

# Solar photocatalytic removal of Cu(II), Ni(II), Zn(II) and Pb(II): Speciation modeling of metal–citric acid complexes

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Received 31 May 2007; received in revised form 21 November 2007; accepted 22 November 2007

Available online 3 January 2008

## Abstract

The present study is targeted on solar photocatalytic removal of metal ions from wastewater. Photoreductive deposition and dark adsorption of metal ions Cu(II), Ni(II), Pb(II) and Zn(II), using solar energy irradiated TiO<sub>2</sub>, has been investigated. Citric acid has been used as a hole scavenger. Modeling of metal species has been performed and speciation is used as a tool for discussing the photodeposition trends.

Ninety-seven percent reductive deposition was obtained for copper. The deposition values of other metals were significantly low [nickel (36.4%), zinc (22.2%) and lead (41.4%)], indicating that the photocatalytic treatment process, using solar energy, was more suitable for wastewater containing Cu(II) ions.

In absence of citric acid, the decreasing order deposition was Cu(II) > Ni(II) > Pb(II) > Zn(II), which proves the theoretical thermodynamic predictions about the metals.

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**Keywords:** Photocatalysis; Citric acid; Metal ions; TiO<sub>2</sub>; Modeling; Dark adsorption

## 1. Introduction

Toxicity and persistence of metals in the environment causes a great environmental concern for heavy metal pollution [1].

Cu(II), Ni(II), Zn(II) and Pb(II), are among the common toxic pollutants found in industrial effluents. Even at low concentrations, these metals can be toxic to organisms, including humans [2].

There is a wide usage of copper in electroplating, electrical industry, machinery, transportation, and military supplies places. Copper is an essential substance to human life, but in high doses it can cause anemia, liver and kidney damage, and stomach and intestinal irritation [3]. While the accumulation of Cu<sup>2+</sup> in human body causes brain, skin, pancreas and heart diseases [4].

Nickel and zinc are widely used in electroplating industry as a protective coating for iron and steel, and in alloys with other metals.

Zinc occurs naturally in air, water and soil, but zinc concentrations are rising due to addition of zinc through industrial activities, such as mining, coal and waste combustion and steel processing [5]. Zn<sup>2+</sup> being in the list of priority pollutants proposed by Environmental Protection Agency (EPA) gives rise to serious poisoning cases [4].

Lead is also found in vehicle exhausts, used motor oil, insecticides, and paints [6]. The storage battery industry wastewater contains lead(II) ion [7]. Lead is extremely toxic and can damage to the nervous system, kidneys and reproductive system [8,9].

Precipitation, activated carbon adsorption, ion exchange, distillation and membrane separations are common methods currently adopted for the safe disposal or recovery of metal ions in wastewater [10]. All these methods have their own advantages and disadvantages. The source of wastewater and the concentration level of contaminants are the two main factors that influence the efficiencies of the above methods. Reduction by semiconductor photocatalysis technology is a relatively new technique for the removal or recovery of dissolved metal ions in wastewater. The process couples low-energy ultraviolet light with semiconductor particles acting as catalyst and is based on the reduction by the photogenerated electrons. The metal ions with rather positive reduction potentials than the conduction band electron

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(potentials less than  $-0.5$  eV) such as  $\text{Cu}^{2+}$ ,  $\text{Cr}^{+6}$ ,  $\text{Au}^{3+}$ ,  $\text{Ag}^{+}$  [11–15] etc. have been widely studied. Whereas, only a few studies are carried out on metal ions that are difficult to reduce like,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  [16–18].

In this study, the possibility of photocatalytic reduction of metal ions,  $\text{Cu}(\text{II})$ ,  $\text{Ni}(\text{II})$ ,  $\text{Pb}(\text{II})$  and  $\text{Zn}(\text{II})$ , is explored using solar energy irradiated  $\text{TiO}_2$  as a photocatalyst, and citric acid as a hole scavenger. The thermodynamic feasibility of reduction of these metal ions is the theoretical basis of the study and modeling is performed for determining the metal speciation. A comparison of, adsorption and photodeposition of these metal ions, is drawn to predict the suitability of the photocatalytic process for the treatment of wastewater containing these metal ions.

### 1.1. Thermodynamic analysis

On the basis of thermodynamic analysis, the possibility of photocatalytic reduction of metal ions can be predicted. In order to photoreduce a 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, photo-oxidation can occur. Therefore, the energy level of the bottom of the conduction band is a measure of the reduction strength of the photogenerated electrons.

Fig. 1 illustrates the positions of valence and conduction bands of  $\text{TiO}_2$  and values of standard electrode potentials of the metals of interest in aqueous solution at  $25^\circ\text{C}$ . The band gap of  $\text{TiO}_2$  is around  $3.2$  eV with energy of conduction band  $-0.3$  eV and valence band  $+2.9$  eV [19]. Therefore, any metal ion in the wastewater, in contact with  $\text{TiO}_2$  surface, which has a

reduction potential less negative than  $-0.3$  eV would potentially be reduced by photogenerated electrons.

On the basis of Fig. 1, and reduction potentials of metal ions, it can be observed that photocatalytic reduction of  $\text{Cu}(\text{II})$ ,  $\text{Ni}(\text{II})$  and  $\text{Pb}(\text{II})$  is thermodynamically feasible, whereas  $\text{Zn}(\text{II})$  cannot be photocatalytically reduced to its corresponding zerovalent state because its reduction potentials is more negative than that of photogenerated electrons. In practice, however, the photocatalytic reduction rate is governed by the reaction kinetics. Sometimes, no measurable reduction is observed owing to the very low reduction rate even though the photocatalytic reaction is thermodynamically feasible. Therefore, the study was performed on all the four metal ions as they are commonly present in wastewater from electroplating industries. Additionally, these metals form complexes with citric acid. The difference in optimum reaction conditions for deposition of these metals could depend on the behavior of the respective complexes formed.

## 2. Materials and methods

### 2.1. Experiment

The experiments were performed using synthetically prepared wastewater containing metal ions  $\text{Cu}(\text{II})$ ,  $\text{Ni}(\text{II})$ ,  $\text{Zn}(\text{II})$  and  $\text{Pb}(\text{II})$ , in an initial concentration of  $20 \text{ mg L}^{-1}$  with and without citric acid dosing. The metal salts,  $\text{CuSO}_4$ ,  $\text{NiCl}_2$ ,  $\text{ZnSO}_4$ , and  $\text{Pb}(\text{NO}_3)_2$  (all Merck) were used to prepare the synthetic wastewater. Distilled water was used to prepare the synthetic wastewater. A separate set of experiments was performed for each metal ion. Citric acid was used as an organic additive in the synthetic wastewater for simulating the organic component of an industrial wastewater and as a hole scavenger. The metal: citric acid concentration was varied in the ratios 1:1, 1:3, 1:5, 1:7 for all the metals. The molar ratios of metal: citric acid are given in Table 1.

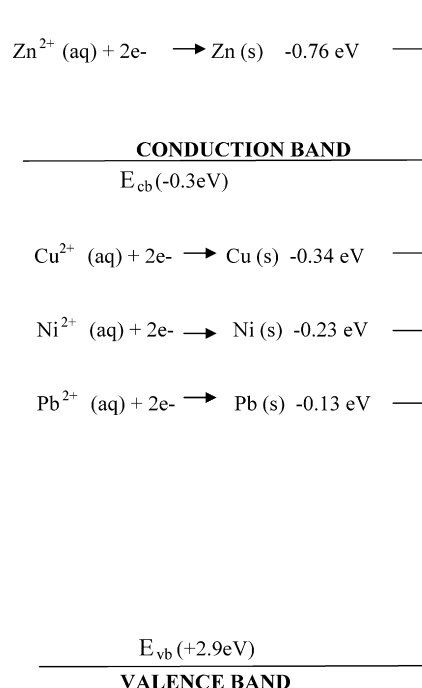


Fig. 1. Positions of valence and conduction bands of  $\text{TiO}_2$ .

Table 1

Notations used for various compositions of simulated wastewater constituents and respective metal: citric acid molar ratios

Ratio of metal: citric acid; metal = $20 \text{ mg L}^{-1}$ , citric acid = variable	Cu (II)	Ni(II)	Zn (II)	Pb(II)
1:0 (Citric acid = 0)	Cu1:0	Ni1:0	Zn1:0	Pb1:0
Molar ratio of metal: citric acid	–	–	–	–
1:1 (Citric acid = $20 \text{ mg L}^{-1}$ )	Cu1:1	Ni1:1	Zn1:1	Pb1:1
Molar ratio of metal: citric acid	3.01	3.269	2.932	0.927
1:3 (Citric acid = $60 \text{ mg L}^{-1}$ )	Cu1:3	Ni1:3	Zn1:3	Pb1:3
Molar ratio of metal: citric acid	1.006	1.089	0.977	0.309
1:5 (Citric acid = $100 \text{ mg L}^{-1}$ )	Cu1:5	Ni1:5	Zn1:5	Pb1:5
Molar ratio of metal: citric acid	0.603	0.653	0.586	0.185
1:7 (Citric acid = $140 \text{ mg L}^{-1}$ )	Cu1:7	Ni1:7	Zn1:7	Pb1:7
Molar ratio of metal: citric acid	0.436	0.472	0.423	0.134

TiO<sub>2</sub> (Merck) was used as a photocatalyst. It was used as received. Anatase was the major crystalline phase in TiO<sub>2</sub>, as determined by XRD analysis (performed by Rigaku RUH 3R instrument) and the surface area is 10.5 m<sup>2</sup> g<sup>-1</sup> [20] and is reported [20] to be the best in the capacity of absorbing photons.

Dose of TiO<sub>2</sub> was fixed to 2 g L<sup>-1</sup>. Photolytic (in absence of TiO<sub>2</sub>) and dark adsorption studies were also performed. All experiments were carried out without altering the pH of the prepared synthetic wastewater. The notations used for various compositions of simulated wastewater are mentioned in Table 1.

All the experiments were performed in a concentrating 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 (Fig. 2). Single axis tracking of the reflector was done manually. The concentration ratio of the solar collector was 4.

The end of the glass tube had a flow control glass tap. The flow rate during all the experiments was maintained to 750 mL min<sup>-1</sup>. 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.

The initial volume of wastewater was 5 L for photocatalytic experiments and 100 mL for dark adsorption experiments. The reactor volume was 1 L. TiO<sub>2</sub> was added in the form of a suspension, after collection of an initial sample of the wastewater. Thereafter, the samples were collected at regular intervals of time. The time period of experiments was fixed from 9 to 17 h.

The adsorption studies were carried out in the dark to study the adsorption of metal ion on the TiO<sub>2</sub> surface under similar experimental conditions as that of photoreduction. For adsorption experiments, batch experiments were performed with 100 mL samples taken in glass flasks. These flasks were kept under ambient conditions but were covered with a thick brown

sheet of paper to avoid the penetration of light. The samples were stirred throughout the experiment using a magnetic stirrer. The time period of experiment was similar to that of the light experiments. The results presented here show an overall adsorption/reduction.

## 2.2. Analysis

Initial metal ion concentration was determined in the wastewater sample collected before the addition of TiO<sub>2</sub>. After sample collection, TiO<sub>2</sub> was removed by centrifugation and samples were analyzed for determining final concentrations of the parameters. The metal concentration was analyzed using Atomic Absorption Spectrophotometer (Shimadzu AA 6300). pH, temperature and solar intensity were monitored regularly throughout the experiment. Solar intensity was measured using a solarimeter (Make- SM 201 Solar, Central Electronic Ltd., India). An alcohol thermometer and a pH meter (make Orion) were used to determine temperature and pH, respectively.

## 2.3. Modeling

Modeling of metal species at the studied pH values was carried out by MINTEQA model [21] to obtain the predominance of various metal species and their percentages in total wastewater components at different pH values. Only the species present in significant percentage (at any pH value) were considered for result interpretation. The modeling results were compared to the experimental results to check the model validity. The input values of the model were the original concentration of metal ions and citric acid (in mg L<sup>-1</sup>) as mentioned in the experimental section and the temperature.

Visual MINTEQA model (version 3.2) was run for calculating the speciation of metal ions. Metal ion and citric acid concentrations were incorporated as input values and the species were determined. The input was the actual concentration, that is 20 mg L<sup>-1</sup> for all the metal ions and 20–140 mg L<sup>-1</sup> of citric acid (separately for all compositions). The initial pH values obtained for the samples (given in Table 7) and a temperature of 25 °C (initial temperature of sample) were the other input values. Only the species present in significant percentage were considered for result interpretation.

The modeling results were used as a theoretical basis for interpreting the experimental results. The experimental results for the modeled wastewater mixes are detailed in the following subsections.

## 3. Results and discussions

### 3.1. Metal complexation with citric acid

The complexes formed with different citric acid concentrations, and their respective percentages in the simulated wastewater, were determined by modeling. The geochemical model MINTEQA was used to simulate the reaction condition and predict the possible speciation in respective percentages.

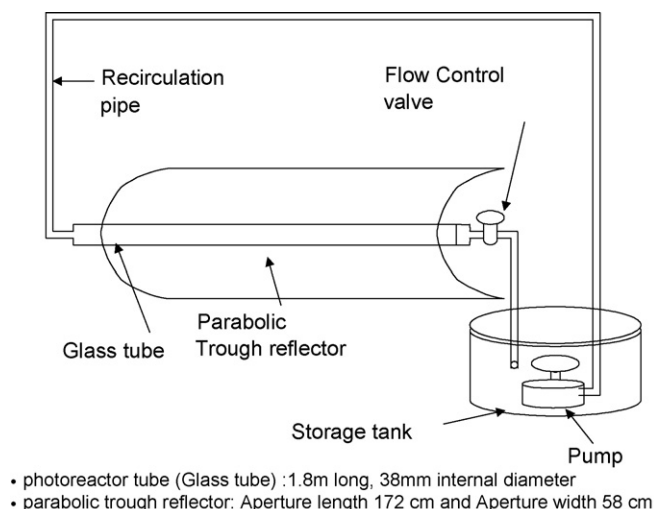


Fig. 2. Line diagram of solar photocatalytic assembly.

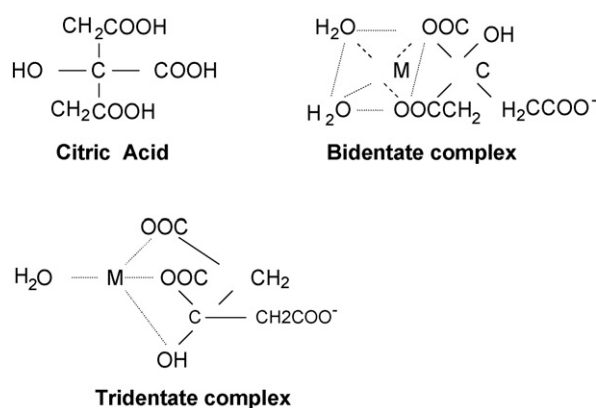


Fig. 3. Possible metal-complex formation of citrate.

Citrate ion forms multidentate, stable complexes with a variety of toxic metals, which alter the behavior of deposition/reduction of these metal ions. The complex could be mononuclear, binuclear or polynuclear depending on the type of metal. Nickel usually forms bidentate, mononuclear complexes, with two carboxylic acid groups of citric acid molecule. Copper and lead form tridentate mononuclear complexes with citric acid involving two carboxylic and one hydroxyl group [22]. The types of metal complexes that can be formed by citrate are given in Fig. 3.

Only the complexes formed in significant percentages were considered in the study. The complexes with percentage of total components less than or equal to 1% were neglected.

The stability constants of the complexes formed on metal citric acid interaction, gives an idea of the possible dissociation of these complexes. These constants are logarithms of equilibrium constants for formation of complexes and solids from metals and ligands.

The values of stability constants for the citrate complexes of these metal ions are mentioned in Table 2 [23]. The magnitude of the stability constant for the association, quantitatively expresses the stability. The greater the association more will be the stability of the compound [24].

That implies that complex ions with large stability constants are more stable than ones with smaller ones [25]. Thereby, higher the stability constant, the lower would be the chances of degradation of that metal complex.

### 3.1.1. Predicted metal speciation by modeling

The results of modeling of Cu(II) species in different wastewater compositions are mentioned in Table 3. It can be observed that the major species of Cu(II) in absence of citric acid were the

Table 2  
Stability constants for formation of various metal citrates and metal hydroxide species

Metal	Complex	Stability Constant
Nickel	Ni-citrate	6.7
	NiH-citrate	10.5
	NiH <sub>2</sub> -citrate	12.9
	Ni(OH) <sub>2</sub>	9.0
	NiOH	4.1
Copper	Cu-citrate	7.2
	CuH-citrate	10.7
	CuH <sub>2</sub> -citrate	13.8
	CuOH-citrate	16.4
	Cu <sub>2</sub> citrate <sub>2</sub>	16.3
	Cu(OH) <sub>4</sub>	16.4
	Cu(OH) <sub>2</sub>	11.8
Zinc	Zn-citrate	6.1
	Zncitrate <sub>2</sub>	6.8
	ZnH-citrate	10.3
	ZnH <sub>2</sub> -citrate	13.3
	Zn(OH) <sub>2</sub>	11.1
	ZnOH	5.0
Lead	Pb-citrate	5.4
	Pbcitrate <sub>2</sub>	8.1
	PbH-citrate	10.2
	PbH <sub>2</sub> -citrate	13.1
	Pb(OH) <sub>2</sub>	10.9
	Pb(OH)	6.3

Compilation by Morel and Hering [23].

cationic and neutral hydroxides of Cu(II), that is, Cu<sub>3</sub>(OH)<sub>4</sub><sup>+2</sup>. The anionic form Cu(OH)<sub>3</sub><sup>-</sup> was present in a very less percentage. On addition of citric acid (Cu1:1), again Cu<sub>3</sub>(OH)<sub>4</sub><sup>+2</sup> predominated and the complex anionic copper citrate was formed.

Further, in the samples Cu1:3, the Cu-citrate species predominated, which has a fair stability constant of 7.2 (Table 2). However, in the samples Cu1:5 and Cu1:7, CuH-citrate was the major species. The other species present were Cu<sup>+2</sup> and CuH-citrate. The stability constant of CuH-citrate is higher than Cu-citrate.

The nickel speciation is depicted in Table 4. The neutral Ni(OH)<sub>2</sub> (aq) was the predominating species in absence of citric acid. Another species in this wastewater was Ni(OH)<sup>+</sup>. The stability constants for these species are 9.0 and 4.1, respectively.

On citric acid addition (Ni1:1), about half of it was converted to nickel citrate and Ni<sup>2+</sup> ions also increased. In the sample Cu1:3, the percentage of cationic Ni<sup>2+</sup> doubled, nickel citrate was increased and NiH-citrate was also formed. The stability

Table 3  
Predicted speciation of Cu(II) by modeling

Sample	Cu <sub>3</sub> (OH) <sub>4</sub> <sup>+2</sup>	Cu(OH) <sub>3</sub> <sup>-</sup>	Cu(OH) <sub>2</sub> (aq)	Cu <sup>+2</sup>	Cu-citrate <sup>-</sup>	CuH-citrate
CuC0	59.44	10.56	27.86	–	–	–
CuC1:1	57.36	–	6.45	–	30.03	–
CuC1:3	–	–	–	28.82	55.54	14.24
CuC1:5	–	–	–	32.16	42.69	23.65
CuC1:7	–	–	–	35.31	34.81	28.03

Table 4  
Predicted speciation of Ni(II) by modeling

Sample	Ni <sup>2+</sup>	Ni(OH) <sub>2</sub> (aq)	Ni(OH) <sub>3</sub> <sup>-</sup>	NiOH <sup>+</sup>	Ni-citrate <sup>-</sup>	NiH-citrate (aq)	NiH <sub>2</sub> -citrate <sup>+</sup>
NiC0	10.47	72.44	6.28	10.81	–	–	–
NiC1:1	18.44	38.40	–	10.41	30.90	–	–
NiC1:3	36.69	–	–	–	46.19	16.67	–
NiC1:5	46.06	–	–	–	25.13	27.23	–
NiC1:7	54.49	–	–	–	13.11	29.11	3.23

Table 5  
Predicted speciation of Zn(II) by modeling

Sample	Zn <sup>2+</sup>	ZnOH <sup>+</sup>	Zn(OH) <sub>2</sub> (aq)	Zn-citrate <sup>-</sup>	ZnH-citrate (aq)
ZnC0	1.83	3.67	93.89	–	–
ZnC1:1	15.30	7.17	43.64	33.81	–
ZnC1:3	48.08	–	–	35.91	16.00
ZnC1:5	63.31	–	–	15.22	21.47
ZnC1:7	74.31	–	–	6.17	19.53

constant of Ni-citrate and NiH-citrate is 6.7 and 10.5, respectively. With the increasing ratios, percentage of Ni<sup>2+</sup> continued to increase. For the ratio of 1:7, NiH<sub>2</sub>-citrate<sup>+</sup> was formed. The stability constant for NiH<sub>2</sub>-citrate is 12.9 showing a high stability.

Table 5 shows the modeling results for zinc speciation. In absence of citric acid, the neutral Zn(OH)<sub>2</sub> (aq) was found to be the prominent species. This is a stable species with a stability constant value of 11.1. On addition of citric acid, sample Zn1:1, Zn<sup>2+</sup> ion and Zn-citrate was formed. Zn-citrate has a stability constant of 6.1, and was in the anionic form. With the increasing concentration of citric acid, for samples Zn1:3, Zn1:5 and Zn1:7, the Zn<sup>2+</sup> ions and zinc hydrogen citrate formation is increased.

The speciation of Pb(II) obtained by modeling is presented in Table 6. It can be observed that Pb(II) existed as a divalent ion and showed lesser extent of complexation with citric acid as compared to other metal ions.

The speciation modeling and their stability constants are used for analyzing the adsorption and deposition trends of metal ions.

### 3.2. Experimental results: dark adsorption and photocatalytic deposition

The solar irradiation, pH and temperature data is mentioned in Table 7. All the experiments were performed at the initial pH values as mentioned in Table 7.

Initially, photolytic experiments (in absence of TiO<sub>2</sub>) were carried out followed by the dark adsorption and photocatalytic

Table 6  
Predicted species of Pb(II) by modeling

Sample	Pb <sup>2+</sup>	Pb <sub>3</sub> (OH) <sub>4</sub> <sup>+2</sup>	PbOH <sup>+</sup>	Pb(OH) <sub>2</sub> (aq)	Pb-citrate <sup>-</sup>	PbH-citrate (aq)	PbH <sub>2</sub> -citrate <sup>+</sup> (aq)
PbC0	–	26.48	29.89	41.48	–	–	–
PbC1:1	59.44	–	–	–	25.42	14.82	–
PbC1:3	78.85	–	–	–	2.94	16.08	2.11
PbC1:5	81.22	–	–	–	1.36	13.95	3.45
PbC1:7	81.71	–	–	–	0.89	12.88	4.50

Table 7  
The values of solar irradiation (average of 8 h), pH and maximum temperature attained during the various experimental runs

Sample	Initial pH value	Final pH value	Average Solar irradiation (W/m <sup>2</sup> )	Maximum temperature attained (°C)
Cu1:0	7.8	8.0	603	56
Cu1:1	7.4	7.7	610	57
Cu1:3	7.1	7.5	640	58
Cu1:5	6.8	7.2	610	57
Cu1:7	6.3	6.8	610	57
Ni1:0	7.2	8.2	603	56
Ni1:1	6.6	7.8	610	57
Ni1:3	6.3	7.6	640	58
Ni1:5	6.0	7.2	610	57
Ni1:7	5.7	6.8	610	57
Zn1:0	8.4	8.6	603	56
Zn1:1	8.3	8.8	610	57
Zn1:3	7.8	8.0	640	58
Zn1:5	7.1	7.3	610	57
Zn1:7	6.5	7.2	610	57
Pb1:0	7.9	8.1	603	56
Pb1:1	7.7	7.9	610	57
Pb1:3	7.2	7.6	640	58
Pb1:5	6.9	7.2	610	57
Pb1:7	6.5	6.8	610	57

studies. There was no significant photolytic reduction in equal quantities of individual metal ions and citric acid (20 mg L<sup>-1</sup> each) showing that the reaction was truly photocatalytic.

#### 3.2.1. Dark adsorption and photoreductive deposition of Cu(II)

The trends of dark adsorption of Cu(II) on TiO<sub>2</sub> surface are depicted in Fig. 4. In absence of citric acid, dark adsorption of copper was significant. 95.8% adsorption was observed for Cu1:0, which was the maximum value for all the experimental runs. It can be observed in Table 7, that the initial pH of the solution for Cu1:0 was 7.8. The TiO<sub>2</sub> surface is negatively charged at this pH value (above pzc). Therefore, the adsorption of positively

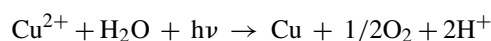
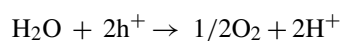
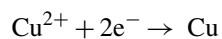
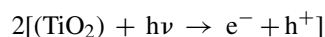
charged  $\text{Cu}_3(\text{OH})_4^{+2}$  ions (Table 3) formed in this wastewater combination, was favorable in this pH range. This could be a possible reason for such a high adsorption. Additionally, in absence of the organic molecule, more sites are available for adsorption of copper ions.

When citric acid was added to the wastewater, complexation of copper ions with citric acid was the outcome. The adsorption value was found to decrease to 53.3%, for the sample Cu1:1. The anionic complex of copper and citrate are repelled by the negatively charged  $\text{TiO}_2$  surface. Moreover, some free Cu(II) species must be present which were possibly adsorbed on the  $\text{TiO}_2$  surface.

On increasing the citric acid concentration further, the percentage adsorption values were 23.9%, 15.0% and 11.2% for Cu1:3, Cu1:5 and Cu1:7, respectively. The reason for such low adsorption values could be predominance of anionic copper citrate complex and repulsion of the complex by negatively charged  $\text{TiO}_2$  surface (pH value of solution being above the pzc of  $\text{TiO}_2$ ).

The trends of reductive deposition were slightly different from that of dark adsorption of copper (Fig. 4). Maximum reduction of 97.5% was obtained in the absence of citric acid, which showed that all the adsorbed copper was reduced and deposited on the catalyst surface. Reiche et al. [26] investigated the photoreduction of Cu(II) in  $\text{TiO}_2$  suspensions. They observed complete reduction of Cu(II) to copper metal in aqueous solutions containing either acetate or no organic species.

The basic reaction for removal of copper on irradiation of Cu(II) solution containing  $\text{TiO}_2$  powder is [26]:



Complete reduction of Cu(II) was also observed by Wang and Wan [27] in UV illuminated  $\text{TiO}_2$  suspensions containing methanol, although, no reduction was possible in the absence of

methanol. Foster et al. [13] reported that Cu(II) could be reduced to Cu(I) only in the presence of suitable organics, such as sodium formate and EDTA, and complete reduction was not observed.

In the present study, the values percentage reduction in presence of citric acid, (samples Cu1:1 and Cu1:3) were similar to those obtained in absence of citric acid. Fig. 4 shows that 97.1% and 96.7% reduction was obtained, for Cu1:1 and Cu1:3, respectively. These values were different from the dark adsorption values obtained for these samples. The presence of citric acid did not affect the reduction of copper significantly, and copper was easily reduced in neutral to alkaline pH range. Possibly, the complexes of Cu–citrate with low stability constants were decomposed by photocatalytic reaction.

As the citric acid concentration was increased, CuH–citrate was formed, which was difficult to degrade due to high stability constant. The percentage reduction was decreased to 85.4% and 73.4% for Cu1:5 and Cu1:7, respectively. The extent of surface coverage by citric acid predominated at this stage leading to lesser reduction. Additionally, the pH of the solution moved to the acidic range making the conditions unfavorable for copper reduction.

The color of copper solution changed to yellow-brown after treatment indicating the reductive deposition of copper ions. Bideau et al. [28] observed the formation of a red Cu– $\text{TiO}_2$  species when solution containing Cu(II) and formate was illuminated in the presence of  $\text{TiO}_2$ .

### 3.2.2. Dark adsorption and photodeposition of Ni(II)

Dark adsorption of nickel was very low as compared to copper. However, the trends of adsorption were similar. Percentage adsorption was found to decrease with increasing concentrations of citric acid (Fig. 5). Maximum adsorption of 31.6% was obtained in absence of citric acid. The positively charged  $\text{Ni}^{2+}$  ion and the nickel hydroxyl species, possibly accounted for this.

On addition of citric acid (Ni1:1) the adsorption value was decreased to 20.6%. The free  $\text{Ni}^{2+}$  ions in the solution, account for this adsorption. The anionic Ni–citrate was repelled by the negatively charged  $\text{TiO}_2$  surface, thereby decreasing the overall adsorption value.

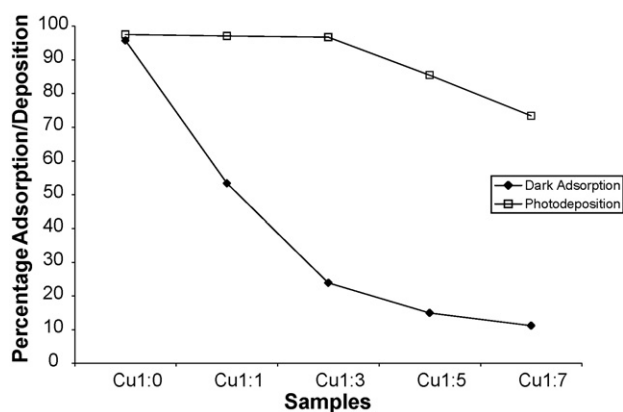


Fig. 4. Dark adsorption and photocatalytic deposition of Cu(II) for different samples (initial metal concentration =  $20 \text{ mg L}^{-1}$ , citric acid = variable,  $\text{TiO}_2 = 1 \text{ g L}^{-1}$ ).

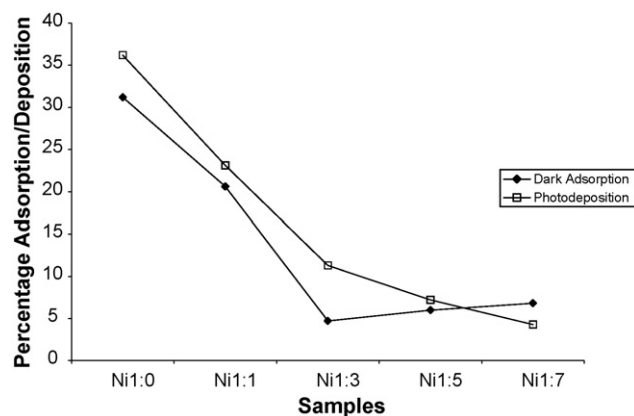


Fig. 5. Dark adsorption and photocatalytic deposition of Ni(II) for different samples (initial metal concentration =  $20 \text{ mg L}^{-1}$ , citric acid = variable,  $\text{TiO}_2 = 2 \text{ g L}^{-1}$ ).

Very less and nearly same adsorption values were obtained for Ni1:3, Ni1:5 and Ni1:7 (4.7%, 6% and 6.8%, respectively). This was due to the higher concentration of Ni–citrates.

The results for Ni(II) deposition on TiO<sub>2</sub> surface are depicted in Fig. 5. Deposition of nickel was found to decrease with increasing citric acid concentration mirroring the adsorption trend. The values of percentage adsorption and deposition were also parallel. In absence of the hole scavenger, maximum deposition of 36.2% was obtained. Whereas, in presence of citric acid, the reduction values were, 23.1%, 11.3%, 7.2% and 4.3% for Ni1:1, Ni1:3, Ni1:5 and Ni1:7, respectively. The trends of deposition show that the removal of nickel is either by adsorption or due to photocatalytic reduction. It is possible that the adsorbed Ni(II) was photoreduced by direct or indirect route.

The complexes of nickel formed with citrate have a comparative stability constant value with that of copper yet the reduction is difficult due to low driving force, at least, by direct electron donation from conduction band to the metal ion.

Although the reduction potential of nickel is a less negative value than the conduction band potential of TiO<sub>2</sub>, yet the driving force for reduction is extremely low which minimizes its possibility to be reduced under most conditions. In the earlier studies [11], no significant reduction for Ni(II) was obtained even in presence of salicylic acid as a hole scavenger at pH 6. In another study [18], indirect photoirradiated removal of nickel using CO<sub>2</sub> formed from the oxidation of oxalate ion, was suggested. Complexation of nickel with EDTA [29], showed that the Ni–EDTA complex is resistant to photocatalysis and the photoefficiency was found to be very less.

Rate of reduction was very low in spite of the presence of hole scavengers, due to less thermodynamic driving force. In the absence of citric acid, deposition was better.

### 3.2.3. Dark adsorption and photodeposition of Zn(II)

The results for dark adsorption of Zn(II) on TiO<sub>2</sub> surface are given in Fig. 6. Dark adsorption was found to increase with increasing citric acid concentration, unlike copper and nickel. There was no adsorption in absence of citric acid. This shows

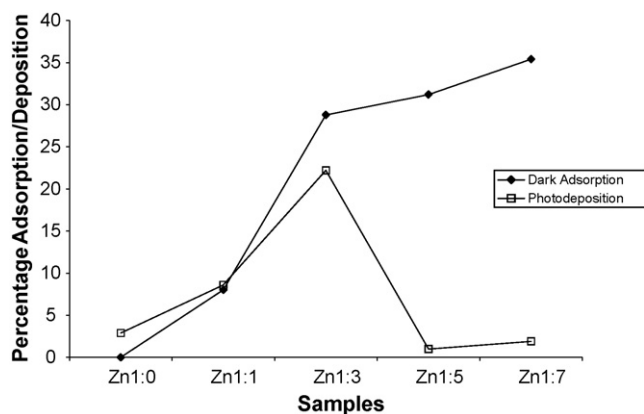


Fig. 6. Dark adsorption and photocatalytic deposition of Zn(II) for different samples (initial metal concentration = 20 mg L<sup>-1</sup>, citric acid = variable, TiO<sub>2</sub> = 2 g L<sup>-1</sup>).

that the neutral Zn(OH)<sub>2</sub>, which was the major species at this stage, does not have an affinity for TiO<sub>2</sub> surface.

In the sample Zn1:1, 8% adsorption was observed. The adsorbed species is the Zn<sup>2+</sup> ion which was attracted towards the negatively charged TiO<sub>2</sub> surface. The anionic Zn–citrate did not have a proclivity for similar charged TiO<sub>2</sub> surface.

The value of adsorption increased to 28.8% for Zn1:3 due to formation of more Zn<sup>2+</sup> ions. The adsorption values of Zn1:5 and Zn1:7 were quite close to the earlier sample, that is, 31.2% and 35.4%, respectively. The values show that equilibrium of adsorption was attained after the sample Zn1:3. This was found to be the maximum adsorption value for Zn<sup>2+</sup> ion, in these reaction conditions, which did not increase, even with higher percentage of zinc ions. The adsorption values also show that zinc was adsorbed more in presence of citric acid.

The photo deposition trends of Zn(II) are also depicted in Fig. 6. The deposition trends were different from the adsorption trends. No significant photodeposition was observed, except for sample Zn1:3. In the absence of citric acid, 2.9% of deposition is observed. On citric acid addition, Zn1:1, 8.6% of the ion was photodeposited. Further in the ratio Zn1:3, a maximum deposition value of 22.2% was observed. This value was close to the dark adsorption value showing that the deposition of zinc was not reductive in nature, but it was only due to adsorption.

The values of solar irradiation, pH and temperature attained are shown in Table 7. It can be observed that no significant pH change was observed in all the experimental runs indicating the absence of any reductive reaction.

For the samples, Zn1:5 and Zn1:7, 1% and 1.9% of deposition was observed which was opposite to the values of dark adsorption, which were highest for these two samples.

It is reported that the direct reduction of zinc by the photo-generated TiO<sub>2</sub> electrons is prohibited thermodynamically [30]. Therefore, some indirect routes have been suggested for zinc reduction through the formation of an organic radical species which could reduce the metal ion [31].

### 3.2.4. Dark adsorption and photodeposition of Pb(II)

Pb(II) is deposited either as a complex or as a free ion on the catalyst surface. Chenthamarakshan et al. [17] suggest that Pb(II) can participate in both oxidative and reductive reactions of photocatalysis.

Fig. 7 shows the trends of dark adsorption of Pb(II). The dark adsorption was lowest in absence of citric acid. 22.4% Pb(II) was found to adsorb on the photocatalyst surface. On adding citric acid, the adsorption value increased to nearly double. 43% adsorption was obtained for Pb1:1. However, on increasing the citric acid concentration further, no significant change in adsorption value was observed. The adsorption was 43.6%, 42.1% and 43.5%, respectively, for Pb1:3, Pb1:5 and Pb1:7. It can be interpreted that the adsorption of Pb(II), attained a maximum value and did not increase further on increasing organic compound.

Fig. 7 also depicts the deposition of Pb(II). It can be observed that the values of adsorption and deposition were quite close. Minimum deposition of 27.8% was obtained in absence of citric acid. On citric acid addition this was increased to 42.9% for Pb1:1.

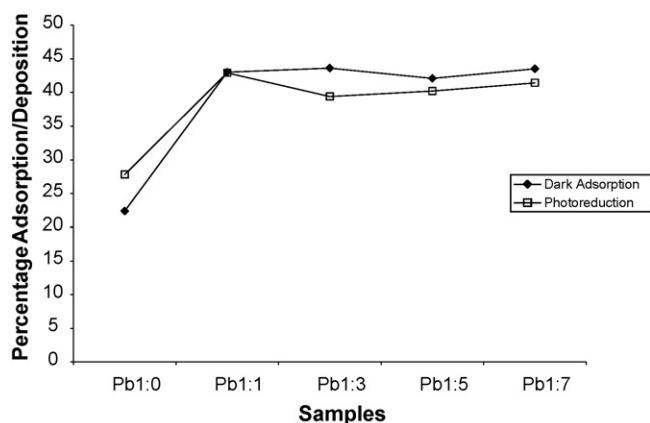


Fig. 7. Dark adsorption and photocatalytic deposition of Pb(II) for different samples (initial metal concentration =  $20 \text{ mg L}^{-1}$ , citric acid = variable,  $\text{TiO}_2 = 2 \text{ g L}^{-1}$ ).

The deposition values obtained for Pb1:3, Pb1:5 and Pb1:7 were 39.4%, 40.2% and 41.4%, respectively. The rate of deposition was very slow. The given percentage values were obtained for deposition in 8 h of solar exposure.

The values being close to adsorption values, suggest that the deposition of Pb(II) was not a reductive or oxidative deposition as suggested by Tanaka et al. [32].

### 3.3. Comparative removal of Cu(II), Ni(II), Pb(II) and Zn(II)

Initial reaction rates, determined for the deposition of these metal ions are shown in Fig. 8. The values show that copper was the only metal, which reduced significantly in two hours of solar exposure. The deposition of Pb(II), Zn(II) and Ni(II) was a kinetically slow process due to less thermodynamic driving forces of these metal ions.

Comparison of percentage deposition at different citric acid concentrations show that the decreasing order of deposition in absence of citric acid was  $\text{Cu(II)} > \text{Ni(II)} > \text{Pb(II)} > \text{Zn(II)}$ . In presence of citric acid, the trend was  $\text{Cu(II)} > \text{Pb(II)} > \text{Zn(II)} > \text{Ni(II)}$ .

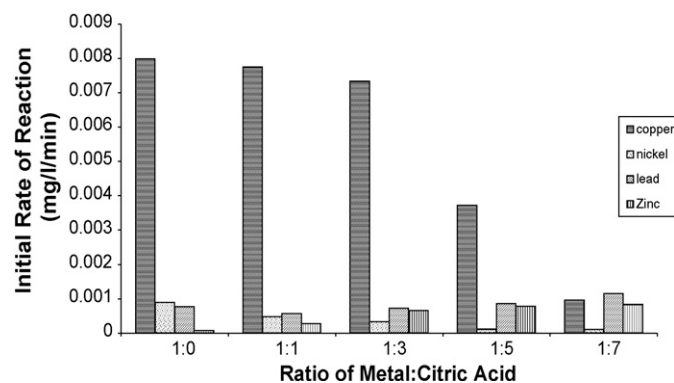


Fig. 8. Comparative initial rate of photodeposition of Cu(II), Ni(II), Zn(II) and Pb(II) on  $\text{TiO}_2$  surface for different samples (initial Metal concentration =  $20 \text{ mg L}^{-1}$ , citric acid = variable,  $\text{TiO}_2 = 2 \text{ g L}^{-1}$ ).

## 4. Conclusions

The major conclusions of the study can be summarized as follows:

1. Ninety-seven percent reductive deposition was obtained for copper. The values of deposition of other metals were significantly lesser [nickel (36.4%), zinc (22.2%) and lead (41.4%)] indicating that the photocatalytic treatment process, using solar energy, was more suitable for wastewater containing Cu(II) ions.
2. Adsorption of copper and nickel decreased with increasing citric acid concentration, zinc adsorption increased with citric acid concentration, whereas lead attained a maximum value which remained almost constant for all the citric acid concentrations.
3. Photocatalytic reduction was most effective for deposition of copper. Reduction of nickel was a slow process and zinc and lead were not possibly reduced but only adsorbed on the catalyst surface.
4. The order of deposition obtained in absence of citric acid,  $\text{Cu(II)} > \text{Ni(II)} > \text{Pb(II)} > \text{Zn(II)}$ , prove the theoretical thermodynamic predictions about the metals. In presence of citric acid, the metals behave differently due to complexation. The complexes were stable and resisted photoreactions.

## Acknowledgements

The authors are thankful to the Ministry of Non-Conventional Energy Sources, New Delhi, India, for providing the financial support for the research.

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