process for reduction of chromium

The addition of H_2O_2 was regarded as a good parameter for the enhancement of photocatalytic degradation process [2]. Light absorbed by a molecule can result in electronic excitation, this makes the excited state more suitable as an oxidizing or reducing agent, which in turn makes it more likely and a highly reactive species such as the hydroxide radical ($OH^{\bullet}$) which can be produced from an electron transfer process between the excited state and contacting medium [14].

In this experiment, the important species observed CrO_4^{2-}, $HCrO_4^-$, and $Cr(OH)_3$ (aq). The CrO_4^{2-} species at pH value 2 and 4 observed less concentration and at pH value 6, 7, 8, and 10 higher concentrations of



(c): TiO_2 = 0 g/L, Citric Acid = 0 mg/L, H_2O_2 = 60 mL/L



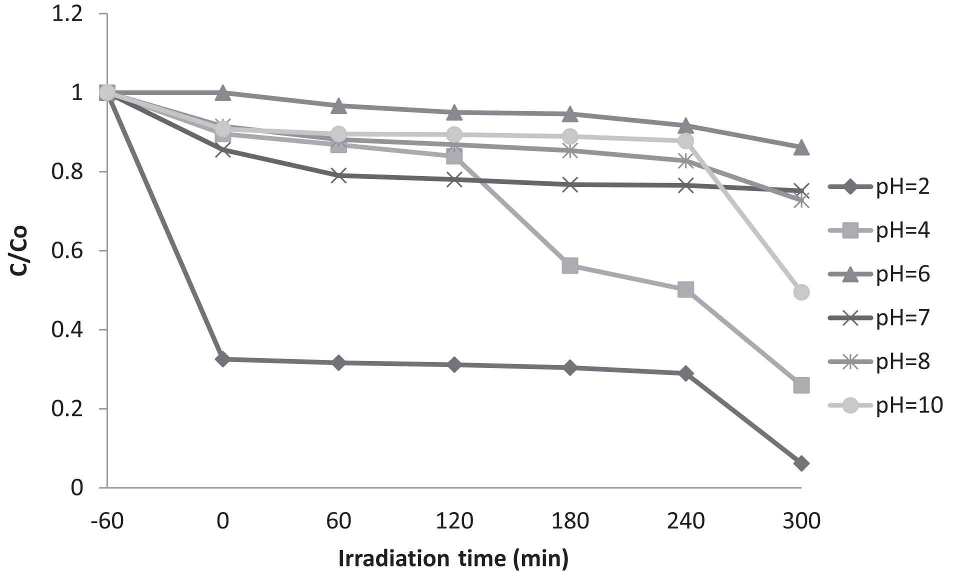
(d): TiO_2 = 2 g/L, Citric Acid = 60 mg/L, H_2O_2 = 0 mL/L

Fig. 6. (*Continued*)

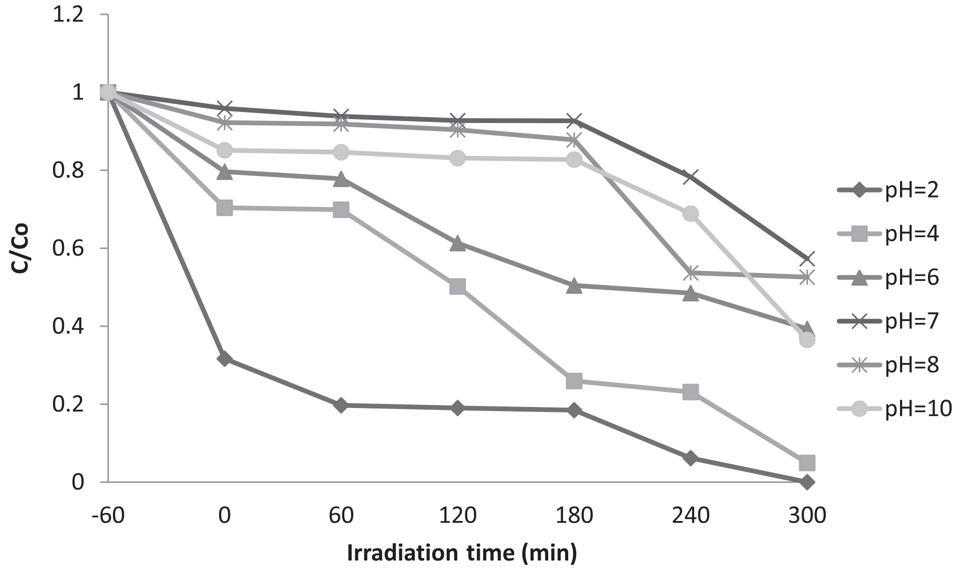
25.25, 76.83, 96.97, and 99.96%, respectively, maximum concentration increases with increasing pH value, depicted in Fig. 3(c). The $HCrO_4^-$ species at pH value 2, 4, and 6 observed 98.28, 98.36, and 73.36% and at pH 7 observed 23.09% and at pH value 8 and 10 observed negligible. The C_r^{3-} species at pH value 2 and 4 observed 98.27 and 29.13%. The $Cr(OH)_3$ (aq) species at pH value 6, 7, 8, and 10 observed 10, 78, 97.7, and 96.58%, respectively.

The chromium reduction was significantly improved by the addition of oxidant [14]. The chromium reduction percentage at pH 2, 4, 6, 7, 8, and 10, were observed 71.95, 49.09, 11.59, 18.98, 12.41, and 47.36%, respectively, depicted in Figs. 5 and 6(c) and the $Cr(OH)_3$ (aq) species shows that reaction was found satisfactory reduction.

In terms of mg/L, chromium deposition was higher and initial pH decreases with the addition of H_2O_2. Fig. 7 shows at pH 2, 4, 6, 7, 8, and 10, the maximum deposition percentage were observed 12.10, 10.34, 4.05, 5.49, 0.78, and 4.39%, respectively, increased due to decrease in pH value.



(e): TiO_2 = 2 g/L, Citric Acid = 0 mg/L, H_2O_2 = 60 mL/L



(f): TiO_2 = 2 g/L, Citric Acid = 60 mg/L, H_2O_2 = 60 mL/L

Fig. 6. (*Continued*)

3.2.4. TiO_2–Citric acid–UV process for reduction of chromium

The beneficial role of the organic additive was quite striking [14]. By the addition of citric acid, the reduction rate was significantly enhanced. The faster degradation can be attributed to minimum electron-hole recombination due to sufficient concentration of hole scavenger. Initially, blank experimental runs were carried out in the absence of citric acid. Thereafter, citric acid was added in the wastewater till a 77.51% reduction of chromium was obtained at pH 2. The percentage of citric acid used with respect to chromium concentration. The relative percentage of chromium in the total quantity of wastewater is also mentioned. Minimal reduction of chromium was obtained in the absence of citric acid.

Fig. 3(d) shows the citrate^{3-} species was found negligible at pH 2 and 4 but at pH 6, 7, 8, and 10 concentrations increased to 31.60, 83.43, 98.03, and 99.98%, respectively. The citric acid as hole scavengers

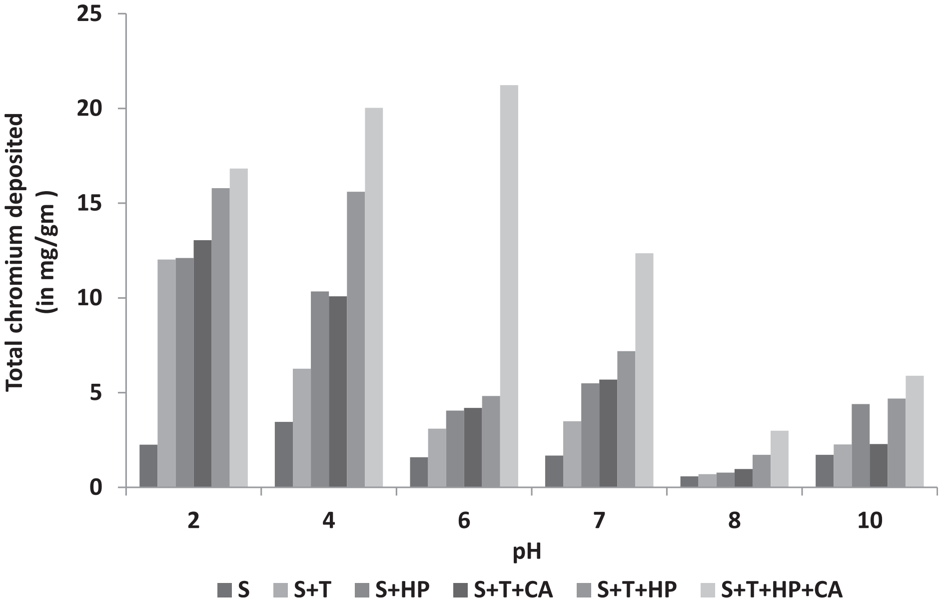


Fig. 7. Milligrams of total chromium deposited per gram of TiO_2 at different pH level ($TiO_2 = 2$ g/L, $H_2O_2 = 60$ mL/L, citric acid = 60 mg/L).

was very beneficial to the experiment, because it generated more complexities as non-hazardous. The H_2-Citrate^{-} species at pH 2 and 4 observed 7.62 and 75.87% only. The H_3-Citrate (aq) species observed maximum at acidic and neutral pH, which at pH 2 and 7 was found to be 92.37% and 16.48%. The H-Citrate^{2-} was observed at pH 4, 6 were observed 14.10% and 65.04% only. The CrO_4^{2-} species was negligible at pH 2 and 4 but at pH 6, 7, 8, and 10 concentrations increased to 25.41, 77.94, 97.23, and 99.97% respectively, which show increase in negative ions as pH increases. Similarly, reverse for the $HCrO_4^{-}$ species that concentration decreases to 98.25%, 98.39%, 73.37%, 21.96%, 2.76%, and 0.02% with increasing pH 2, 4, 6, 7, 8, 10, respectively. The $Cr_2O_7^{2-}$ species observed fewer amounts. The $Ti(OH)_4$ species shows higher concentration at pH 2, 4, 6, 7, 8, and 10 were observed 57.63, 99.32, 99.99, 99.99, 99.98, and 98.92%, respectively.

Figs. 5 and 6(d) show that at pH 4, 6, 7, 8, and 10, the percentages were 47.87, 11.99, 19.67, 15.37, and 24.69%, respectively, observed percentage increases as the pH value decreases. There was a steep decrease in the chromium concentration in the first three hours which contributed a maximum reduction to the UV, TiO_2/UV, and H_2O_2/UV. Citric acid also decreased the solution pH, thereby favoring Cr^{6+} reductions. Almost complete reduction of Cr^{6+} in the presence of citric acid is also reported by Colon et al. [17] at pH 4, however, significant deposition was seen which were expected to be of $Cr(OH)_3$ species.

Fig. 7 shows, in terms of mg/L, chromium deposition was higher at initial pH and decreases with the addition of TiO_2 and citric acid. At pH 2, 4, 6, 7, 8, and 10, the percentage deposition was increased to 13.04, 10.08, 4.19, 5.69, 0.97, and 2.29%, respectively, due to the decrease in pH value.

3.2.5. TiO_2–H_2O_2–UV process for reduction of chromium

In this present study, Figs. 5 and 6(e) show maximum treatment efficiency of chromium reduction with TiO_2 and H_2O_2 concentration, respectively, that is more efficient than the H_2O_2/UV process. As shown, H_2O_2 reacts with conduction band electrons and with superoxide radicals produced between oxygen and electron to generate $OH^{\bullet}$, also, H_2O_2 produces $OH^{\bullet}$ directly by the photolytic split [14,17].

When this experiment started, the reaction generates different types of species. Firstly, it generates the CrO_4^{2-} species was observed negligible at pH 2 and 4, butat pH 6, 7, 8, and 10 its concentrations increased to 25.24, 76.82, 96.97, and 99.97%, respectively, shown in Fig. 3(e). The $HCrO_4^{-}$ species was decreasing to 98.24, 98.35, 73.54, 23.08, 3.02, and 0.03% with increase of pH, 2, 4, 6, 7, 8, and 10, respectively. The $Cr(OH)_2^{1+}$ species at pH 6 and 7 were observed to be 24.62 and

17.99% only. The Cr^{3+} species at pH 2 and 4 were observed 98.42 and 29.24% only. Similarly, the $CrOH^{2+}$ species at pH 4 and 6 were observed 66.44 and 51.07% only. The $Ti(OH)_4$ species generated by the photocatalyst shows maximum of 99.99% at all pH and only pH 2 shows 57.51% only.

At pH 2, 4, 6, 7, 8, and 10, shows the chromium percentage reduction were 93.83, 74.05, 13.80, 24.84, 27.23, and 50.51%, respectively, shows that increased percentage as well as decrease pH depicted in Figs. 5 and 6(e). In terms of mg/L, chromium deposition was higher and decreases initial pH with addition of H_2O_2. Fig. 7 shows at pH 2–10, the deposition percentage were observe 15.79, 15.60, 4.82, 7.18, 1.71, and 4.68%, respectively, was increased due to decrease in pH value.

The same results were also obtained in previous works and it had been reported that photocatalytic oxidation of same organics as well as reduction of few metals is possible by coupling TiO_2 with UV light [27]. In this process, the removal efficiency for chromium at acidic or basic pH was higher than that at neutral pH value. The addition of H_2O_2, in the TiO_2/UV process increased the reduction efficiency for the treatment of heavy metals. Photocatalysis/H_2O_2 processes had been employed for the removal of four metal ions Cr, Cu, Ni, and Zn present in the wastewater [28]. Finally, the degradation efficiency of the TiO_2/oxidant/UV process was much greater when H_2O_2 was used as the oxidant [17].

3.2.6. TiO_2–Citric acid–H_2O_2–UV process for reduction of chromium

The addition of citric acid to the TiO_2/H_2O_2/UV process enhances its photoreduction rate. This may be due to the production of a greater amount of OH radicals in this process compared with the production in other process. At pH 4 the reduction continued till the end of reaction time period but the fastest reduction was achieved in 2–4 h with maximum reduction was achieved only by the end of reaction time period. Fig. 6(f) shows the trends of reduction of chromium were quite different from the adsorption trends for the acidic pH values. The chromium reduced was much higher than the adsorbed at pH 2 and 4. Therefore, lower the pH value, faster would be the reduction of chromium [14]. At the pH 6–8, very less quantities of chromium were found to reduce.

The CrO_4^{2-} species at pH 2 and 4 were negligible, but increases at pH 6, 7, 8, and 10 observed percentage of reduction 25.98, 77.98, 97.23, and 99.97%, respectively, shown in Fig. 3(f). The $HCrO_4^-$ species found higher concentration at lower pH and lower concentration at higher pH shows that at pH 2, 4, 6, 7, 8, and 10 were observed 98.24, 98.34, 72.79, 21.92, 2.76, and 0.02%, respectively. The $Cr(OH)_2^{1+}$ species was observed only 23.60 and 18.25% at pH 6 and 7. The Cr^{3+} species generate at lower pH 2 and 4 were observed only 98.42 and 29.59%. The $Cr(OH)_2^{1+}$ species were found 66.02 and 50.79% at pH 4 and 6. The $Ti(OH)_4$ species, similarly, the photocatalyst at all pH shows 99.99% maximum only while pH 2 shows 57.51% only. The $Citrate^{3-}$ species were negligible at pH 2 and 4, but increased in concentration with increase in pH from 6, 7, 8, and 10 observed 32.74, 83.48, 98.03, and 99.98%, respectively.

The results in Figs. 5 and 6(f) show greatest treatment efficiency of chromium reduction with TiO_2, citric acid and H_2O_2 at pH 2 which was give a complete reduction. At pH 4 to 10 was observed 95.07, 60.69, 42.69, 47.42, and 63.49%, respectively. That was more efficient than the H_2O_2/UV process**.** In terms of mg/L, chromium deposition was higher at initial pH with the addition of TiO_2, citric acid, and H_2O_2. Fig. 7 shows at pH 2, 4, 6, 8, and 10, the deposition percentage were observed 16.82, 20.03, 21.22, 12.35, 2.99, and 5.89%, respectively, which was increased due to decrease pH level.

The color of catalyst was found to change from white to light green after treatment for the samples in which complete reduction of chromium occurred indicating the deposition of Cr^{3+}. The color of wastewater changed from yellow to characteristic light green color of Cr^{3+} after treatment.

The pH was found to increase and decrease by the end of the experiment. This could be due to reduction-oxidation process by TiO_2, citric acid, and H_2O_2 formation of metal hydroxide after the reduction of metals (Cr, Cu, Ni, and Zn). There was an overall increase in about 2 pH units for maximum samples depicted in Table 2.

3.3. Removal of copper, nickel, and zinc at different pH values

Other metals like copper, nickel, and zinc were found in the wastewater in significant quantity. At a pH 6, copper has solubility of 20 mg/L, and at pH 8, the solubility is 0.05 mg/L. Nickel has a similar curve but it occurs at 3 pH. At a pH 8, nickel has solubility of 70 mg/L, and at a pH 10.2, the solubility is 0.1 mg/L. Several metals such as chromium and zinc are amphoteric, being soluble at both alkaline and acidic conditions [25].

On the basis of the reduction potentials of metal ions, one can see in reactions (Eqs.10–12) that

Table 2
Percentage reduction of chromium and corresponding pH change with UV irradiance and maximum temperature attained

pH (initial)	S pH (final)	S+T pH (final)	S+T+CA pH (final)	S+T+HP pH (final)	S+T+CA+HP pH (final)	UV irradiance (W/m^2)	Max. temp. (℃)
pH 2	1.86	1.87	1.84	1.7	1.84	30	42
pH 4	4.03	4.03	3.91	3.46	3.55	30	39
pH 6	8.2	8.06	6.93	7.01	6.12	30	42
pH 7	8.47	8.46	7.6	7.02	6.83	30	47
pH 8	8.52	8.49	8.34	8.35	8.02	30	47
pH 10	9.55	9.57	9.72	9.11	9.05	30	47

Note: Where T = TiO_2 Photocatalyst (2 g/L), CA = Citric Acid (60 mg/L), HP = H_2O_2 (60 mL/L).

photocatalytic reduction of copper, nickel is thermodynamically feasible, whereas Zn^{2+} cannot be photocatalytically reduced to its corresponding zero-valent state because its reduction is more negative than that of photogenerated electrons. Thermodynamically, the driving force for and Ni^{2+} is also extremely low which minimizes their possibility to be reduced under most conditions [29].

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \quad -0.34\,eV \tag{10}$$

$$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s) \quad -0.23\,eV \tag{11}$$

$$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s) \quad -0.76\,eV \tag{12}$$

3.3.1. *Influence of pH on copper speciation*

The speciation prediction of copper in presence of TiO_2 and citric acid shows a predominance of Cu^{2+} ions at higher pH level, showing maximum reduction with citric acid. The formation of Cu-citrate, H_2-Citrate$^-$, H_3-Citrate (aq) species decreased with pH up to 6 and formation of hydroxide of Cu^{2+} begin at lower pH 2 revealed in Fig. 8(a)–(c).

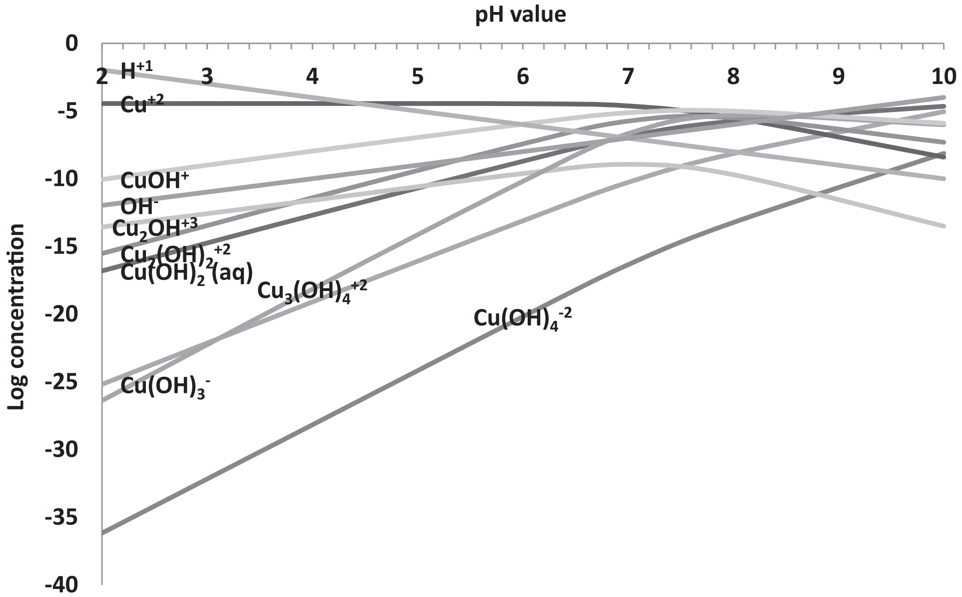
The complexation favored the copper due to reduction in the electron hole recombination due to oxidation of citrate complexes with copper.

3.3.1.1. Dark adsorption of copper. The dark adsorption of copper is depicted in Fig. 9. At pH 4, the maximum adsorption for all experimental sequence of UV, TiO_2/UV, H_2O_2/UV, TiO_2/citric acid/UV, TiO_2/H_2O_2/UV, and TiO_2/H_2O_2/citric acid/UV process were obtained 69.88, 78.69, 81.17, 84.87, 88.75, and 95.81%, respectively. Adsorption of copper was found to increase with decrease in pH level but the overall adsorption values were minimal. The reason for low-adsorption values could be the different species predominating at different pH level. In the acidic range, high adsorption was justified as the Cu^{2+} ions was the dominant species, which was repelled by positively charged TiO_2.

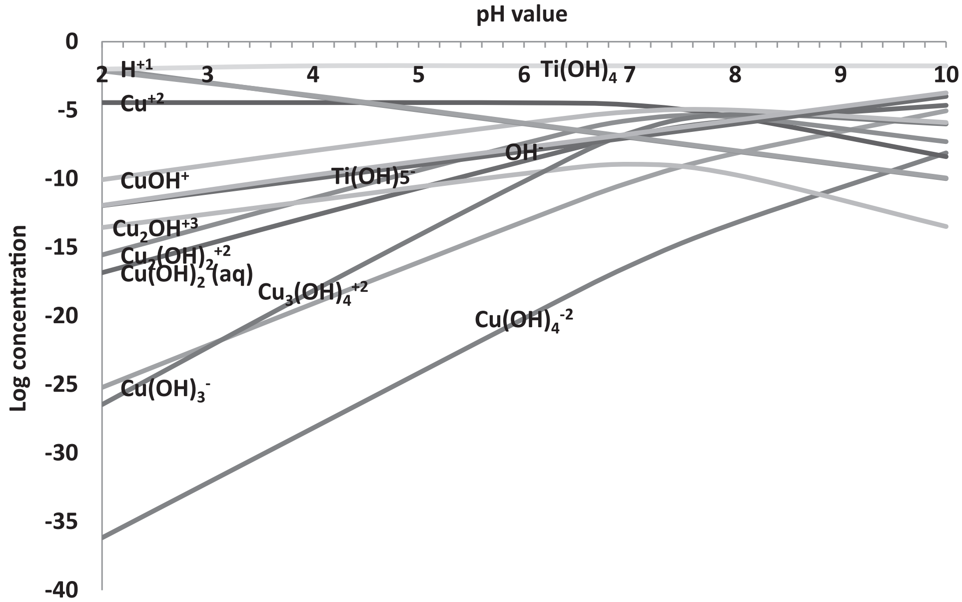
3.3.1.2. Photoreduction and photodeposition of copper. The copper was overall combinations rate of reduction found to be very less at pH 7 and 8. The experimental results for the similar concentrations were described in following subsections of dark adsorption. The Cu^{2+} was not found to reduce or adsorb very significantly at all pH values except for pH 8 where was 28.05% reduction observed (Fig. 10). The rate of reduction of copper was found to be very less due to its low concentrations in the wastewater. The UV, TiO_2/UV, H_2O_2/UV, TiO_2/citric acid/UV, TiO_2/H_2O_2/UV, and TiO_2/H_2O_2/citric acid/UV process were maximum copper reduction at pH 4, the values of reduction increase to 77.82, 80.99, 85.23, 88.23, 94.75, and 99.87%, respectively.

The trend of photodeposition and photoreduction of copper were similar. In terms of mg/L, copper deposition was higher as well as decreases initial pH with used of TiO_2, citric acid and H_2O_2. The UV, TiO_2/UV, H_2O_2/UV, TiO_2/citric acid/UV, TiO_2/H_2O_2/UV, and TiO_2/H_2O_2/citric acid/UV process maximum deposition at pH 4 were observed 1.78, 1.86, 1.95, 2.02, 2.17, and 2.29%, respectively. The copper deposition percentage at pH 2, 4, 6, 7, 8, and 10 were observed 2.19, 2.29, 1.75, 0.94, 0.64, and 1.23%, respectively, which was increased due to decrease in pH level (Fig. 11). The maximum reduction and deposition of copper support sequence at pH 4, 2, and 6.

The removal of copper has been [30] reported in absence of any organic species or in presence of acetate. Wang and Wan [31] have reported the reduction in the presence of methanol. In this study, since the



(a): TiO_2 = 0 g/L, Citric Acid = 0 mg/L, H_2O_2 = 0 mL/L



(b): TiO_2= 2 g/L, Citric Acid = 0 mg/L, H_2O_2 = 0 mL/L

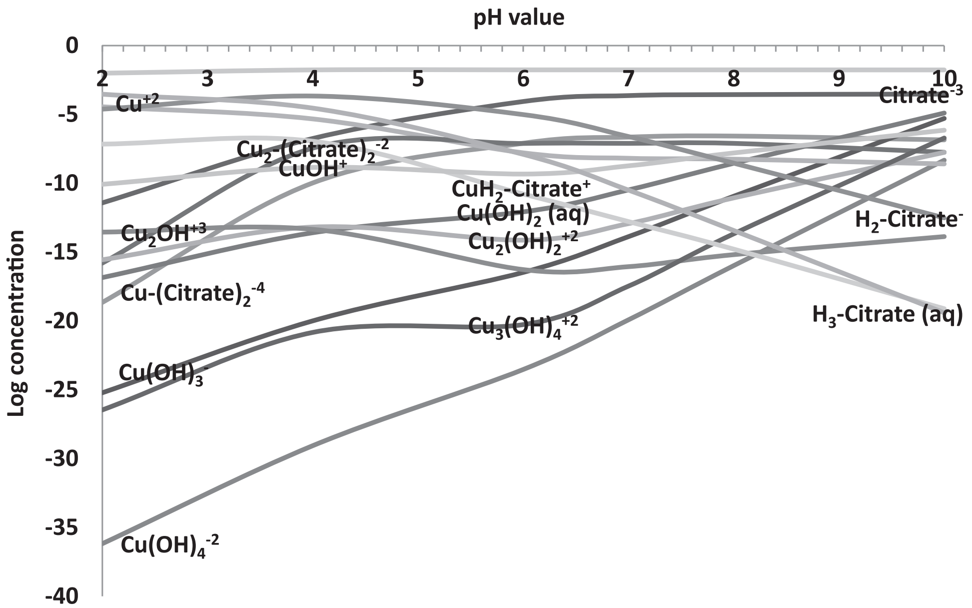
Fig. 8. Speciation of copper at different pH level determined by "Visual MINTEQ Model" (a) without TiO_2, (b) with TiO_2, and (c) TiO_2 and citric acid.

concentration of copper is quite low, the reduction rates were unpredictable.

3.3.2. *Influence of pH on nickel speciation*

The behavior of nickel in terms of speciation was showing no complexation at pH 2 without any dose shown as Fig. 12(a)–(c). The cationic Ni^{2+} was predominant in the alkaline pH 8–10. The complexation with citric acid increased with pH up to 8 but the cationic Ni^{2+} was present even at pH 7 and 8 indicating less complexation. Even at pH 10, the percentage of Ni-Citrate^{-}, NiH_2-Citrate, Ni-$(Citrate)_2^{-4}$, and $Ni(OH)_2$ (aq) species were minimum.

3.3.2.1. Dark adsorption of nickel. The dark adsorption of nickel was found at pH 8 with UV, TiO_2/UV, and H_2O_2/UV process and obtained 76.55, 91.70, and 93.29



(c): TiO_2 = 2 g/L, Citric Acid = 60 mg/L, H_2O_2 = 0 mL/L

Fig. 8. (*Continued*)

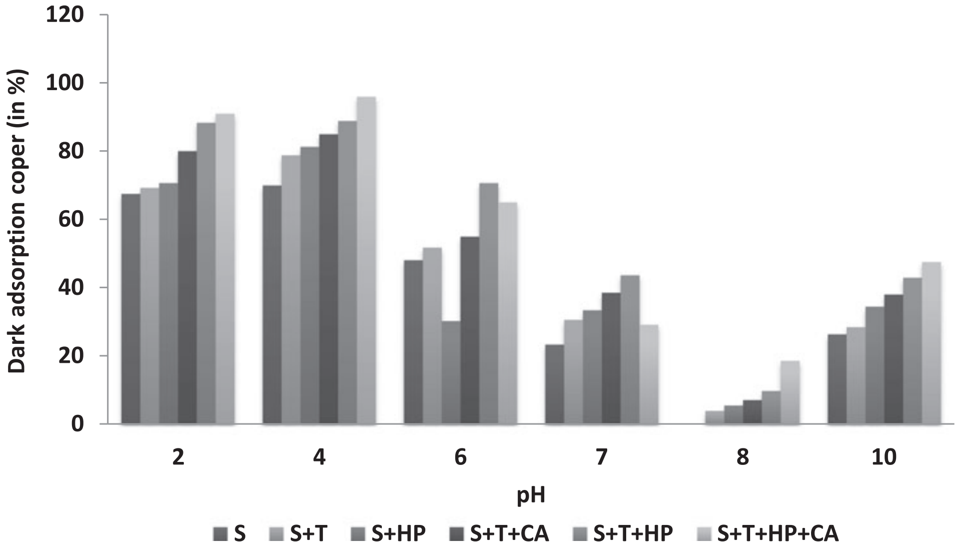


Fig. 9. Dark adsorption of copper at different pH level (TiO_2 = 2 g/L, H_2O_2 = 60 mL/L, citric acid = 60 mg/L).

and at pH 2 with TiO_2/citric acid/UV and TiO_2/H_2O_2/citric acid/UV obtained 91.70%, 91.17% and at pH 10 with TiO_2/H_2O_2/UV process obtained 67.51% (Fig. 13). The maximum dark adsorption with TiO_2/H_2O_2/citric acid/UV combinations were obtained at pH 2, 6, and 4 but other combination with less adsorption.

3.3.2.2. Photoreduction and photodeposition of nickel. Minimal reduction was observed for nickel in the acidic pH range depicted in Fig. 14. However, at pH 10, 8, and 7 significant maximum removals were observed. The maximum complete reduction was favored more in the alkaline and neutral pH range. The reason for this could be the surface characteristics of the catalyst. TiO_2 surface has a more negative charge in the alkaline pH range, thereby having an affinity for the positively charged nickel ion.

The lesser reduction rates can be attributed to the low-thermodynamic driving force for nickel due to its

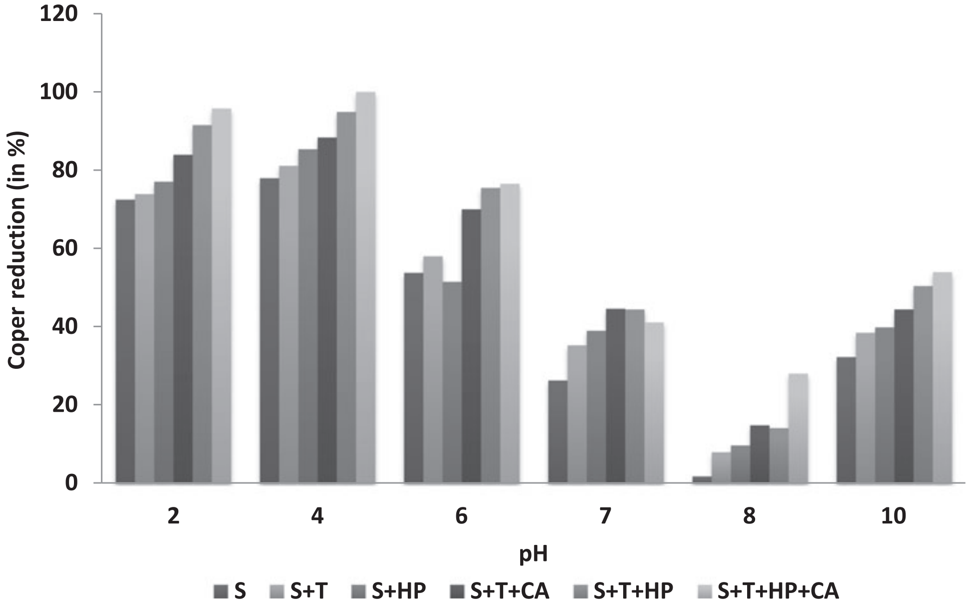


Fig. 10. Percentage reduction of copper at different pH level ($TiO_2 = 2$ g/L, $H_2O_2 = 60$ mL/L, citric acid = 60 mg/L).

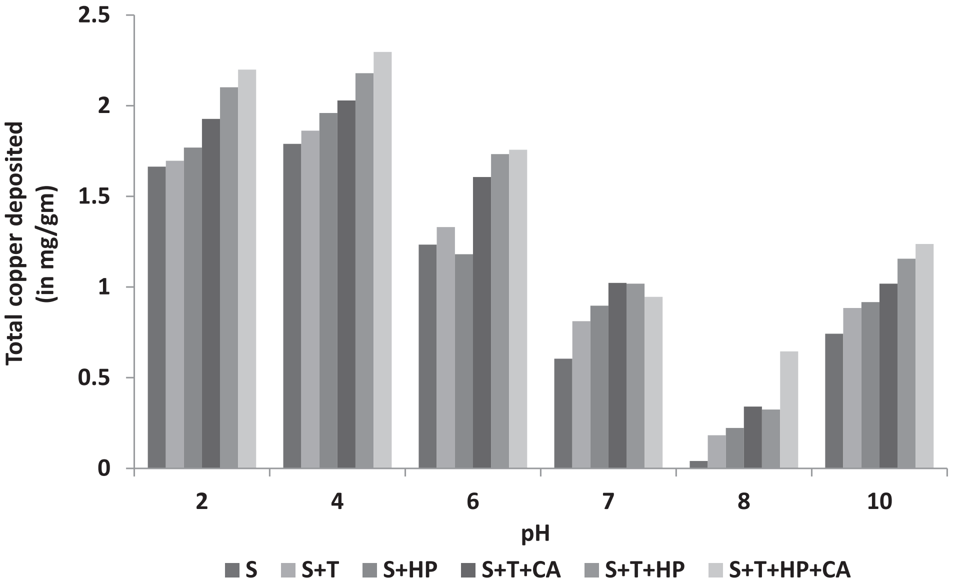


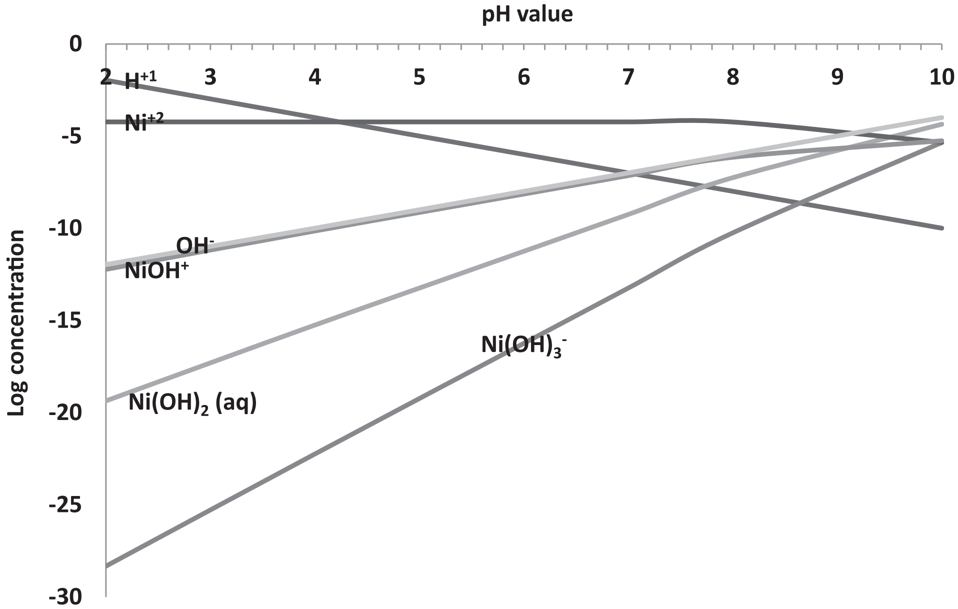
Fig. 11. Milligrams of total copper deposited per gram of TiO_2 at different pH level ($TiO_2 = 2$ g/L, $H_2O_2 = 60$ mL/L, citric acid = 60 mg/L).

lower reduction potential. The all combinations show complete removal percentage. For nickel, the removal obtained was very less concentration; in the absence of citric acid, no removal was observed. In the presence of citric acid, nearly similar reduction was observed for all concentrations of citric acid and H_2O_2. On the basis of thermodynamic considerations, Chen and Ray [32] suggested that the reduction would be favorable in the alkaline pH range. Since the pH value was lower in these reactions due to the high concentrations of citric acid in the wastewater, the reduction was not favorable. The pH studies carried out further ensured that the reduction was likely to occur more in the alkaline pH range.

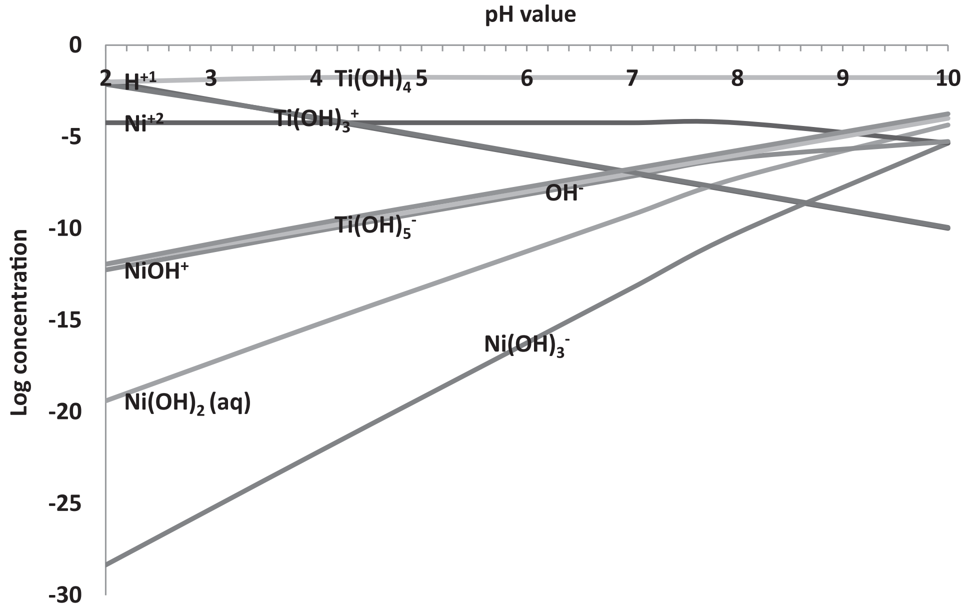
The photodeposition values were found to increase with increase in pH values but that was similar to the reduction values. The combinations show complete deposition. As expected, TiO_2, H_2O_2, and citric acid, no more photodeposition at pH 2, 4, and 6 were observed (Fig. 15). Low-adsorption values and lesser thermodynamic force were the probable reasons for this. The trend of nickel deposition showed increasing percentage with pH but the overall deposition of nickel on TiO_2 was very less.

3.3.3. Influence of pH on zinc speciation

The speciation of zinc in presence of citric acid is depicted in Fig. 16(a)–(c) and the percentages of species at different pH values were mentioned. Formation

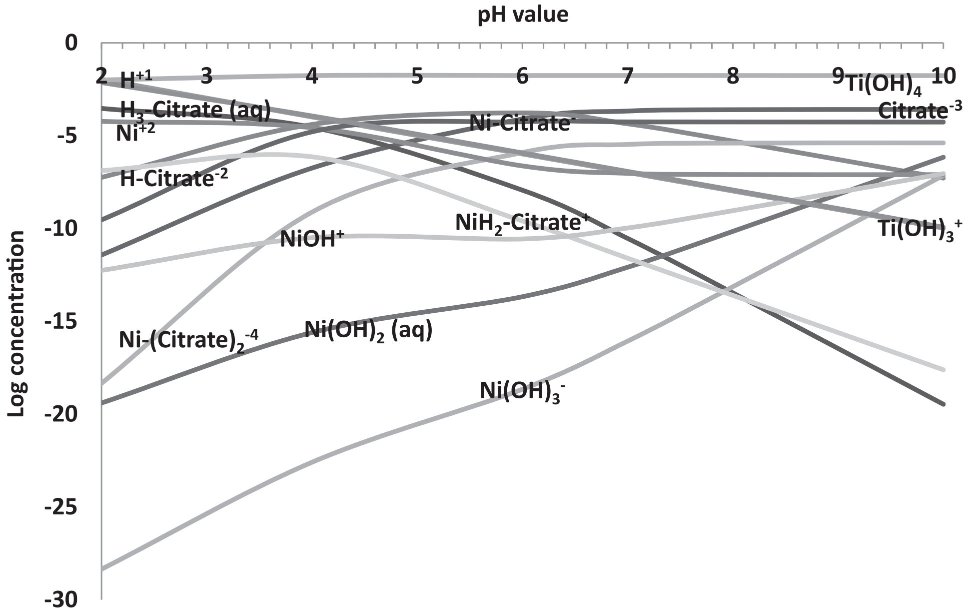


(a): TiO_2 = 0 g/L, Citric Acid = 0 mg/L, H_2O_2 = 0 mL/L



(b): TiO_2 = 2 g/L, Citric Acid = 0 mg/L, H_2O_2 = 0 mL/L

Fig. 12. Speciation of nickel at different pH level determined by "Visual MINTEQ Model" (a) without TiO_2, (b) with TiO_2, and (c) TiO_2 and citric acid.



(c): TiO_2 = 2 g/L, Citric Acid = 60 mg/L, H_2O_2 = 0 mL/L

Fig. 12. (*Continued*)

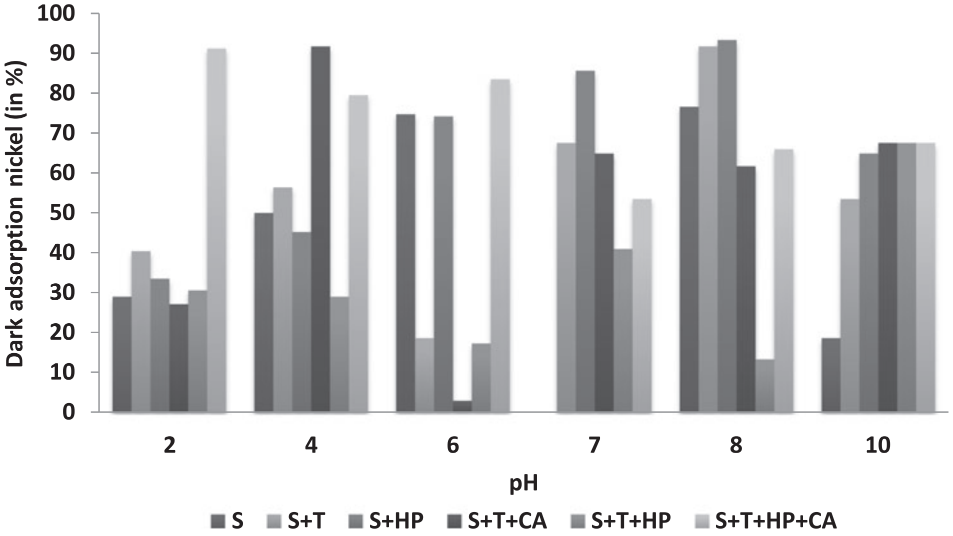


Fig. 13. Dark adsorption of nickel at different pH level (TiO_2 = 2 g/L, H_2O_2 = 60 mL/L, citric acid = 60 mg/L).

of Zn-Citrate$^-$, $Zn(OH)_2$ (aq), Zn-(Citrate)$_2^{4-}$, Zn $(OH)_3^-$, $Zn(OH)_4^{2-}$ were very less at pH 6, 7, and 8. Further at pH 10, the complexation was very less and the hydroxides of Zn^{2+} predominate. The high proclivity of Zn-citrate and neutral $Zn(OH)_2$ was the reason for the high-adsorption values.

3.3.3.1. *Dark adsorption of zinc.* The results of dark adsorption for zinc are depicted in Fig. 17. This adsorption was due to the anionic Zn-citrate adsorption on TiO_2 surface due to attraction of opposite charges. The zinc metal was complete adsorbed at pH 7, TiO_2 and H_2O_2 combinations as the surface

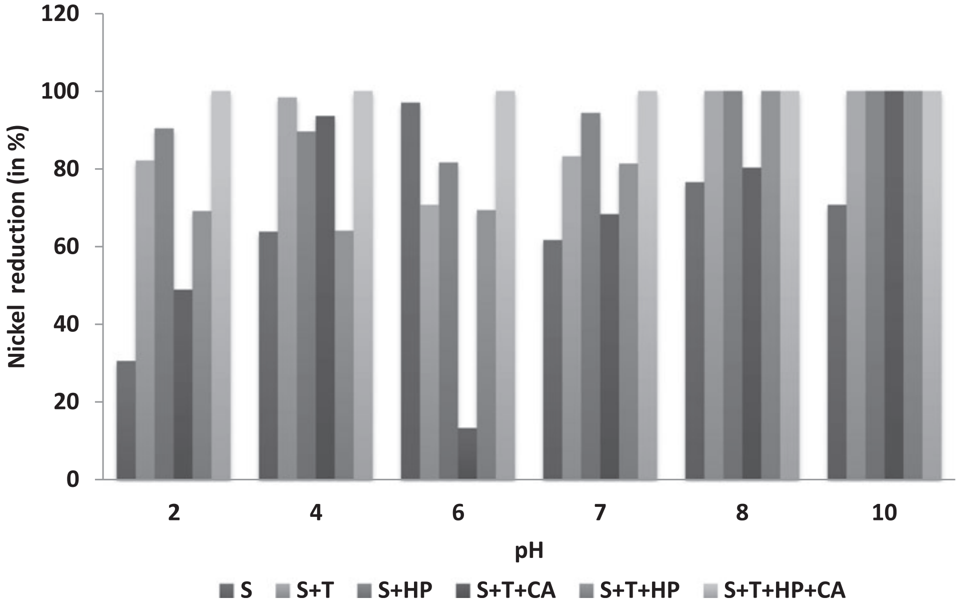


Fig. 14. Percentage reduction of nickel at different pH level ($TiO_2 = 2$ g/L, $H_2O_2 = 60$ mL/L, citric acid = 60 mg/L).

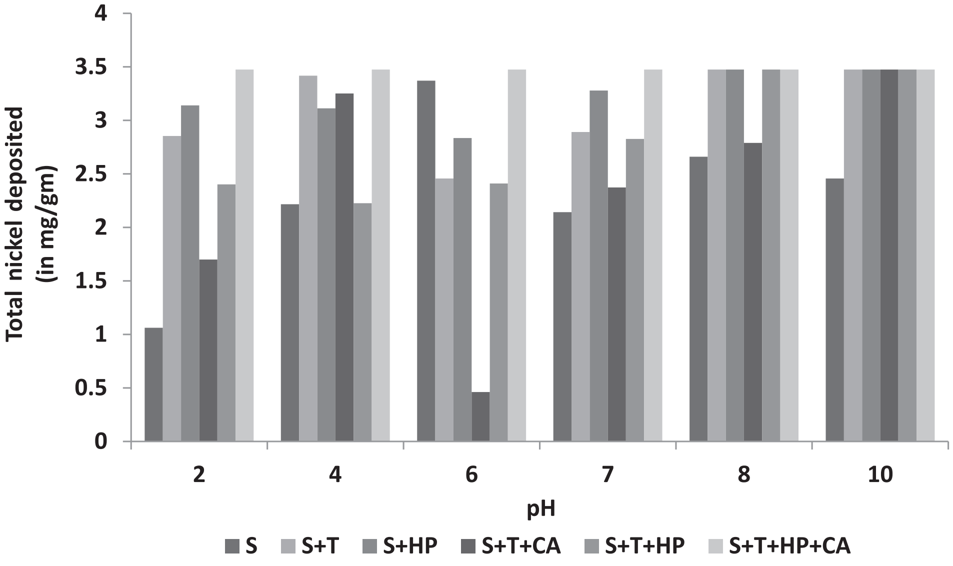


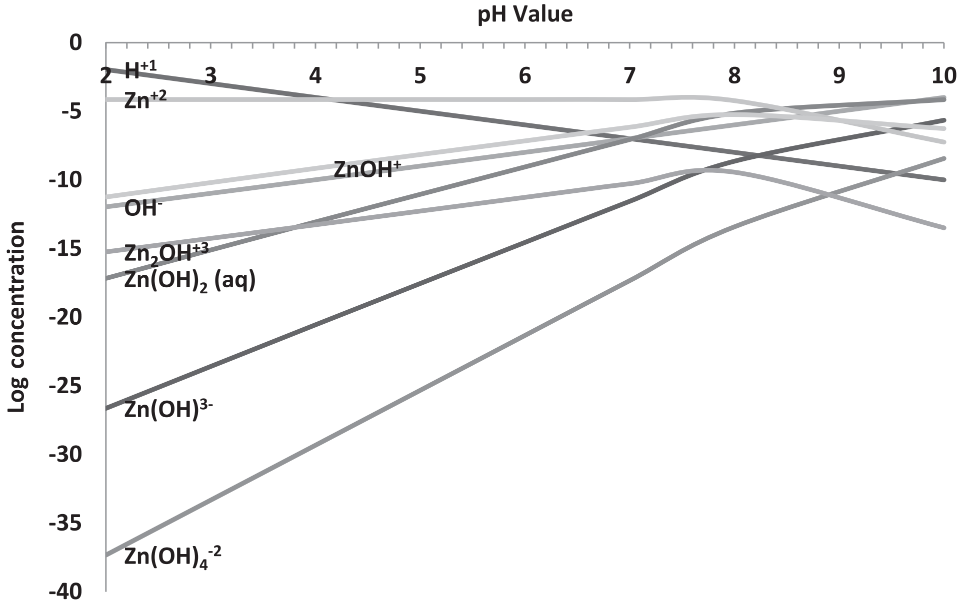
Fig. 15. Milligrams of total nickel deposited per gram of TiO_2 at different pH level ($TiO_2 = 2$ g/L, $H_2O_2 = 60$ mL/L, citric acid = 60 mg/L).

charge of TiO_2 was negative. At pH 8, with H_2O_2/UV and TiO_2/citric acid significant increase to couplet adsorbed was seen and at pH 10 with H_2O_2/UV and TiO_2/H_2O_2/citric acid/UV of zinc was adsorbed.

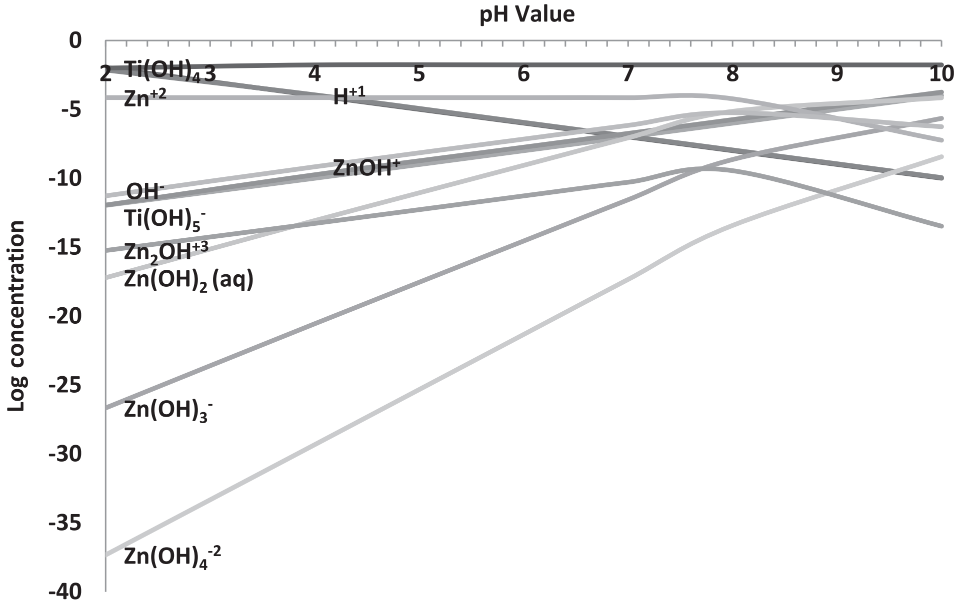
3.3.3.2. Photoreduction and photodeposition of zinc. The maximum reduction of zinc was observed at the neutral pH range and found to increase with the increase in pH level. Insignificant removal was observed at pH 2 and 4. The complete reduction was obtained at pH 7, 8, and 10 (Fig. 18). The removal condition of zinc was quite similar to that of nickel.

Fig. 19 shows the deposition at pH 7 was complete at all combination, similar to increased at pH 8 to H_2O_2/UV, TiO_2/citric acid/ UV, and TiO_2/citric acid/H_2O_2/UV were complete deposition. At pH 10 with H_2O_2/UV, TiO_2/ H_2O_2/ UV, and TiO_2/citric acid/H_2O_2/UV were complete deposition. These values were quite similar to the adsorption indicating that the deposition of zinc was possibly not reductive but only due to adsorption.

Nearly, same percentage of metal was photodeposited and photoreduced. No more reduction was observed for lower pH of citric acid and H_2O_2. Zinc was found to reduce more in the samples which show complete reduction at pH 7, 8, and 10. Meshkov et al. [33] were also not observed the deposition, adsorption, and photoreduction. The lower values of deposition as compared to adsorption further indicate that some of the zinc was desorbed due to weaker surface bonding.



(a): TiO_2 = 0 g/L, Citric Acid = 0 mg/L, H_2O_2 = 0 mL/L



(b): TiO_2 = 2 g/L, Citric Acid = 0 mg/L, H_2O_2 = 0 mL/L

Fig. 16. Speciation of zinc at different pH level determined by "Visual MINTEQ Model" (a) without TiO_2, (b) with TiO_2, (c) TiO_2 and citric acid.

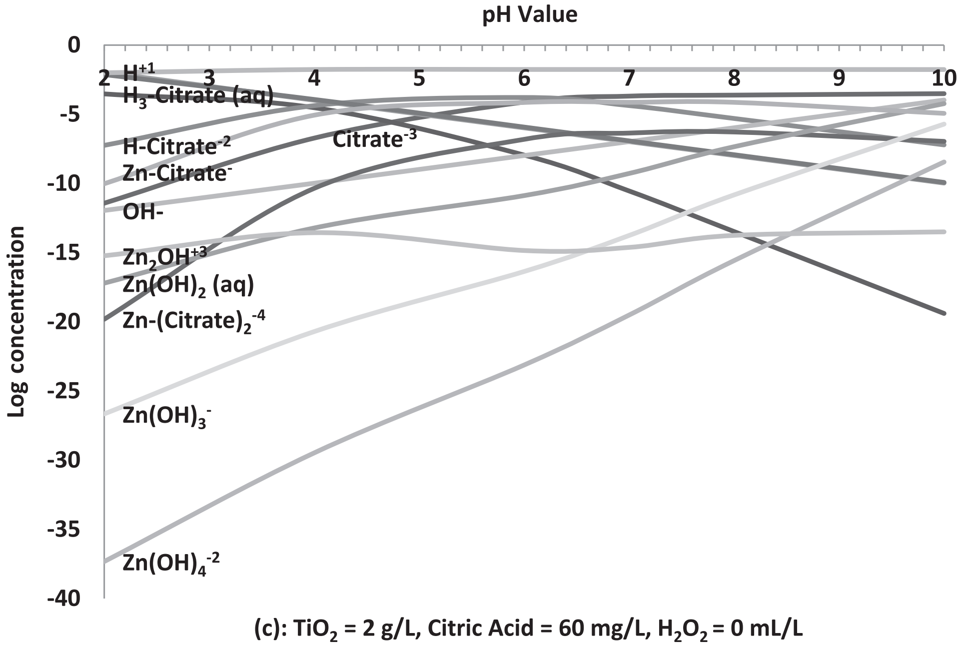


Fig. 16. (*Continued*)

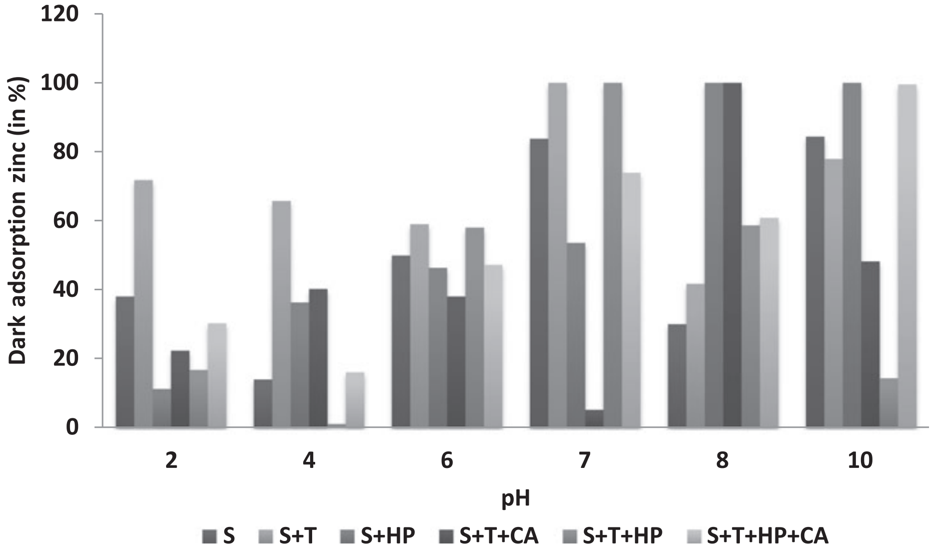


Fig. 17. Dark adsorption of zinc at different pH level ($TiO_2 = 2$ g/L, $H_2O_2 = 60$ mL/L, citric acid = 60 mg/L).

4. Kinetic analysis of photocatalytic reduction of all metal ions

According to the Langmuir–Hinshelwood kinetics model (Eq. 13 and 14) confirming the heterogeneous catalytic character of the system with the rate "r" varying proportionally with the surface coverage θ as [7,14]:

$$r = k\theta = \frac{k(KC)}{1 + KC} \tag{13}$$

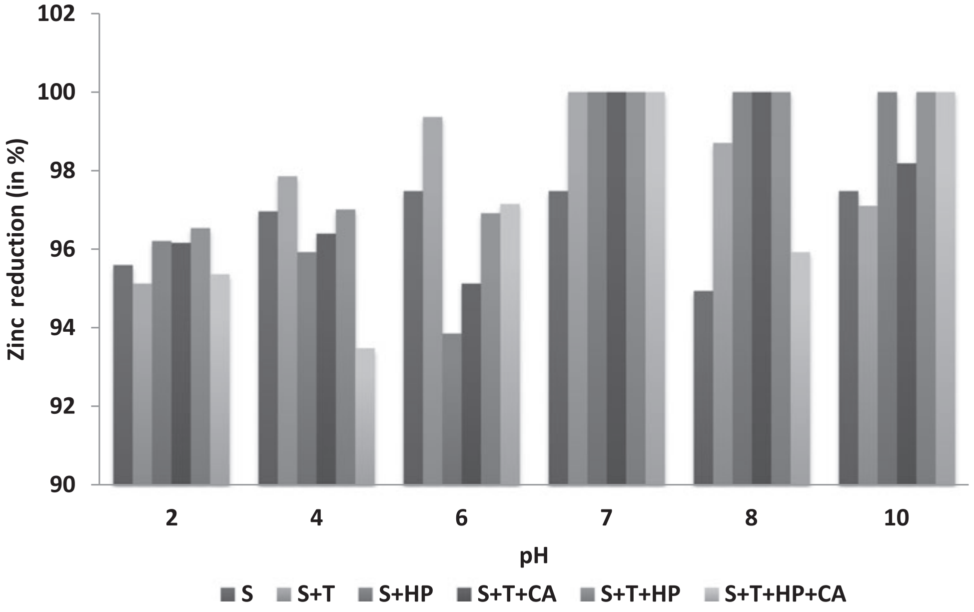


Fig. 18. Percentage reduction of zinc at different pH level ($TiO_2 = 2$ g/L, $H_2O_2 = 60$ mL/L, citric acid = 60 mg/L).

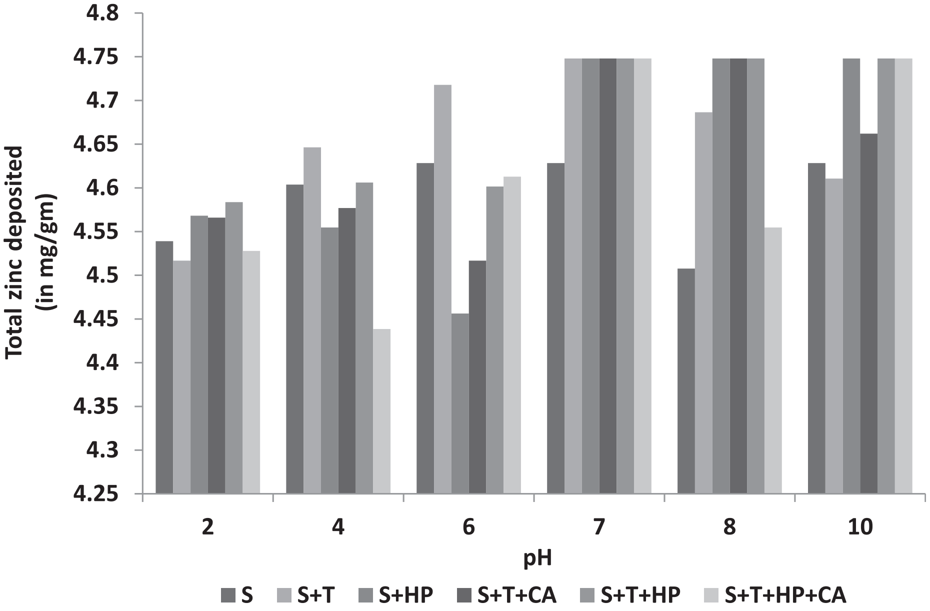
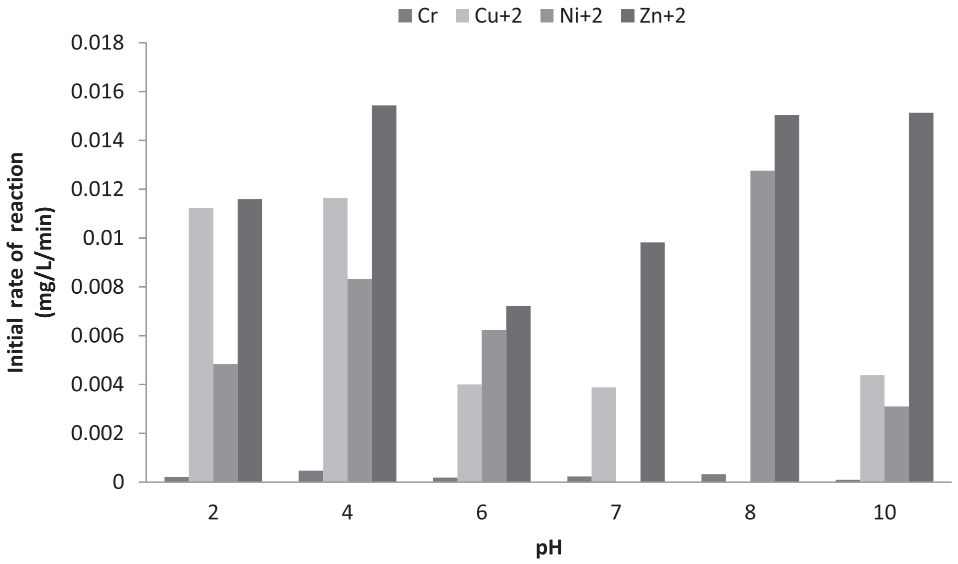


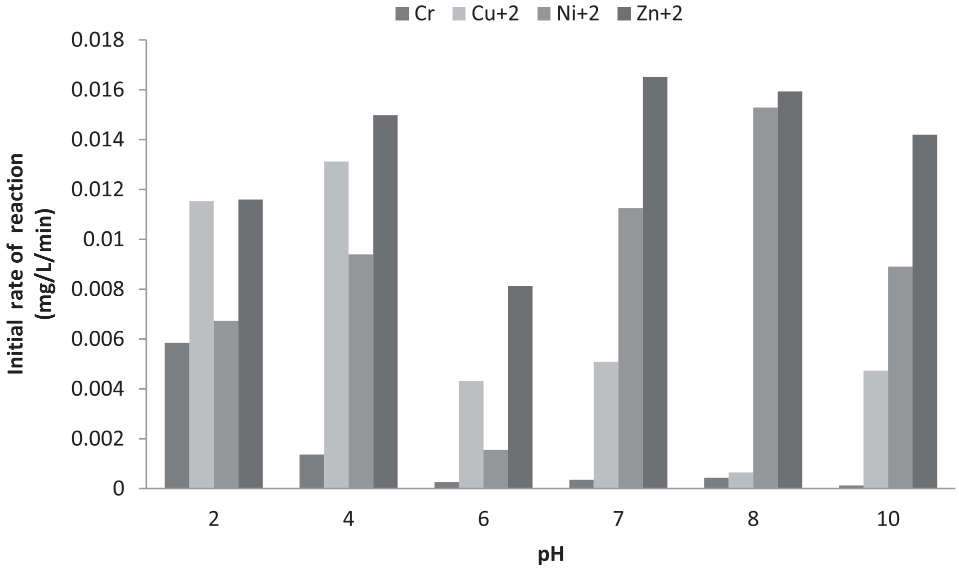
Fig. 19. Milligrams of total Zinc deposited per gram of TiO_2 at different pH level ($TiO_2 = 2$ g/L, $H_2O_2 = 60$ mL/L, citric acid = 60 mg/L).

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) was determined and evaluated at different citric acid and H_2O_2 concentrations to find out the values at which maximum efficiency (k_{max}). The following experiments are described by assuming a pseudo-first-order reaction. Then, an approximation of L-H expression can be used [7,14]:



(a): TiO_2 = 0 g/L, Citric Acid = 0 mg/L, H_2O_2 = 0 mL/L



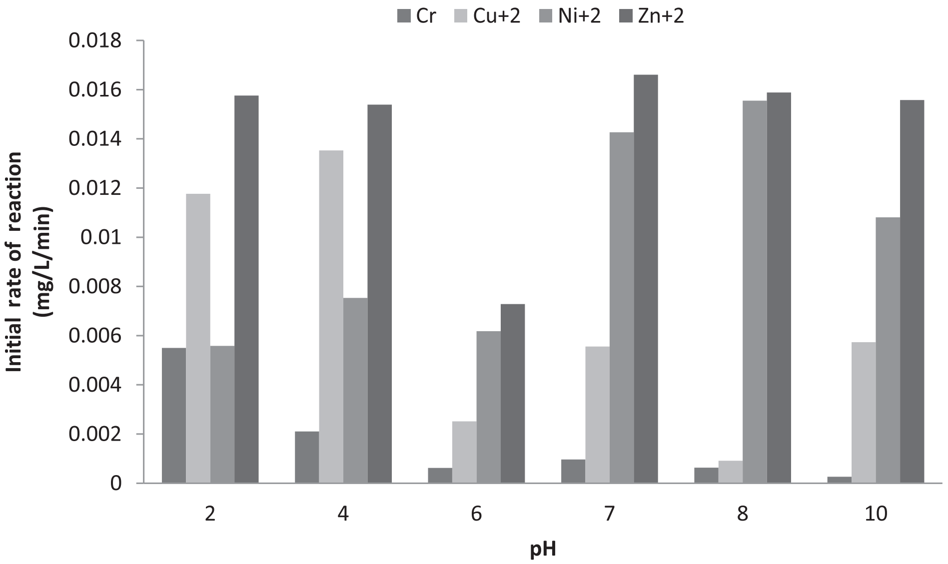
(b): TiO_2 = 2 g/L, Citric Acid = 0 mg/L, H_2O_2 = 0 mL/L

Fig. 20. Comparative initial reaction rates of chromium, copper, nickel and zinc metal ions at different pH level: (a) without TiO_2, (b) with TiO_2, (c) with H_2O_2, (d) TiO_2 and citric acid, (e) TiO_2 and H_2O_2, and (f) TiO_2, citric acid, and H_2O_2.

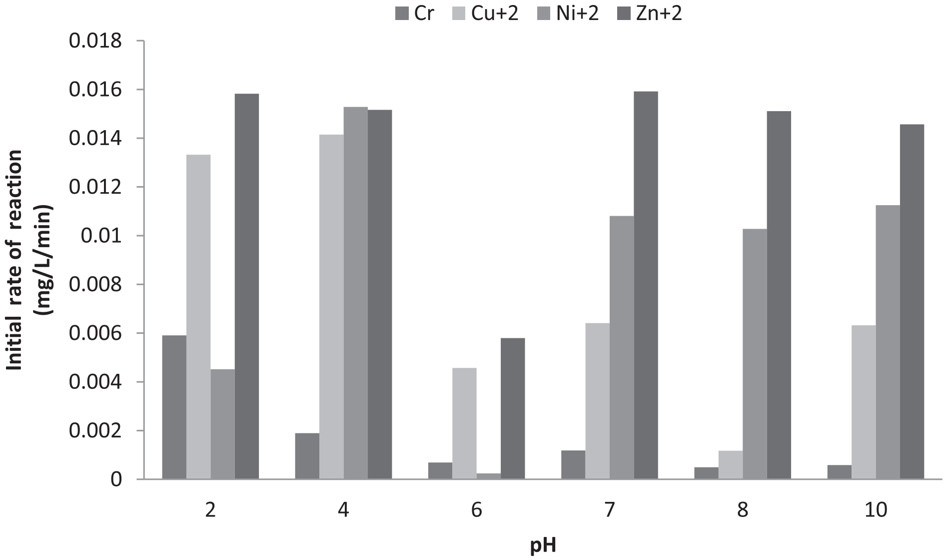
$$\frac{-\mathrm{d}(C)}{\mathrm{d}t} = k(C) \tag{14}$$

where k was the pseudo-first-order reaction rate constant.

The photocatalytic reduction rate was governed by the reaction kinetics. Sometimes, no measurable reduction was observed owing to the very low reduction rate, even though the photocatalytic reaction was thermodynamically feasible. Therefore, under the guideline of above thermodynamic analysis, kinetic study of the photocatalytic reduction for different metal ions of interest becomes more important and meaningful [2,6,14]. Therefore, Fig. 20 shows the higher initial rate of reaction for all metals with over



(c): TiO_2 = 0 g/L, Citric Acid = 0 mg/L, H_2O_2 = 60 mL/L



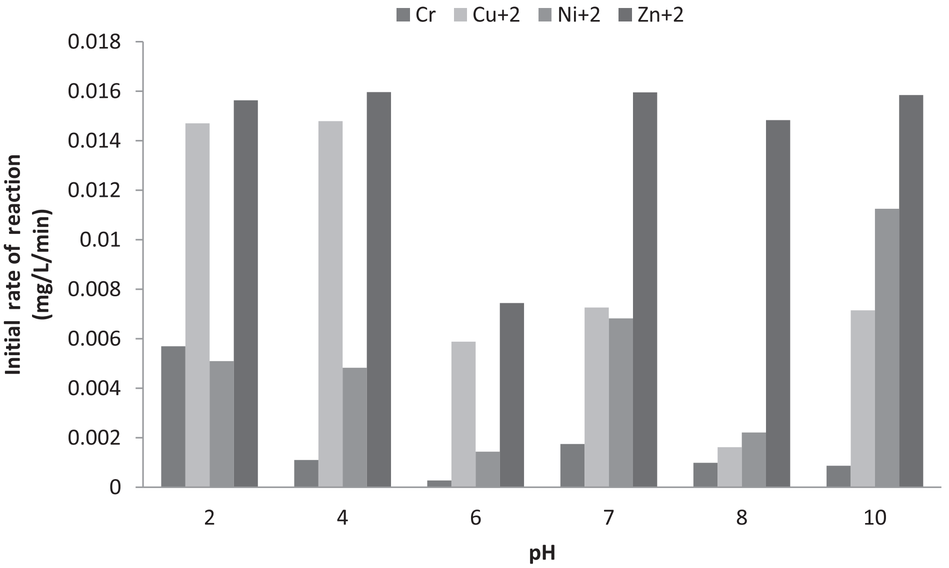
(d): TiO_2 = 2 g/L, Citric Acid = 60 mg/L, H_2O_2 = 0 mL/L

Fig. 20. (*Continued*)

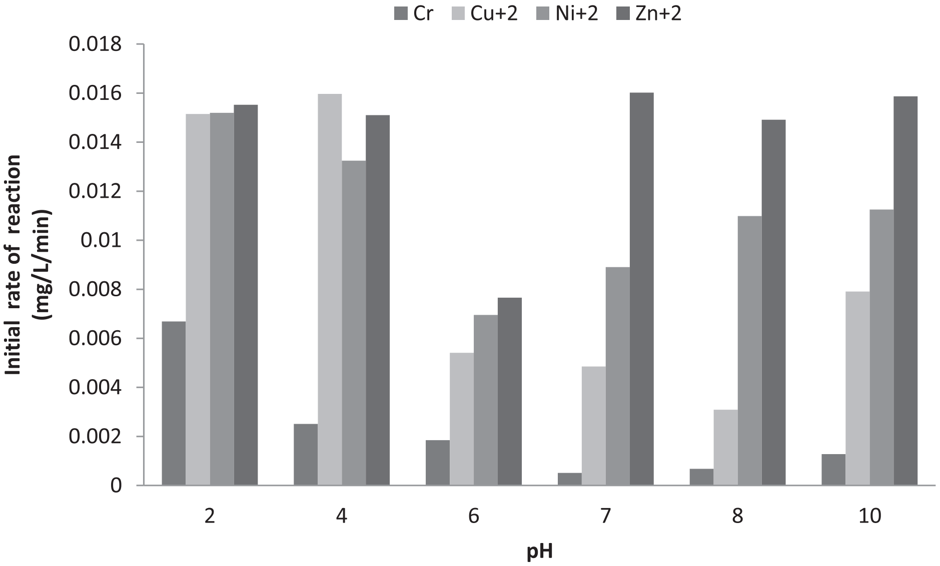
all combinations at pH 2 and 4 level, but vary to $Zn^{2+} > Cu^{2+} > Ni^{2+} > Cr$ at all pH level.

It can be observed that the reaction rate of chromium was steadily decreased with the increase in pH level. The rate of reaction for copper was found to increase at lower pH 2 and 4. In the alkaline range, the rate of reactions was nearly similar. For zinc metal, the reaction rate was found to be higher at neutral pH, but was found to increase with acidic and alkaline pH level. Nickel metal was shows maximum reaction rates at pH 8, 7, and 10 with TiO_2/UV, H_2O_2/UV, and at pH 4, 2 with TiO_2/citric acid/UV, TiO_2/H_2O_2/UV, and TiO_2/citric acid/H_2O_2/UV.

The greater the association more will be the stability of the compound. This implies that complex ions with large stability constants are more stable than the ones with smaller ones. Thereby, the higher the stability constant, the lower would be the chances of degradation of that metal complex [2,25].



(e): TiO_2 = 2 g/L, Citric Acid = 0 mg/L, H_2O_2 = 60 mL/L



(f): TiO_2 = 2 g/L, Citric Acid = 60 mg/L, H_2O_2 = 60 mL/L

Fig. 20. (*Continued*)

5. Conclusions

The chromium reduction was very sensitive for the type of organics that was being simultaneously reduced. In general, the more easily oxidized organics produce higher photocatalytic reduction rates. Chromium photoreduction was increased with decreasing pH values, suggesting an acid-catalyzed behavior. For the reduction of chromium, even at very low catalyst concentrations, effective reduction was attained at acidic pH level. The process can be made economically more feasible if it carried out in acidic conditions, as less catalyst was required. The pH being regularity requirement for discharge of wastewater, it was safer to conduct the photocatalytic treatment at around pH 2–4 for chromium which gives sufficient reduction of chromium and deposition of Cr^{3+} on the photocatalyst surface ensuring overall maximum removal of total chromium and final pH well in the discharge limits. Titania was able to catalyze the reduction of chromium in the presence of UV-light were obtained at pH lower than 2 and the activity of the catalyst remains constant. Acidic pH was found to be favorable for photocatalytic reduction of chromium but unfavorable for the removal of Ni^{2+} and Zn^{2+}, supporting the thermodynamic feasibility of the reaction.

For Cu^{2+} was maximum photoreduction occurred at pH 4 and 2, which was a usual pH of wastewater. At pH 6, therefore, not much reduction adjustment would be required for removal of Cu^{2+}. The photoreduction of Cu^{2+} was maximum at acidic condition, however, Ni^{2+} and Zn^{2+} was favorable in the alkaline condition. For reduction of Ni^{2+} and Zn^{2+} support, neutral to alkaline pH 7–10 was found to be most suitable but the overall removal was low. The acidic pH for Cr^{6+}, Cu^{2+} and alkaline pH for Zn^{2+}, Ni^{2+} were found to be suitable for photoreduction and deposition of metal ions. The photocatalyst, H_2O_2 and citric acid were performed higher reduction and oxidation efficiency of metals because support to generate various complexes and speciation's at different pH level. The combination process, whose treatment and maintenance expenses are cheaper, seems to have more advantages for the reuse of wastewater and industrial wastewater.

Acknowledgments

The authors are thankful to Rajiv Gandhi National Fellowship MPhil/PhD from University Grant Commission, Delhi (India), for providing the financial support for the research and also to Energy and Environmental Studies, Devi Ahilya University, Indore (India), for giving the opportunity for this research work.

References

[1] C. Singh, R. Chaudhary, K. Gandhi, Solar photocatalytic oxidation and disinfection of municipal wastewater using advanced oxidation processes based on pH, catalyst dose and oxidant, J. Renew. Sustainable Energy 5 (2013) 1–11.

[2] R.S. Thakur, R. Chaudhary, C. Singh, Fundamentals and applications of the photo-catalytic treatment for the removal of industrial organic pollutants and effects of operational parameters: A review, J. Renew. Sustainable Energy 2 (2010) 042701–37. doi:10.1063/1.3467511.

[3] S. Kothari, A. Kumar, R. Vyas, R. Ameta, P.B. Punjabi, Cadmium sulfide photocatalysed reduction of malachite green by ascorbic acid and EDTA as reductants, J. Braz. Chem. Soc. 20(10) (2009) 1821–1826.

[4] A.B. Araújo, O.P. Amarante Junior, E.M. Vieira, J.P.S. Valente, P.M. Padilha, A.O. Florentino, Photodegradation of soluble and emulsive cutting fluids using TiO_2 as catalyst, J. Braz. Chem. Soc. 17(4) (2006) 737–740. http://dx.doi.org/10.1590/S0103-50532006000400015.

[5] F. Shafqat, H.N. Bhatti, M.A. Hanif, A. Zubair, Kinetic and equilibrium studies of Cr(III) and Cr(VI) sorption from aqueous solution using rosa gruss an teplitz (red rose) waste biomass, J. Chil. Chem. Soc. 53(4) (2008) 1667–1672.

[6] C. Singh, R. Chaudhary, R.S. Thakur, Performance of advanced photocatalytic detoxification of municipal wastewater under solar radiation—A mini review, Int. J. Energy Environ. 2(2) (2011) 337–350.

[7] S.P. Parra Cardona, Coupling of photocatalytic and biological processes as a contribution to the detoxification of water: catalytic and technological aspects [Doctoral Theses No. 2470], EPFL, Lausanne, 2001. Available from: http://library.epfl.ch/theses/?nr=2470.

[8] E. Vassileva, Use of high surface area TiO_2 for pre concentration and following determination of Cr species by on-line flow injection inductively coupled plasma atomic emission spectrometry, Analusis 28 (2000) 878–884.

[9] D.D. Dionysiou, M.T. Suidan, E. Bekoua, I. Baudin, J.-M. Laîné, Effect of ionic strength and hydrogen peroxide on the photocatalytic degradation of 4-chlorobenzoic acid in water, Appl. Catal. 26(3) (2000) 153–171. doi:10.1016/S0926-3373(00)00124-7.

[10] J.B. Galvez, S.M. Rodriguez, Solar Detoxification Technology,(2003), p. 20. http://www.unesco.org/science/wsp/publications/solar.htm.

[11] Li-Yang Chang, Alternative chromium reduction and heavy metal precipitation methods for industrial wastewater. Environ. Prog. 22(3) (2003) 174–182.

[12] L.B. Khalil, W.E. Mourad, M.W. Rophael, Photocatalytic reduction of environmental pollutant Cr(VI) over some semiconductors under UV/visible light illumination, Appl. Catal., B 17 (1998) 267–273.

[13] H. Chung, B. Ku, J.G. Regory, Development of an advanced water treatment system for wastewater reuse, Environ. Prog. 29 (2008) 931–939.

[14] R. Chaudhary, R.S. Thakur, Photocatalytic treatment of industrial wastewater containing chromium as a model pollutant-effect on process parameters and kinetically studies, J. Renew. Sustainable Energy 4 (2012) 053121–19. doi:10.1063/1.4757629.

[15] Hydroxide Precipitation/Hoffland Environmental Inc. http://www.hofflandenv.com/hydroxide-precipitation/.

[16] S. Malato, J. Blanco, A. Vidal, C. Richter, Photocatalysis with solar energy at a pilot plant scale: an overview, Appl. Catal., B 37(1) (2002) 1–15.

[17] G. Colón, M.C. Hidalgo, J.A. Navío, Influence of carboxylic acid on the photocatalytic reduction of Cr(VI) using commercial TiO_2, Langmuir 17(22) (2001) 7174–7177. doi:10.1021/la010778d.

[18] W. Lin, C. Wei, K. Rajeshwar, Photocatalytic reduction and immobilization of Hexavalent chromium at titanium dioxide in aqueous basic media, J. Electrochem. Soc. 140 (1993) 2477–2482.

[19] S.G. Schrank, H.J. José, R.F.P.M. Moreira, Simultaneous photocatalytic Cr(VI) reduction and dye oxidation in a TiO_2 slurry reactor, J. Photochem. Photobiol., A 147 (2002) 71–76.

[20] S.X. Liu, Removal of copper (VI) from aqueous solution by Ag/TiO_2 photocatalysis, Bull. Environ. Contam. Toxicol 74 (2005) 706–714.

[21] K. Young, I. Jung, Photocatalytic reduction of Cr(VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide, Water Res. 35(1) (2001) 135–142.
[22] S. Srivastava, I.S. Thakur, Evaluation of biosorption potency of Acinetobacter sp. for removal of hexavalent chromium from tannery effluent, Biodegradation 18 (5) (2007) 637–646. http://www.ncbi.nlm.nih.gov/pubmed/17203372.
[23] F. Juan, C. Gonzalez, A.R. Ismael, Hexavalent chromium removal by a paecilomyces. Fungal strain isolated from environment, Hindawi Publishing Corporation Bioinorg. Chem. Appl. 2010 (2010) 1–6.
[24] K. Kabra, R. Chaudhary, R.L. Sawhney, Solar photocatalytic removal of metal ions from industrial wastewater, Environ. Prog. 27(4) (2008) 487–495.
[25] K. Kabra, R. Chaudhary, R.L. Sawhney, Effect of pH on solar photocatalytic reduction and deposition of Cu(II), Ni(II), Pb(II) and Zn(II): Speciation modeling and reaction kinetics, J. Hazard. Mater. 149 (2007) 680–685.
[26] X. Wang, S.O. Pehkonen, A.K. Ray, Removal of aqueous Cr(VI) by a combination of photocatalytic reduction and co precipitation, Ind. Eng. Chem. Res. 43 (2004) 1665–1672.
[27] M.R. Samarghandi, J. Nouri, A.R. Mesdaghinia, A.H. Mahvi, S. Nasseri, F. Vaezi, Efficiency removal of phenol, lead and cadmium by means of UV/TiO_2/H_2O_2 processes, Int. J. Environ. Sci. Tech. 4(1) (2007) 19–25.
[28] R. Chaudhary, C. Singh, Removal of metal ions by means of solar oxidation processes based on pH, TiO_2 and oxidants, J. Desalin. Water Treat. 5 (2013) 1–9.
[29] Z. Ji, Synthesis and engineering of titanosilicate ETS-10 for enhanced photocatalytic activity in an optical fiber reactor [Chemical Engineering Dissertations] (2009), Paper 2. http://hdl.handle.net/2047/d10019145.
[30] H. Reiche, W.W. Dun, A.J. Bard, Heterogeneous photocatalytic and photosynthetic deposition of Copper on TiO_2 and WO_3 powders, J. Phys. Chem. 83(17) (1979) 2248–2251.
[31] Y.Y. Wang, C.C. Wan, Investigation of photo electrochemical reduction of cupric ions over TiO_2 in the presence of methanol, J. Photochem. Photobiol., A 84 (1994) 195–202.
[32] D. Chen, A.K. Ray, Removal of toxic metal ions from wastewater by semiconductor photocatalysis, Chem. Eng. Sci. 56 (2001) 1561–1570.
[33] N.K. Meshkov, L.R. Skubal, T. Rajh, Removal of heavy metals from aquous waste streams using surface-modified nanosized TiO_2 photocatalysts. in: Third International Conference on TiO_2 Photocatalytic Purification and Treatment of Water and Air, Orlando, FL (1997).