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Removal of metal ions by means of solar oxidation processes based on pH, TiO_2 and oxidants

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ABSTRACT

The present study is targeted at the feasibility of photocatalytic treatment of wastewater containing metal ions. The relatively newest of which is photo catalysis with titanium dioxide which may also be used, plus hydrogen peroxide as a hole scavenger to improve the treatment rate. In this study, photocatalysis/hydrogen peroxide processes had been employed for the removal of four metal ions Cr, Cu, Ni, and Zn present in the wastewater. Experiments were carried out to find an optimum dose of H_2O_2, used as hole scavenger. The absorption and reduction of the metal ions at different pH values (7.2, 2, 4, 6, 8 and 10) were also investigated. The detention time was kept constant (300 min). Results indicated that at pH 2, complete reduction was achieved for Cr. However, Cu, and Zn reduced completely even at alkaline and natural pH in a minimum time period; and 94.8% reduction of Ni at the alkaline pH was obtained by solar radiation. On the other side without solar radiation, the percentage of removal of metals are very less.

Keywords: Solar; Metals; Photocatalysis; Hydrogen peroxide; Chemical oxygen demand; pH

1. Introduction

A wastewater treatment system has been designed to reduce the environmental impacts of discharging untreated wastewater. Various options available for wastewater treatment have different performance characteristics and also different direct impacts on the environment. The removal of toxic contaminants from water remains a huge challenge for industrial and municipal wastewater treatments. In most cases, wastewater often contains a lot of inorganic and organic pollutants. The major inorganic pollutants are toxic heavy metals, such as Cr, Cu, Ni, and Zn, which have become a serious problem for the aquatic environment. To date, however, there has been little progress in the use of visible light-induced photocatalysis for the simultaneous removal of organic matter and metal ions from polluted water [1–3].

Advanced oxidation processes (AOP) are upcoming techniques for wastewater treatment. The effectiveness of which depends largely on the oxidation potential of OH radicals (2.8 V vs. standard hydrogen electrode) and has been extensively demonstrated [4]. The TiO_2/UV process is particularly attractive for use in regions where UV photons can be provided by sunlight. An overview of the work on solar heterogeneous photocatalysis is given by [5]. The photoreduction

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reaction involves metal ions being reduced to form metal deposits on the surface of the semiconductor catalyst. The deposited metal can, subsequently, be recovered by mechanical and/or chemical methods [6]. A potential, and very attractive practical, application of light-driven photocatalytic reduction is the deposition of toxic metals and recovery of noble metals from industrial wastes [7].

A pictorial representation of the mechanism of TiO_2 photocatalysis is shown in Fig. 1. This study was carried out to identify the effects due to the presence of hydrogen peroxide on the removal efficiency of metal ions at different parameters, such as intensity of solar irradiation, concentration of photocatalyst, time, and different pH values. Therefore, the following redox reaction cycle (photo catalytic oxidation and reduction) takes place:

$$TiO_2 + hv(\lambda \leqslant 380\ \text{nm}) \rightarrow TiO_2(e^- + h^+) \quad (1)$$

$$M^{n+} + e \rightarrow M^{(n-1)+} \quad (2)$$

$$Mn^+ + H_2O \xrightarrow{TiO_2(hv)} M^o nH^+ + \frac{n}{4}O_2 \quad (3)$$

$$OH^- + h^+ \rightarrow OH^0 \quad (4)$$

$$\begin{aligned} OH^0 + RH &\rightarrow R^0 + H_2O \\ &\rightarrow CO_2 + H_2O + \text{Mineral acids} \end{aligned} \quad (5)$$

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \quad (6)$$

where M represents the metal ion and RH organic compounds.

For reduction in the photocatalytic chemical species, the conduction band of the semiconductor photocatalyst must be more negative than the reduction potential of the chemical species. By contrast, only when the potential of the valence band is more positive than the oxidation potential of the chemical species, photooxidation can occur. Therefore, the energy level of the bottom of the conduction band is a measure of the reduction strength of the photo-generated electrons [8]. Fig. 2. illustrates the positions of valence and conduction bands of anatase TiO_2 photocatalyst in contact with an aqueous electrolyte solution at different pH and compares them with the reduction potentials of relevant metal ions. It is worth noting that the positions of both conduction and valence bands are pH-dependent.

Recently, the application of photocatalytic technology for effluent treatment has received much attention. The advantages of the technology are that the oxidative and reductive reactions occur simultaneously, solar light can be utilized, and this technology can be comparatively low cost [9].

The Cr (VI) was selected as a model metal ion since it is one of the most toxic ions present in the environment, posing toxicity to most organisms at concentrations greater than 0.05 mg/L [10]. The visible light could induce photocatalytic reduction in Cr, with efficiency increasing with decrease in pH from 10 to 2. The removal of Cr at lower pH values may be attributed to the large number of H^+ ions which were neutralized to negatively charged or converted to a neutral group [11]. Chromium exists in two oxidation states, Cr (III) and Cr (VI). The hexavalent form is 500 times more toxic than the trivalent form [12]. It is

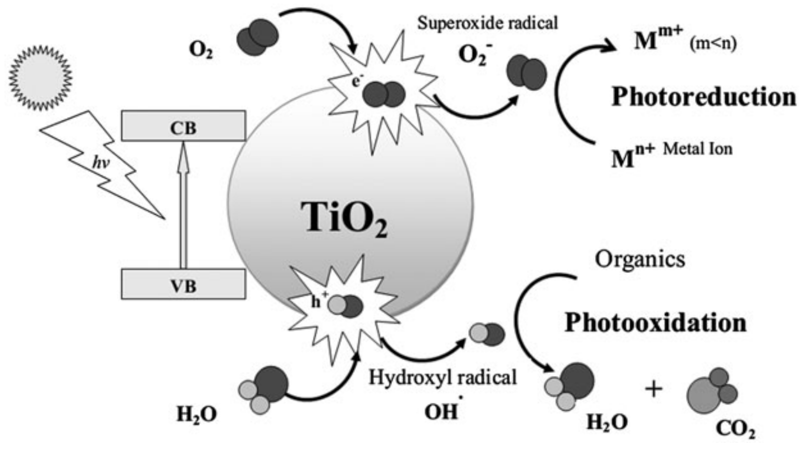

Fig. 1. Mechanism of photocatalysis.

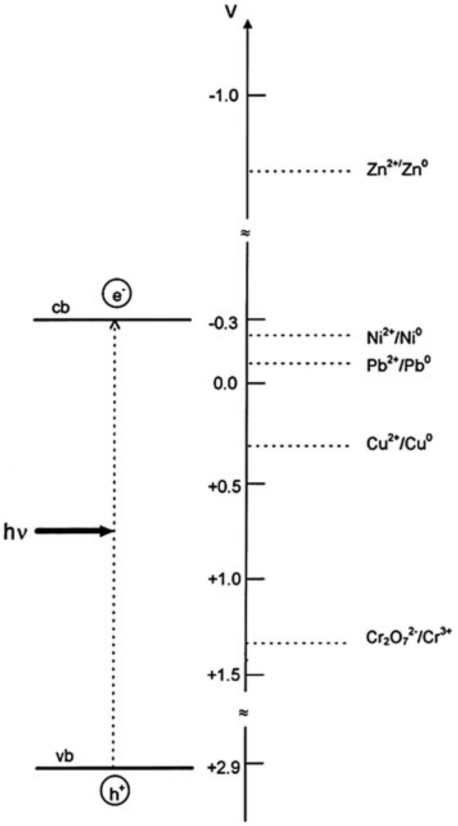

Fig. 2. The redox potentials of various metallic couples relative to the energy levels of the conduction and valence bands of Degussa P25 TiO_2[9].

toxic to microorganisms, plants, animals, and humans [13]. Several studies have shown that trace amount of chromium (VI) are considered to be essential for normal metabolic processes [14]. Chromium, discharged in to the sewage system, causes a serious environmental impact [15].

$$Cr_2O_7^{2-} + 6e + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O\ (E^o = +1.50\ \mathrm{V}) \quad (7)$$

The decrease in the metal concentration of Cr(VI) and Cu(II) is caused by photocatalytic reduction, which occurs by capturing the released electrons from the photolysis of water with TiO_2 as the photocatalyst [16] as depicted by reactions (1), (7), and (8):

$$Cu^{2+} + 2e^- \rightarrow Cu^o (E^o = +0,34V) \quad (8)$$

The more effective photocatalytic reduction of Cr (VI) as compared to that of Cu (II) is consistent with their reduction potential values, as presented in reactions (7) and (8).

On the basis of Fig. 2, and the reduction potentials of metal ions one can see that photocatalytic reduction of Cu and Ni is thermodynamically feasible, whereas Zn cannot be photo catalytically reduced to its corresponding zero valency state because its reduction is more negative than that of photo-generated electrons. Thermodynamically, the driving force for Zn and Ni is also extremely low which minimizes their possibility to be reduced under most conditions.

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) - 0.76\ \mathrm{eV} \quad (9)$$

$$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s) - 0.23\ \mathrm{eV} \quad (10)$$

The study focuses on the determination of organic and inorganic ions formed during the process. Although many researches have been performed on the use of photocatalysis processes in treatment of different wastewaters, this study should be regarded as new because the efficiency of visual light/TiO_2/H_2O_2 process has been determined for the first time in simultaneous removal of heavy metals "Cr, Cu, Ni and Zn as four inorganic pollutants" underdifferent conditions of treatment.

India is located in the equatorial sun belt of the earth, thereby receiving large quantity of radiant energy from the sun. In most parts of India, clear, sunny weather is experienced for 250–300 days a year, making India a suitable site for solar-based treatment processes. The solar radiation intensity was 650 W/m^2 during most experimental runs. Average mean peak irradiance of Solar UV–A is 47–66 W/m^2 and average mean peak irradiance of Solar UV–B is 0.195–0.3384 W/m^2, corresponding to Indore field conditions.

The major objective is to study the possibility of solar energy based photocatalytic treatment of wastewater containing organic and inorganic metal ions. The reaction conditions were optimized by determination of an optimum dose of hole scavenger and optimum pH value for solar photocatalytic wastewater treatment. The municipal wastewater treatment plant (MWWTP) was used for the study, which contained Cr, Cu, Ni, and Zn as major metal constituents, and hydrogen peroxide was used as a hole scavenger.

All the photoreaction experiments were performed under ambient conditions on the open roof of the building of School of Energy and Environmental Studies, Devi Ahilya University campus, located in Indore from 1 Oct 2011 to 30 Oct 2011 under natural light irradiation. The study area is situated at 22°43′N, 75° 48′E.

2. Experimental

2.1. Materials and methods

The wastewater sample was collected before entering the treatment cycle of the MWWTP. The physicochemical characterization of wastewater sample is shown in Table 1. Cr, Cu, and Ni were the major constituents of the wastewater.

Photocatalytic experiments were performed for the study. Hydrogen peroxide was used as a hole scavenger. Initially, blank experimental runs were carried out in absence of hydrogen peroxide. Thereafter, an optimum hydrogen peroxide dosage was determined. The dosage of hydrogen peroxide varied with metal ions concentration of the wastewater treatment. The hydrogen peroxide dose was increased until a complete metal reduction was achieved. The removal rate increased with increasing initial concentration of H_2O_2. However, as the initial concentration of H_2O_2 reached a certain value, the increase in decomposition rate became less [17]**.** TiO_2 was used as a photocatalyst. Dose of TiO_2 was fixed to 1 g/L. Experiments were also carried out at different pH values 2, 4, 6, 8, and 10, using optimum dose of hydrogen peroxide at which maximum reduction of metal ions was achieved. NaOH and H_2SO_4 were used to adjust the pH solution.

2.2. Batch reactor description

All the experiments were performed in a concentrated solar collector with a parabolic trough reflector except for the experiments of dark adsorption. The photoreactor used was a transparent borosilicate glass tube with 38-mm internal diameter, 1.8 m length, mounted on a parabolic trough reflector of aperture length 172 cm and aperture width 57.75 cm. Single-axis tracking of the reflector was done manually. The end of the glass tube had a flow control glass tap. The flow rate during all the experiments was maintained at 750 $\text{ml}^{-\text{min}}$. The wastewater was collected in a covered collection tank and was recirculated through the glass tube with the help of a low rpm water pump. The storage tank, recirculating pipes, connectors, and motor parts in contact with the wastewater were made of PVC material to avoid the problem of corrosion and metal leaching. A schematic diagram of the photocatalytic system is reported in Elsevier [18].

The initial volume of wastewater was 5 L. TiO_2 was added in the form of a suspension, after collection of an initial sample of the wastewater mixed with hydrogen peroxide. Thereafter, the samples were collected at regular intervals of time. The time period of experiments was fixed at 5 h.

For the adsorption experiments, 200-ml samples were taken in glass flasks covered with a thick aluminum sheet to avoid the penetration of light. The time period of experiment was similar to that of the light experiments.

Table 1
Characteristics of the municipal wastewater obtained from the pilot plant

Characterization parameters	Units	Values
pH		7.2
Temperature	℃	31
COD	mg/L	352 ± 5
Cr	mg/L	0.75 ± 0.05
Cu	mg/L	0.52 ±0.0 5
Ni	mg/L	0.33 ± 0.05
Zn	mg/L	0.23 ± 0.05

2.3. Chemical analysis

Initial metal ions concentration was determined in the wastewater sample collected before the addition of TiO_2. After sample collection, TiO_2 was removed by centrifugation and samples were analyzed for determining final concentrations of the parameters. Chemical oxygen demand (COD) was analyzed according to the Standard Methods [19] under section 5,220. TiO_2 (Marck) photocatalyst was used as available. Anatase was the major crystalline phase in TiO_2 as determined by XRD analysis (performed by Rigaku RUH 3R instrument) and the surface area is $10.5\,\text{m}^2/\text{g}$ [20]. Solar intensity, temperature, and pH were monitored regularly throughout the experiment. Solar intensity was measured using a solar meter (Make-SM 201 Solar, Central Electronic Ltd., India). 0.1 N H_2SO_4 and 0.1 N NaOH were used to adjust the solution pH. Temperature and pH levels were monitored by using a digital temperature indicator and pH meter. COD was estimated before and after treatment. The determination of chromium, copper, nickel, and zinc was done by Atomic Absorption Spectrophotometer (Shimadzu AA 6300) [19].

2.4. Treatment

All these experiments had been accomplished in reactor with a capacity of 5 L, and the variables studied include pH, TiO_2, and H_2O_2 concentrations. The two main stages of tests were as follows:

Without the use of solar irradiation: in the first phase, this study tested four different concentrations of H_2O_2

and 1 g/LTiO_2 at different pH values 7.2, 2, 4, 6, 8, and 10, for treatment. The detention time of these experiments was 300 min. To determine the efficiency of treatment, enough samples were regularly taken before and after chemicals' addition and were, then, analyzed for heavy metals and COD measurements.

By use of solar irradiation: the above-mentioned tests were also accomplished by the use of solar irradiation. For this phase of the study, TiO_2 and H_2O_2 concentrations used were somehow similar. Different concentrations of H_2O_2 (10, 20, 30, and 40 ml/L) at the different pH values had been selected for these treatment tests.

3. Results and discussion

The physicochemical and heavy metal characterization of wastewater is mentioned in Table 1. The degradation of COD and metal ions Cr, Cu, Ni, and Zn took place by AOP treatment. Various parameters, like pH, sunlight, catalyst, and dose of hydrogen peroxide, were found to affect the degradation of pollutants. The reduction of COD is dealt with separately in detail because of its high concentration in the wastewater.

3.1. Effect of hydrogen peroxide

As shown in Table 2, for different hydrogen peroxide doses, results can be classified into experimental stage (Stage B1 and S1 to S4 for experimental runs without solar irradiation; and Stage B2 and S5 to S8 for experimental runs with solar irradiation).

Table 2
Ratios of TiO_2 and hydrogen peroxide in various experimental samples

Experimental stage	TiO_2 (1 g/L):hydrogen peroxide (ml/L)	Experiment
Without solar irradiation	1:0	B1 (Blank)
	1:10	S1
	1:20	S2
	1:30	S3
	1:40	S4
With solar irradiation	1:0	B2 (Blank)
	1:10	S5
	1:20	S6
	1:30	S7
	1:40	S8

3.1.1. Effect of hydrogen peroxide concentration on COD reduction

Initially, B1 and S1–S4 Stages were carried out in the absence of light; B1 Stage was carried out in the absence of hydrogen peroxide and COD. Thereafter, in S1–S4 stages, hydrogen peroxide was added in increasing quantities in the wastewater till an optimum reduction of COD was obtained. The different concentrations of hydrogen peroxide used in different experiments are mentioned in Table 2. There was an increase in the initial COD of the wastewater after adding hydrogen peroxide to it. The decrease of COD of the wastewater is also measured for the samples. The overall percentage reduction of COD is depicted in Fig. 3. Although, the percentage of COD reduction was different for all the samples due to different initial concentrations of hydrogen peroxide added, the overall COD reduction (in mg/L) was nearly similar for all the samples (350 ± 5 mg/L). It can be observed (Fig. 3) that the trend of reduction was quite similar for most of the samples and maximum reduction of COD was achieved in 5 h of solar irradiation.

B2 and S5–S8 stages were carried out in the presence of solar irradiation; B2 stage was carried out in the absence of hydrogen peroxide and COD. Thereafter, for S5–S8 stages, hydrogen peroxide was added in increasing quantities in the wastewater till a complete reduction of COD was obtained. The different concentrations of hydrogen peroxide used in different experiments are mentioned in Table 2. There was an increase in the initial COD of the wastewater after adding hydrogen peroxide to it. The decreasein COD of wastewater is also measured for the samples. The overall percentage reduction of COD is depicted in Fig. 4. Although, the percentage of COD reduced was different for all the samples due to different initial concentrations of hydrogen peroxide added, the overall COD reduction (in mg/L) was nearly similar for

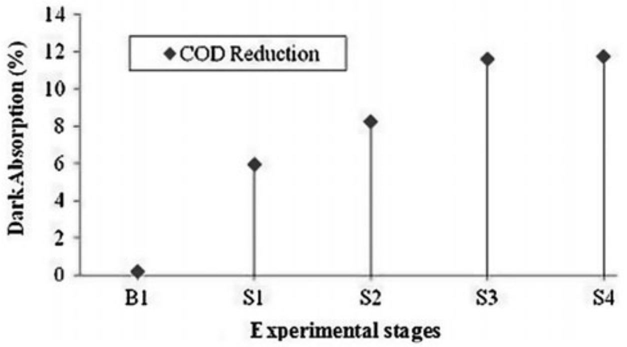

Fig. 3. Dark absorption of COD for different experimental stages.

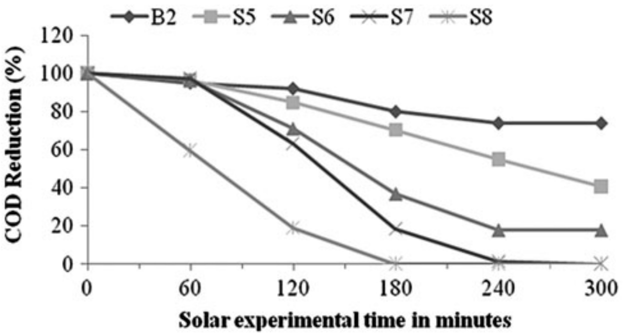

Fig. 4. Percentage COD reduction for different concentration of hydrogen peroxide.

all the samples (350 ± 5 mg/L). On addition of hydrogen peroxide in increasing quantities, a complete reduction of COD was achieved for stage S7 and S8. It can be observed (Fig. 4) that the trends of reduction were quite similar for most of the samples and maximum reduction of COD was achieved in the first 4 h of solar irradiation. After 3–4 h of irradiation, the reduction continued in the samples with higher quantities of hydrogen peroxide.

3.1.2. *Effect of hydrogen peroxide concentration on reduction of Cr, Cu, Ni and Zn*

Other metals found in the wastewater were Cr, Cu, Ni, and Zn of these metals, chromium was present in significant quantities. The percentage removal observed for these metals is depicted in Fig. 5. At the B1 stage, minimum reduction of Cr was obtained in the absence of light and hydrogen peroxide. At B2 stage, without hydrogen peroxides in the presence of solar irradiation, the electron-hole recombination was more dominating because the hole scavenger is absent. It can be observed (Fig. 5) that there was an overall decrease in total chromium concentration in the wastewater. This decrease was higher for the samples in which more reduction of Cr occurred (samples S8).

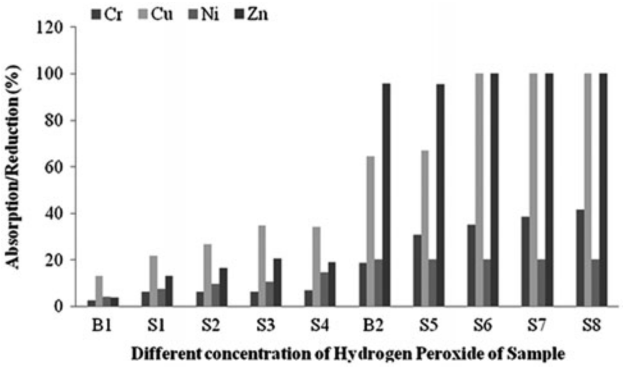

Fig. 5. Absorption/reduction of Cr, Cu, Ni, and Zn at different concentration of hydrogen peroxide.

The removal of Cu has been a controversial topic. Reiche et al. [21] reported a complete reduction of copper in the absence of any organic species or in the presence of acetate. Wang and Wan [22] have reported the reduction in the presence of methanol. In this study, since the concentration of copper is quite low, the reduction rates were unpredictable. It can be observed from Fig. 5 that more reduction was obtained in the presence of hydrogen peroxide. On addition of hydrogen peroxide in increasing quantities, complete reduction of Cu was achieved for experiments S6–S8.

For nickel, the removal obtained was very low. At the B1 stage, in the absence of hydrogen peroxide, no removal was observed. At the S1–S4 stages, in the presence of hydrogen peroxide, Ni reduction was low. At the B2 and S5–S8 stages, nearly similar reduction was observed for all concentrations of hydrogen peroxide. On the basis of thermodynamic considerations, Chen and Ray [8] suggested that the reduction would be favorable in the alkaline pH range. The pH studies carried out, (reported after this section) further ensured that the reduction is likely to occur more in the alkaline pH range.

The removal conditions of Zn were quite similar to that observed for Cu. It can be observed from Fig. 5 that nearly same percentage of metal is removed in the presence of hydrogen peroxide and for the high concentrations of hydrogen peroxide. On addition of hydrogen peroxide in increasing quantities, complete reduction of Zn was achieved for stage S6–S8.

The reduction of Cr, Cu, Ni, and Zn shows that the rate of reduction was independent of the concentration of hydrogen peroxide unlike Cu and Zn. Possibly, a minimum concentration of hole scavengers was sufficient for the reduction of these metal ions. Additionally, water was also an equally efficient hole scavenger for these metals [23].

3.2. *Effect of pH studies*

At different pH values, the results can be classified into experimental stage (Stage B1 and S1–S4 experimental runs without solar irradiation and Stage B2 and S5–S8 experimental runs with solar irradiation).

3.2.1. *Reduction of COD at different pH values*

Significant COD reduction in dark is observed at all pH values except at pH 2. The photocatalytic

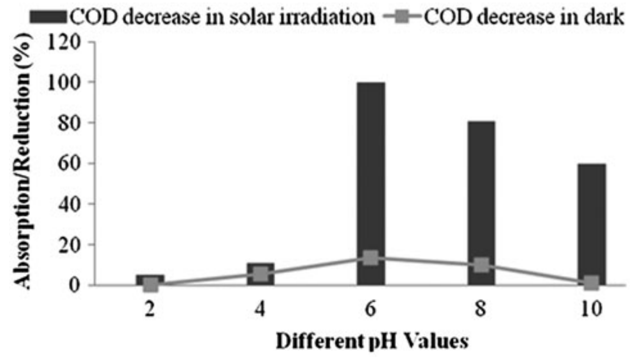

Fig. 6. Absorption/reduction of COD for stage S8 at different pH values.

oxidation trends were similar to the dark adsorption observed in Fig. 6. The low reduction and adsorption at pH 2 could be possibly due to the neutral surface of TiO_2 at the point of zero charge, which would be unfavorable for the adsorption and subsequent oxidation of hydrogen peroxide. On addition of hydrogen peroxide in increasing quantities, complete reduction of COD was achieved for stage at pH 6.

3.2.2. Reduction of Cr, Cu, Ni, and Zn at different pH values

The thermodynamic studies show that the reduction potential of all the metal ions is independent of pH. Consequently, the photoreduction of most of the metals was favored at high pH. Similar trends were observed in this study for the metal ions studied [23]. Studies at different pH values 2, 4, 6, 8, and 10 were carried out to observe the influence of pH on the reduction of metals (Cr,Cu,Ni, and Zn). The stage S4 and S8 (TiO_2/H_2O_2 and solar irradia-

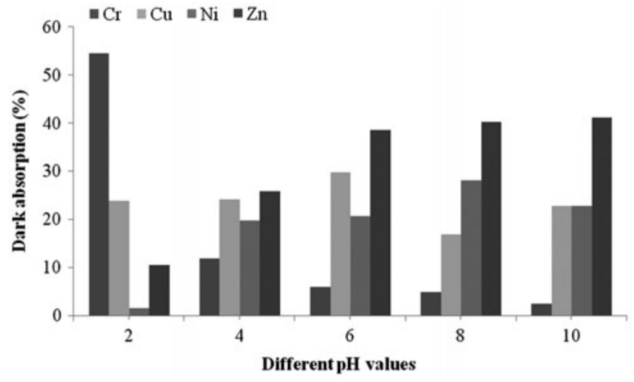

Fig. 7. Dark absorption of metals for stage S4 at different pH values.

Table 3
Removal efficiency (%) of metals ions (Cr, Cu, Ni, and Zn) in different pH (2, 4, 6, 8 and 10) in the various stages of experiments

Experiments	Removal efficiency																			
	(2 pH)				(4 pH)				(6 pH)				(8 pH)				(10 pH)			
	Cr	Cu	Ni	Zn	Cr	Cu	Ni	Zn	Cr	Cu	Ni	Zn	Cr	Cu	Ni	Zn	Cr	Cu	Ni	Zn
Blank (B1)	6.1	4.2	0	0	5.1	8.4	5.7	1.5	4.2	6.9	6.9	1.3	2.9	15.6	15.2	5.1	1.7	10.3	9.6	6.8
S1	10.2	12.3	2.2	2.8	7.6	13.1	3.9	6.6	4.8	12	7.6	16	3.3	15.8	20.2	17.3	1.9	10.8	15.4	37.7
S2	12.3	18.9	2.3	4.8	11	19.6	14.6	13.2	5.9	19.6	14.7	16.2	4.7	13.6	23.7	34.4	2.5	20	20	41.3
S3	13.5	23.1	4.6	6.5	11.8	24.8	15.3	9.9	5.9	27.6	18	31	4.7	16.3	23.6	42.3	2.5	21.5	21.5	45.3
S4	54.5	23.9	1.5	10.5	11.8	24.2	19.8	25.8	5.9	29.8	20.6	38.6	4.8	16.9	28.1	40.3	2.5	22.8	22.8	41.2
Blank (B2)	81	36.4	6.6	19.6	43	19.9	14.2	37.2	47.1	29.3	28.1	85.6	50.6	29.2	81.5	93.3	37.8	36.5	77.1	98.3
S5	98.2	40.1	11.2	88.5	43	43.8	57.7	94.7	55.8	55.8	40.3	92	63.6	30.7	87	99.9	47.2	56.8	86.4	99.9
S6	99.2	43.1	35.4	90.3	89.5	65.3	63.2	94.6	68.6	72.7	65.4	96.6	65.9	63.5	87.8	99.9	60.1	78.5	89.9	100
S7	100	78.6	55.4	94.3	90.1	89.6	79.3	95.8	75.3	100	87	97.4	72.5	100	88.8	100	69.4	89.5	94.8	100
S8	100	89.5	67.4	96.3	90.1	100	76.1	95.6	75.8	100	80.7	97.4	72.9	100	90.8	100	69.1	98.9	94.7	100

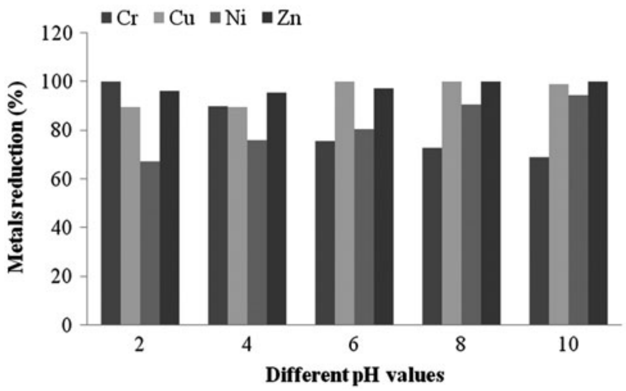

Fig. 8. Percentage reduction of metals for Stage S8 at different pH.

tion/TiO_2/H_2O_2) which gave a maximum reduction of Cr and Zn in our study was used for pH study.

In accordance with the above theory, adsorption of Cr in dark, decreased with increasing pH, as observed in Fig. 7. At S4 stage, the trend of reduction of Cr was quite different from the dark absorption trend for different pH values which is observed in Table 3. The chromium reduction was higher at pH 2 as compared to pH 4 (Fig. 7). For pH 6 and 8, very less quantities of Cr were found to reduce. No reduction was found to occur at pH 10. At S8 stage and pH 2, complete reduction was achived in 3 h of exposure. Minimal reduction was found to occur at pH 10 (Fig. 8).

Cu was found to reduce or absorb very significantly at all the pH values except for S4 stage, at pH 6 where maximum 29.8% adsorption and (Table 3) S8 stage, at pH 4, 6,and 8 complete reduction was observed (Figs. 7 and 8).

Maximal adsorption and reduction were observed for Ni in the alkaline pH range (Figs. 7 and 8). At pH 7.2 and 8, significant removal was seen for the metal. Adsorption was favored more in the alkaline and neutral pH range. Results can be observed in Table 3. 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 [23].

The reduction and adsorption of Zn was observed most in the alkaline pH range and was found to increase with the increasing pH values. Results can be observed in Table 3**.** Insignificant reduction was observed at pH 2 (Fig. 7). Complete reduction was obtained at pH 8 and 10 (Fig. 8).

4. Conclusions

It can be concluded that different pH values of 7.2 (natural pH), 2, 4, 6, 8, and 10, can be used for metal removal. Since, the main purpose of this study was to find a suitable treatment condition by which simultaneous reduction of COD and removal of metals could be accomplished, it can be concluded that even at significantly high concentration of hydrogen peroxide and sufficient solar intensity, the reaction rate was dependent on pH. At pH 2, complete reduction (100%) was achieved for Cr in a minimum time period (120 min.) and the time period required for the reduction was found to increase with increasing pH values. In the alkaline pH range, Cu, Ni, and Zn were found to absorb and were removed significantly. A complete reduction was achieved for Cu and Zn, and 94.8% reduction was achieved for Ni at the alkaline pH values.

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References

[1] H.X. Fu, G.X. Lu, S.B. Li, Photocatalytic reduction of Cr^{6+} ion in the presence of organics, Acta Phys. Chim. 13 (1997) 106–112.

[2] R. Vinu, G. Madras, Kinetics of simultaneous photocatalytic degradation of phenolic compounds and reduction of metal ions with nano-TiO_2, Environ. Sci. Technol. 42 (2008) 913–919.

[3] N. Wan, L.H. Zhu, K.J. Deng, Y.B. She, Y.M. Yu, H.Q. Tang, Visible light photocatalytic reduction of Cr(VI) on TiO_2 *in situ* modified with small molecular weight organic acids, Appl. Catal. B: Environ. 95 (2010) 400–407.

[4] K. Kabra, R. Chaudhary, R.L. Sawhney, Treatment of hazardous organic and inorganic compounds through aqueous-phase photo-catalysis: A review, Ind. Eng. Chem. Res. 43 (2004) 7683–7696.

[5] S. Malato, J. Blanco, M.I. Maldonado, I. Oller, W. Gernjakand, L. Perz-Estrada, Coupling solar photo-fenton and biotreatment at industrial scale: Main results of a demonstration plant, J. Hazard. Mater. 146 (2007) 440–446.

[6] V.N.H. Nguyen, R. Amal, D. Beydoun, Effect of format and methanol on photoreduction/removal of toxic cadmium ions using TiO_2 semiconductor as photocatalyst, Chem. Eng. Sci. 58 (2003) 4429–4439.

[7] 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. Technol. 4 (2007) 19–25.

[8] D. Chen, K.A. Ray, Removal of toxic metal ions from wastewater by semiconductor photocatalysis, Chem. Eng. Sci. 56 (2001) 1561–1570.

[9] Ji. Zhaoxia, Synthesis and engineering of titanosilicate ets-10 for enhanced photocatalytic activity in an optical fiber reactor, Northeastern University Boston, Massachusetts, MA, March 2009.

[10] R. Qiu, D. Zhang, Z. Diao, X. Huang, C. He, J.L. Morel, Y. Xiong, Visible light induced photocatalytic reduction of Cr (VI) over polymer-sensitized $TiO_2$and its synergism with phenol oxidation, Water Res. 46 (2012) 2299–2306.

[11] A. Idris, N. Hassan, N.S.M. Ismail, E. Misran, N.M. Yusof, A.F. Ngomsik, A. Bee, Photocatalytic magnetic separable beads for chromium (VI) reduction, Water Res. 44 (2010) 1683–1688.

[12] Z. Kowalski, Treatment of cromic tannery wastes, J. Hazard. Mater. 37 (1994) 137–141.

[13] C.G. Maria, Toxic and mutagenic effects of chromium(VI): A review, Polyhedron 15 (1996) 3667–3689.

[14] M.A. Barkat, Y.T. Chen, C.P. Huang, Removal of toxic cyanide and Cu(II) Ions from water by illuminated TiO_2catalyst, Appl. Catal. B 53 (2004) 13–20.

[15] V.S. Shrivastava, Photocatalytic degradation of methylene blue dye and chromium metal from wastewater using nanocrystalline TiO_2 semiconductor, Arch. Appl. Sci. Res. 4 (2012) 1244–1254.

[16] P.J.M. Carrot, M.M.L.R. Carrot, J.M.V. Nabais, J.P.P. Ramalho, Influence of ionization on the adsorption of aqueous zinc species by activated carbon, Carbon 35 (1997) 403–410.

[17] 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. (IJEE) 2 (2011) 337–350.

[18] K. Kabra, R. Chaudhary, R.L. Sawhney, Photocatalytic reduction of Cr(VI) in aqueous titania suspensions exposed to concentrated solar radiation, Int. J. Sustainable Energy 26 (2007) 195–207.

[19] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, (Eds.), Standard methods for the examination of water and wastewater, twentieth ed., American Public Health Association, APHA/AWWA/WEF, Washington, DC, 1998, pp 3–65–3–67, 5–13–1–15.

[20] L. Palmisano, V. Augugliaro, R. Compostrini, M. Schiavello, A proposal for the quantitativeassessment of heterogeneous photocatalytic processes, J. Catal. 143 (1993) 149–154.

[21] H. Reiche, W.W. Dunn, A.J. Bard, Heterogeneous photo-catalytic andphotosynthetic deposition of Cu on TiO_2 and WO_3 powders, J. Phys. Chem. 83 (1979) 2248–2251.

[22] 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: Chem. 84 (1994) 195–202.

[23] K. Kabra, R. Chaudhary, R.L. Sawhney, Solar photocatalytic removal of metal ions from industrial wastewater, Am. Inst. Chem. Eng. 27 (2008) 487–495.