

Effect of pH on solar photocatalytic reduction and deposition of Cu(II), Ni(II), Pb(II) and Zn(II): Speciation modeling and reaction kinetics

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Abstract

The present study is targeted on the effect of pH 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 TiO₂, has been investigated at pH values 2, 4, 7, 8 and 10. Modeling of metal species at the studied pH values has been performed and speciation is used as a tool for discussing the photodeposition. The decreasing order of metal deposition at pH 2 and 4 was found to be Pb(II) > Cu(II) > Ni(II) \cong Zn(II). In the neutral and alkaline pH conditions (pH 7, 8 and 10) the order was Cu(II) > Zn(II) > Ni(II) > Pb(II).

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1. Introduction

pH is a crucial factor for designing a solar photocatalytic wastewater treatment facility. It not only influences the surface charge properties of the photocatalyst used (like TiO₂ in this study), but also pollutant adsorption on the photocatalyst surface. The amount of sludge generated in the wastewater treatment facility is also dependent on pH. Additionally, the final discharge pH of treated wastewater is a mandatory regulatory requirement, making it an important parameter for wastewater treatment.

In case of metal treatment, study of pH is even more relevant because the speciation of some of the metals and metal complexes are altered at different pH values, thereby changing their toxicity. Additionally, adsorption plays an important role in photocatalytic reduction of metal ions. Metal adsorption is usually strongly pH-dependent and a function of metal complex formation and ionic strength. Therefore, a detailed study of effect of pH is necessary in order to optimize photocatalytic reduction of metal ions.

Very few studies have been performed on pH variation in photocatalytic reactions. A study [1] on Cu(II) photodeposition and oxidation in presence of TiO₂ showed reversible photore-

duction and deposition in pH range 1.84–6.60. Another study on the treatment of EDTA (ethylenediamine tetraacetic acid) and its metal complexes using photocatalysis, performed by Madden et al. [2] showed that the degradation of EDTA was enhanced at lower pH (pH 4). The thermodynamic aspects of the photocatalytic reduction of Cr(VI) on TiO₂ were discussed and contrasted for pH 0 and pH 10 aqueous media by Lin et al. [3]. They concluded that the thermodynamic driving force for Cr(VI) reduction on TiO₂ in basic aqueous solutions was less than that in acidic media. They also found hole transfer to be thermodynamically more favorable than photocorrosion of TiO₂ in basic media.

In this study, solar photodeposition of toxic metals species Ni(II), Cu(II), Zn(II) and Pb(II) has been investigated at different pH values. Geochemical modeling is used as a tool for predicting the metal speciation. The major objective is to determine the effective photocatalytic removal of Ni(II), Cu(II), Zn(II) and Pb(II) in acidic, neutral and alkaline wastewaters.

2. Materials and methods

Photocatalytic and dark adsorption experiments were performed at pH values 2, 4, 7, 8 and 10 to observe the influence of pH. The pH ranges, acidic, neutral and alkaline were selected so as to ensure the best pH suitable for reduction.

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2.1. Experiment

The experiments were performed using synthetically prepared wastewater containing metal ions Cu(II), Ni(II), Zn(II) and Pb(II) in an initial concentration of 20 mg l^{-1} . The metal salts, CuSO_4 , NiCl_2 , ZnSO_4 , and $\text{Pb}(\text{NO}_3)_2$ (all Merck) were 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. The quantity of citric acid was fixed to 140 mg l^{-1} . After addition of citric acid to the wastewater, the pH values were adjusted to 2, 4, 7, 8 and 10 in different experiments. No attempt was made to maintain these pH values thereafter. Sodium hydroxide and sulphuric acid were used to adjust the pH of the wastewater. Photocatalyst TiO_2 (Merck) was added to the wastewater after pH adjustment. Dose of TiO_2 was fixed to 2 g l^{-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. 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 to 750 ml min^{-1} . 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. TiO_2 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 h to 17 h.

The adsorption studies were carried out in the dark to study the adsorption of metal ion on the TiO_2 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.

2.2. Analysis

Initial metal ion 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. The metal concentration was analyzed using Atomic Absorption Spectrophotometer (Shimadzu AA 6300). pH, tem-

perature 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 MINTEQ model 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.

Visual MINTEQ 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 pH values were fixed to the 2, 4, 7, 8 and 10 (pH values at which experiments were performed) separately and the species were determined.

3. Results and discussions

Thermodynamically the reduction of Ni(II), Cu(II), Pb(II) and Zn(II) is favored in the alkaline pH range. The results obtained were close to the theoretical thermodynamic predictions. However, another consideration was the surface of TiO_2 , which has a point of zero charge value around pH 7 as reported by a number of authors [4,5]. Below this pH, the TiO_2 surface has a net positive charge and above this pH, it has a negative charge. 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 photoreaction product formed, would decide whether it remains deposited on the catalyst surface or is desorbed.

3.1. Speciation determination by modeling

Modeling was performed for the synthetic wastewater mixes, on which actual experiments were carried out. A fixed concentration of metal ions Cu(II), Ni(II), Zn(II) and Pb(II) (20 mg l^{-1}) and citric acid (140 mg l^{-1}) was used. pH was variable. The species of these metals were modeled at pH 2, 4, 7, 8 and 10 to study the citric acid complexation of these metals. The speciation results determined by modeling for metal ions Cu(II), Ni(II), Zn(II) and Pb(II) are depicted in Figs. 1–4, respectively.

At pH 2, all the studied metal ions Cu(II), Ni(II), Zn(II) and Pb(II) were found to exist in their cationic forms indicating no complexation with citric acid.

At pH 4, the complexation was maximum for copper (nearly half was complexed forming citrates of Copper). About 20–30% Nickel and Zinc was complexed. But negligible complexation was observed for Pb. At pH 7 and 8, nearly 65% of all the metal ions were complexed with the exception of Pb, which showed nearly 90% of complexation.

At pH 10, Cu, Zn and Pb were converted to their hydroxides in a significant percentage, however Ni speciation

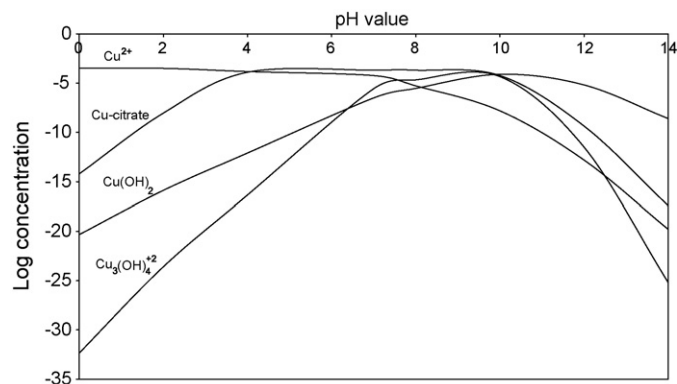


Fig. 1. Speciation of Cu(II) in presence of citric acid at different pH values determined by Minteq model (Initial concentration of metal = 20 mg l^{-1} , citric acid concentration = 140 mg l^{-1}).

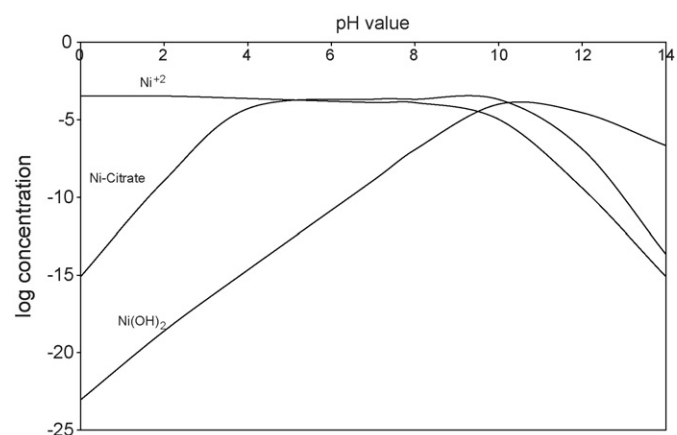


Fig. 2. Speciation of Ni(II) in presence of citric acid at different pH values determined by Minteq model (Initial concentration of metal = 20 mg l^{-1} , citric acid concentration = 140 mg l^{-1}).

showed a majority of citrates indicating a stable complexation.

The complexation of all metal ions is found to increase with pH value up to pH 8, except for Pb, which shows an anomalous behavior at pH 4 showing very little complexation.

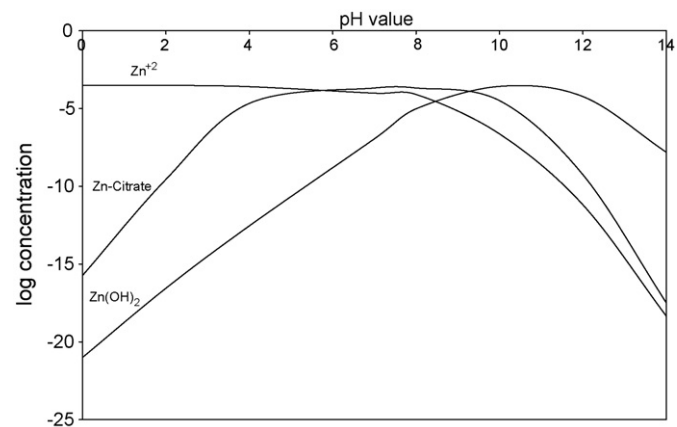


Fig. 3. Speciation of Zn(II) in presence of citric acid at different pH values determined by Minteq model (Initial concentration of metal = 20 mg l^{-1} , citric acid concentration = 140 mg l^{-1}).

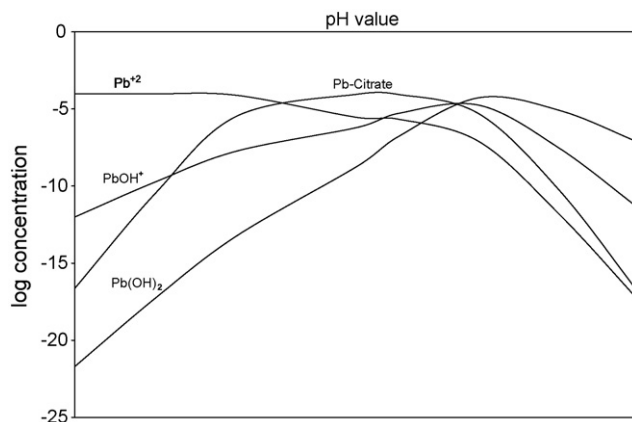


Fig. 4. Speciation of Pb(II) in presence of citric acid at different pH values determined by Minteq model (Initial concentration of metal = 20 mg l^{-1} , citric acid concentration = 140 mg l^{-1}).

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.

3.2. Experimental results

The pH of the wastewater not only affects the metal speciation but also the surface charge of TiO_2 . Therefore, these two factors jointly determine the fate of adsorption and photocatalytic deposition of the metal. The synthetically prepared wastewater was exposed to solar radiation in different experiments at pH values 2, 4, 7, 8 and 10. The change of pH, solar irradiance and temperature is reported in Table 1

The average value of solar irradiation was nearly same for all the pH experimental runs because the experiments were carried out on similar days or days of a month with nearly constant solar irradiations. It is in the range of $705\text{--}862 \text{ W/m}^2$, which is an average value of solar irradiation data collected for the 8 h of experimental runs during a day (Table 1).

3.2.1. Dark adsorption and photodeposition of Cu(II)

The dark adsorption values of copper are presented in Fig. 5. Adsorption of copper was found to increase with increasing pH values but the overall adsorption values were minimal. No adsorption was observed at pH 2, which increased to merely 0.4% at pH 4. At pH 7 and 8, 1.2% and 3.6% of copper respectively was found to adsorb. The maximum adsorption of 7.7% was obtained for pH value 10.

The reason for low adsorption values could be the different species predominating at different pH values. In the acidic range low adsorption values were justified as the Cu^{2+} ions was the dominant species (Fig. 1), which was repelled by positively charged TiO_2 . At pH 7 and 8, the major species was the anionic Cu-citrate, which again did not have an affinity for the negatively charged TiO_2 surface above pzc.

The major differences in the values of dark adsorption and photoreaction (Fig. 5) show that the reduction of copper from

Table 1
Solar irradiation (average of 8 h), pH and maximum temperature attained for experimental runs at different pH values

Metal	pH	Initial pH value	Final pH value	Average solar irradiation (W/m ²)	Maximum temperature attained (°C)
Cu(II)	2	2	1.9	862	54
	4	4	5.2	705	54
	7	7	7.5	767	52
	8	8	7.8	767	52
	10	10	8.8	767	52
Ni(II)	2	2	2	855	54.5
	4	4	5.8	847	51
	7	7	7.6	828	52.5
	8	8	7.7	828	52.5
	10	10	8.9	825	52.5
Pb(II)	2	2	1.8	780	51
	4	4	6.1	824	52
	7	7	7.4	786	51.5
	8	8	7.8	786	51.5
	10	10	9.1	786	51.5
Zn(II)	2	2	2	780	51
	4	4	5.4	824	52
	7	7	7.3	786	51.5
	8	8	7.6	786	51.5
	10	10	9.0	780	52

the wastewater is not merely due to adsorption but it is due to reductive deposition. The percentage reduction value at pH 2 was just 10.2%. This showed that in acidic pH conditions the thermodynamic driving force for metal reduction is significantly low.

At pH 4, the values of reduction increased to 65%. For pH 7, 8 and 10, the percentage reduction further increased to 99%, 95% and 82%, respectively. The speciation of copper obtained for the pH 7 and 8 shows that the Cu-citrate species was predominating for these pH values. The complexation of copper with citric acid, favored the reduction of copper due to decreased electron hole recombination. At pH 10, again the concentration of Cu-citrate decreased which can be accounted for the decreased (82%) values at this pH, as compared to pH 7 and 8. It is reported [6] that the reductions of Cu(II,I), Cu(I,0) and Cu(II) couples are more favorable with increasing pH.

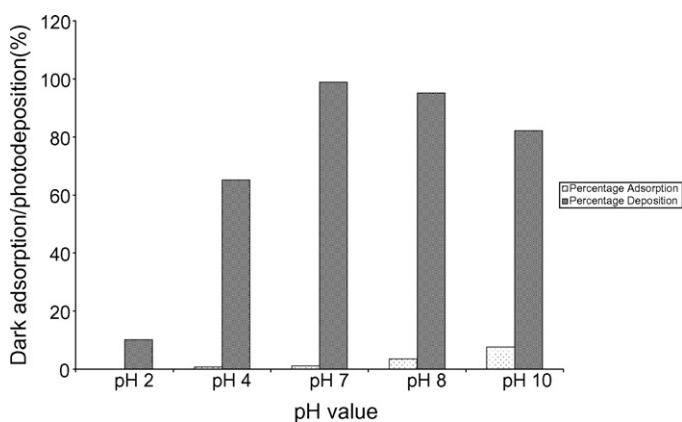


Fig. 5. Percentage dark adsorption and photodeposition of Cu(II) at different pH values (Initial concentration of metal = 20 mg l⁻¹, citric acid concentration = 140 mg l⁻¹, TiO₂ = 2 g l⁻¹).

3.2.2. Dark adsorption and photodeposition of Ni(II)

The dark adsorption of nickel was maximum at pH 7 (Fig. 6). After pH 7, it was found to decrease for pH 8 and 10. No adsorption was obtained at pH 2 and 4. The species Ni²⁺ that predominates at these two pH values does not adsorb on TiO₂ due to similar charges. Additionally, the neutral NiH-citrate found at pH 4, also does not have a proclivity for TiO₂ surface.

The maximum adsorption of 30.7%, obtained at pH 7 was possibly contributed more by cationic Ni²⁺ ion. A decrease in adsorption of 28.2% and 21.3% was observed at pH 8 and 10 showing that the adsorption at pH 7 was again of Ni²⁺ species, the percentage of which decreased at pH 8 and 10. At these two pH values the Ni-citrate ion present was repelled by TiO₂ surface due to identical charges.

The photodeposition values were found to increase with increasing pH values but the percentage deposition was slightly

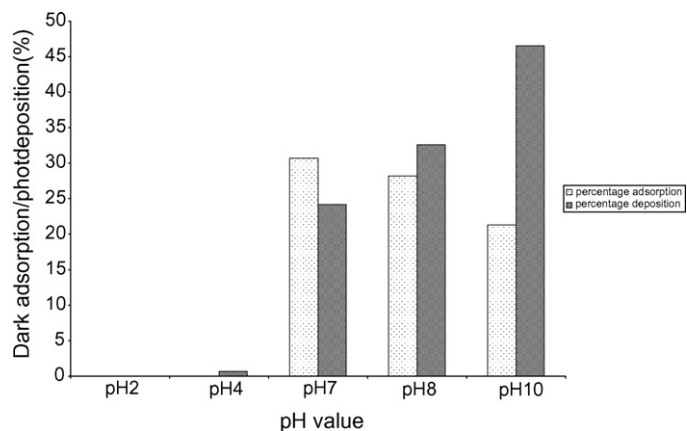


Fig. 6. Percentage dark adsorption and photodeposition of Ni(II) at different pH values (Initial concentration of metal = 20 mg l⁻¹, citric acid concentration = 140 mg l⁻¹, TiO₂ = 2 g l⁻¹).

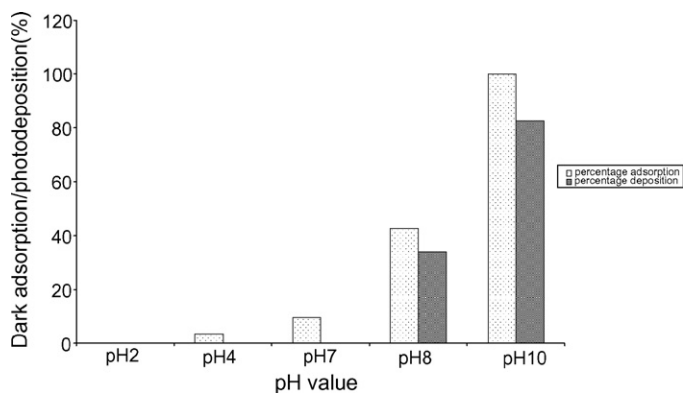


Fig. 7. Percentage dark adsorption and photodeposition of Zn(II) at different pH values (Initial concentration of metal = 20 mg l^{-1} , citric acid concentration = 140 mg l^{-1} , $\text{TiO}_2 = 2 \text{ g l}^{-1}$).

different from the adsorption values. As expected, no photodeposition at pH 2 and 0.7% at pH 4 was observed (Fig. 6). Low adsorption values and lesser thermodynamic force were the probable reasons for this.

The trend of Ni(II) deposition showed increasing percentage with pH but the overall deposition of nickel on TiO_2 was very less. The values increased to 24.2%, 32.6% and 46.5% for pH 7, 8 and 10, respectively. The lesser reduction rates can be attributed to the low thermodynamic driving force for nickel due to its lower reduction potential.

3.2.3. Dark adsorption and photodeposition of Zn(II)

The results of dark adsorption for Zn(II) are depicted in Fig. 7. No adsorption of Zn(II) on TiO_2 was observed at pH 2. The adsorption value increased to 3.5% at pH 4. This adsorption was due to the anionic Zn-citrate adsorption on TiO_2 surface due to attraction of opposite charges. At pH 7, 9.6% Zn(II) was adsorbed as the surface charge of TiO_2 was negative at and above this pH value. At pH 8, significant increase of 42.6% was seen and at pH 10, 95% of Zn(II) was adsorbed. The high proclivity of Zn-citrate and neutral $\text{Zn}(\text{OH})_2$ were the reasons for the high adsorption values.

The percentage photodeposition of Zn(II) is also depicted in Fig. 7. No deposition of Zn(II) is obtained at pH 2, 4 and 7, closer to the adsorption trends. It indicates that even the minimally adsorbed Zn(II) at pH 4 and 7 was desorbed possibly due high reaction temperature. The deposition at pH 8 was 34.1%, which was significantly increased at pH 10 to 82.5%. These values were quite similar to the adsorption values indicating that the deposition of zinc was possibly not reductive but only due to adsorption.

The color change of catalyst to grey, as observed by Meshkov et al. [7] was also not seen in this study showing that the deposition was merely adsorption and not photoreduction. The lower values of deposition as compared to adsorption further indicate that some of the Zn(II) was desorbed due to weaker surface bonding.

3.2.4. Dark adsorption and photodeposition of Pb(II)

Significant adsorption of Pb(II) was obtained in the acidic pH range with a maximum at pH 4 in all the pH values stud-

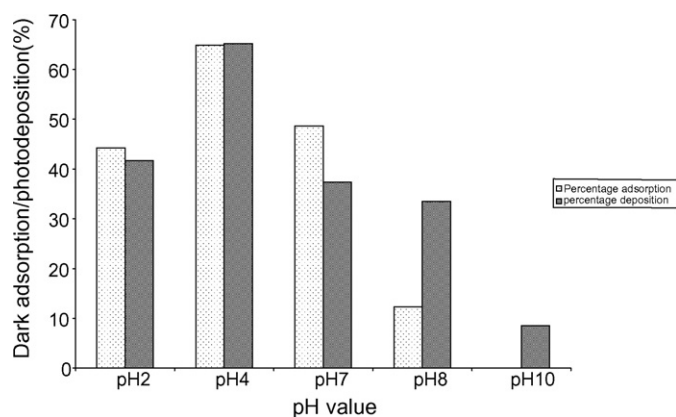


Fig. 8. Percentage dark adsorption and photodeposition of Pb(II) at different pH values (Initial concentration of metal = 20 mg l^{-1} , citric acid concentration = 140 mg l^{-1} , $\text{TiO}_2 = 2 \text{ g l}^{-1}$).

ied (Fig. 8). 44.2% adsorption was obtained at pH 2. At pH 4 this increased to 64.9%. After this pH, the adsorption started decreasing. At pH 7, 48.6% of Pb(II) was adsorbed, which further decreased to 12.3% and finally no adsorption occurred at pH 10.

The photodeposition mirrored the adsorption trend. The values of deposition were also similar to that of dark adsorption in most of the cases (Fig. 8). 41.7% deposition was obtained for pH 2. 65.2% deposition, which was the maximum deposition among all pH values, was obtained for pH 4, similar to that of adsorption. Lawless et al. [8] also reported that Pb(II) dispersions at a pH of 3.7 were optimal for use of Pt/ TiO_2 photocatalyst in the absence of hole scavengers.

The deposition values then decreased to 37.4% at pH 7 and further to 33.5% at pH 8. A minimum deposition of 8.5% was observed at pH 10. The behavior of Pb(II) was unlike that observed for Ni(II), Zn(II) and Cu(II). However, the resemblance of dark adsorption and photodeposition values indicates the deposition to be non-reductive and merely adsorptive.

4. Conclusions

The major conclusions of this study are as follows:

- (1) The photodeposition of Pb(II) is favorable at pH 4 whereas that of Cu(II), Ni(II), Pb(II) and Zn(II) is favorable in the alkaline condition.
- (2) The acidic pH values are found to be suitable for photoreduction/deposition of metals in the order $\text{Pb}(\text{II}) > \text{Cu}(\text{II}) > \text{Ni}(\text{II}) \cong \text{Zn}(\text{II})$. In the alkaline pH (pH 7 and above 7) the order is $\text{Cu}(\text{II}) > \text{Zn}(\text{II}) > \text{Ni}(\text{II}) > \text{Pb}(\text{II})$.
- (3) For Cu(II), maximum photodeposition occurred at pH 7, which is a usual pH of wastewater. Therefore, not much of the pH adjustment would be required for removal of Cu(II). For removal of Ni(II) and Zn(II) alkaline pH 10 is found to be most suitable but the overall removal is low. Some other modified conditions (like catalyst doping) should be used for effective photocatalytic removal of these metal ions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jhazmat.2007.04.028](https://doi.org/10.1016/j.jhazmat.2007.04.028).

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