

Photocatalytic Removal of Zinc (II) in UV -Irradiated Titania Suspensions

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Abstract:The photocatalytic reduction of zinc(II) in aqueous suspensions of TiO₂ on UV illumination was investigated. Synthetic wastewater containing zinc with an initial concentration of 160 mg/L was used in this study. The zinc removal efficiency is reported respectively as a function of solution pH, mass of TiO₂, hole scavenger species and reactor types. It was found that direct photoreduction removed very little zinc (II) due to its negative reduction potential compared to the conduction band edge potential of TiO₂. The studied hole scavengers (formate and acetate ions) played a major role in reducing zinc (II) from synthetic wastewater. The best condition found to decrease the zinc (II) concentration to lower than the standard level (5 mg/l) was at pH 1.6 with a TiO₂ loading of 20 g/l and 1 M of formate ions. This system successfully removed zinc in the quartz reactor within 5 hours reaction time. Results from this study may be beneficial to zinc (II) removal from industrial wastewater.

Keywords: Zinc (II) removal, photocatalysis, titanium dioxide, TiO₂, heavy metal removal.

Introduction

There has been a tremendous amount of interest in semiconductor photocatalysis for the past two decades and much background information is available in the literature [1-3]. It is a well-known fact that a wide variety of organic and inorganic toxic chemicals can be oxidized or reduced by heterogeneous photocatalysis using TiO₂ as a catalyst. Upon illumination of the semiconductor-electrolyte interface with light of energy higher than the semiconductor band gap, electron-hole pairs (e-h⁺) are formed in the conduction and valence bands of the semiconductor, respectively. These charge carriers, which migrate to the semiconductor surface, are capable of reducing or oxidizing pollutant species in solution having suitable redox potential

Even though there has been a huge amount of work done regarding the kinetics and photocatalytic mineralization of organic pollutants, studies related to the inorganic species, particularly heavy metal ions, are rather limited [4-5]. Little research investigates the removal of metals, which are hardly reduced by photocatalytic process due to their relatively negative redox potential compared to the conduction band edge potential of TiO₂. The metal species that fall into this category are Zn, Cd, Tl and Ni. In the present study, we investigated the photocatalytic conditions that afford facile conversion of Zinc (II) ions in UV -irradiated TiO₂ aqueous suspensions.

Methods

All chemicals were reagent grade or better and were used as received. The TiO₂ (Degussa P-25) was predominantly anatase and had a specific surface area of ~60 m² g⁻¹. Figure I shows a schematic of the photoreactor which was employed in this study. A 10 W low-pressure Hg UV-lamp was used as the radiation source. A glass reactor was the major photoreactor used in this study, except when otherwise specified. This reactor consisted of two compartments, the outer for containing wastewater and the inner for housing a UV lamp. The inner compartment was water-jacketed to maintain the solution temperature at 25°C for all tests, and equipped with a magnetic stirrer.

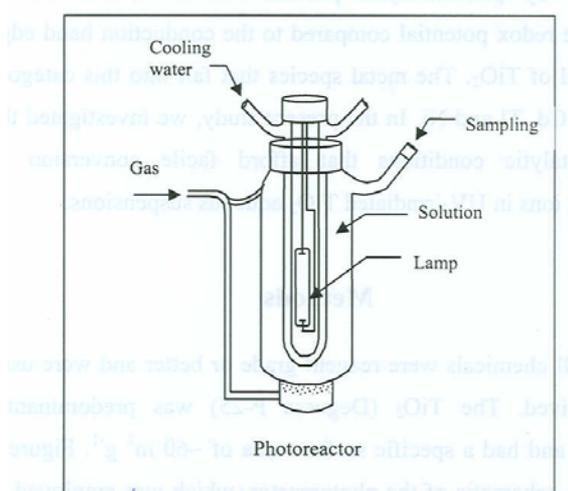


Figure 1. A chematic of the photoreactor employed in this study.

The concentration of TiO_2 was nominally 20 g/L, unless otherwise specified. Synthetic wastewater containing zinc (II) ions was simulated following the real chemical solution used in electroplating wastewater. Zinc ions were obtained from zinc oxide (Merck) and zinc chloride (Merck) in addition to ammonium chloride (Merck) with the ratio of $\text{ZnO}:\text{ZnCl}_2:\text{NH}_4\text{Cl}$ as 1:2:5. The initial concentration of zinc (II) in all experiments was 160 mg/l. The wastewater loaded TiO_2 suspensions were equilibrated in the dark for 2 hours (see dark adsorption results). After the equilibration period, the ultraviolet light (UV) was turned on and the solution was syringed out periodically. The solution was sampled at various times during each experiment by withdrawing milliliters of aliquots and removing the suspended catalyst by filtration. All the samples were covered by aluminum paper to avoid sunlight illumination. The solution pH was adjusted using NaOH (basic range) from and H_2SO_4 (acidic range). All experiments were accomplished at normal temperature ($25\pm 2^\circ\text{C}$). Zinc concentrations for all experiments were measured by an Atomic Absorption Spectrophotometer (Hitachi, Model Z9000).

Results and Discussion

Dark adsorption of chromium on titanium dioxide surface

Zinc (II) adsorption at different pH values was examined as a function of time to obtain the equilibration time prior to irradiation. The results of this set of experiments (get are shown in Figure 2. It is important to note that the ordinate value at time zero represents the amount of zinc (II) in solution after the precipitation period. For all experiments in this set, the loaded TiO_2 was 3 g/l and the initial concentration of zinc (II) was 160 mg/l. At the beginning of the experimental period, the precipitation of zinc at pH higher than 5 was obviously pronounced. The maximum adsorption amounts of zinc (II) were read when the system reached the equilibrium period, which was at 120 minutes. Apparently adsorption exerted a small effect on zinc removal from the studied wastewater.

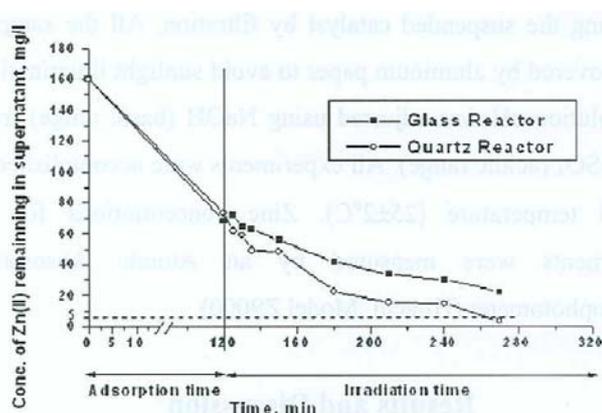


Figure 2. The equilibrium adsorption of Zinc(II) at different pH with 3g/l of loaded TiO_2 .

Effect of pH on Zn (II) removal by photocatalytic process

A series of experiments was conducted to investigate the removal efficiency of zinc(II) in different pH solutions. Figure 3 shows the results of zinc reduction after 120 minutes adsorption and 180 minutes irradiation.

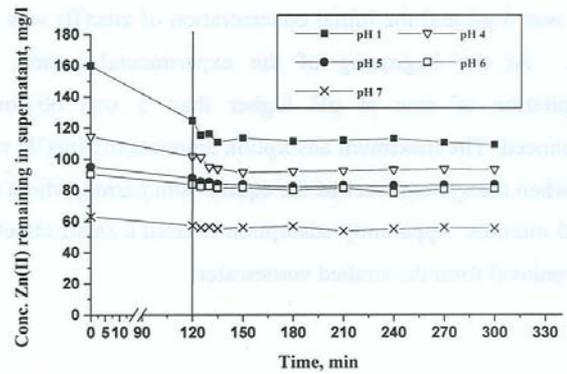
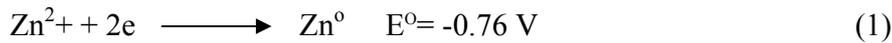


Figure 3. Photocatalytic reduction of Zinc(II) at different pH using 3 g/l loaded- TiO₂.

As seen from the graph, zinc (II) removal was mainly the result of the adsorption process during the first 120 minutes. Compared with the earlier result, the irradiation process exhibited less effect on the zinc removal. Apparently, there tends to be minimal removal by this UV-irradiated titania suspension over all ranges of solution pHs. This behavior might be explained by considering the thermodynamics of the photocatalytic reaction. The redox potential level to reduce the oxidation state from divalent to zero-valent can be shown as:



The position of this redox potential lies above the flat band of TiO₂ as seen in Figure 4. In this case, electrons generated by the conduction band of TiO₂ are hardly transferred to the zinc ions. The photoreduction of zinc might not be possible. This phenomenon suggests that the adsorption process is likely to be the key mechanism of zinc decrease in this system rather than the irradiation process.

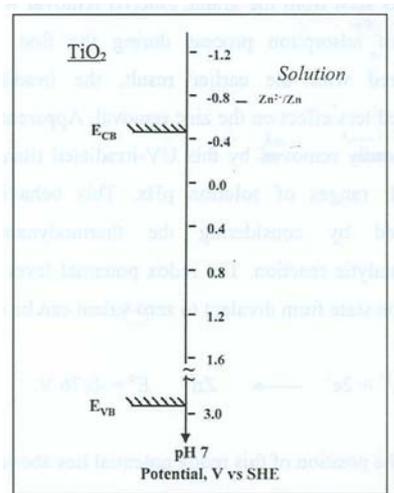


Figure 4. Redox potential of Zinc(II)/Zn compared to conduction band edge potential of TiO₂.
Effect of loaded- TiO₂ on Zinc (II) removal by photocatalytic process

Figure 5 shows the effect of loaded-TiO₂ on the photoreduction of Zinc(II). It is apparent that the removal of the zinc(II) ions was remarkably affected by the different amounts of TiO₂ particles in the solution during the equilibrium period. However, there was little change in zinc concentration during the irradiation period. It is also found that the adsorption of zinc(II) increased in proportion to the increasing amounts of TiO₂ added to the solution. However from experimental observation, it is worth noting that an excess TiO₂ causes a reduction in removal efficiency due to the inhibition of light scattering caused by TiO₂ itself.

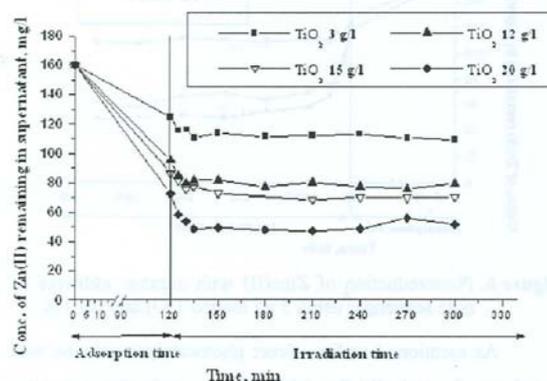


Figure 5. Direct photoreduction of Zinc(II) using different amounts of TiO₂ at pH1.

Effect of hole scavengers on Zinc(II) removal by photocatalytic process

Figure 6 shows the effect of hole scavengers on the photoreduction of Zinc(II). In this study, the hole scavengers were formate and acetate ions. Formate ions were obtained from formic acid (HCOOH), while acetate ions were obtained from acetic acid (CH₃COOH). The solution pH after adding these ions was 1.6. No precipitation was seen in this region.

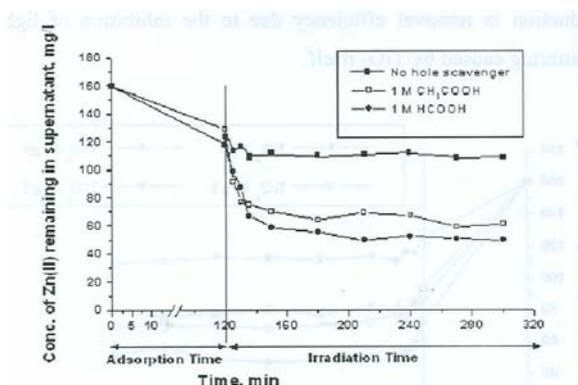


Figure 6. Photoreduction of Zinc(II) with organic additives as hole scavengers using 3 g/l loaded TiO₂ and pH 1.6.

As mentioned earlier, direct photocatalysis of zinc was not thermodynamically favorable for zinc reduction in water. When hole scavengers were presented into the system, the photoreduction of zinc(II) was improved. The role of this addition of hole scavengers can be described in that these ion species serve to intercept hole carriers which maintains the photooxidation process. With this conjugate reaction, the recombination of electron-hole pairs is inhibited. A second explanation on

the influence of organic additives (which has also been discussed by previous authors [6]) describes how the formate and acetate ions, which are anchor species, presumably capture the photogenerated holes from TiO_2 resulting in the transfer of the needed electrons to the bound metal ions to complete the photocatalytic reduction reaction. To confirm this reaction pathway, we also measured the reduction of COD with the assumption that if formate was employed as expected, the COD of the solution should be decreased from the original value. As evidence, the supernatant COD decreased quite remarkably. These findings support the proposal that hole scavengers might enhance the efficiency of the zinc(II) photocatalytic reduction.

Effect of reactor materials on Zinc(II) removal by photocatalytic process

To study the effect of reactor materials, two types of reactor were used in this study. As mentioned in the experimental section, all earlier experiments were performed using a glass reactor. For this experimental set, a quartz reactor was used to investigate the photoreduction of Zinc(II) to compare its efficiency with that obtained from the glass reactor. Results of this experimental set are shown in Figure 7. This experiment set was conducted with 20 g/l of loaded TiO_2 using 1 M of formate ions as hole scavengers and was performed at pH 1.6.

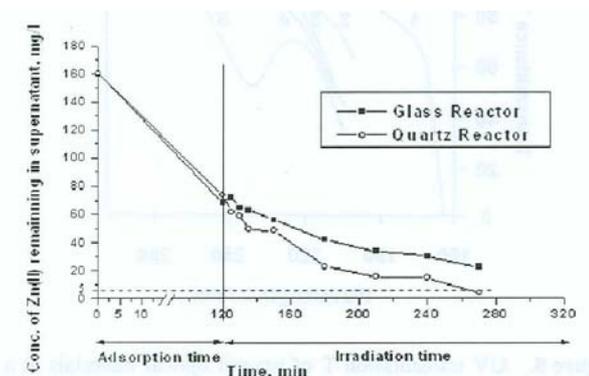


Figure 7. Photoreduction of Zinc(II) using glass and quartz reactors.

With irradiation of 20 g/l of TiO_2 assisting formate ions as hole scavengers in a quartz reactor, zinc(II) was drastically reduced to low concentrations and to even lower than 5 mg/l, which is the standard level for treated industrial wastewater for environmental discharge. This achievement could be found with prolonged irradiation in the quartz reactor. It is anticipated that the glass reactor could also achieve this accomplishment with a longer irradiation period than quartz. The difference in the efficiency of both types of reactor arises from the transmission spectra of different types of glass as seen in Figure 8. The internal transmittance also decreases with increasing thickness according to the Beer-Lambert law [7]. For this zinc(II) removal, both reactors "can be used effectively" for the photoreduction process with different reaching times.

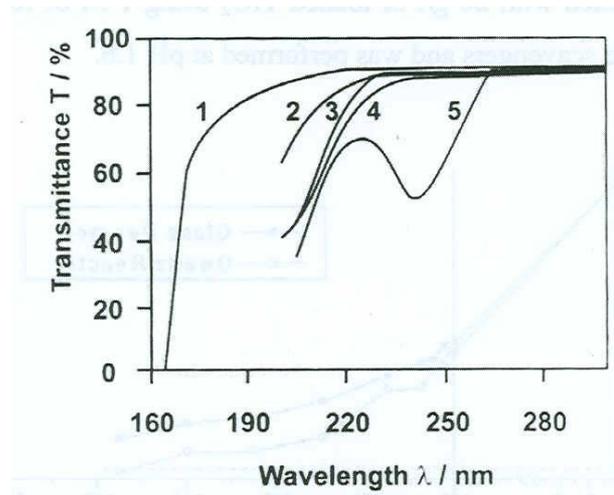


Figure 8. UV transmission T of several optical materials at a thickness of 10 mm (1 = Suprasil quartz; 2= quartz; 3=Ultrasil; 4= Infrasil; 5=Optisil, adapted from [7]).

Conclusions

The major findings of this study are as follows:

- Direct photoreduction is not favorable for zinc(II) removal due to its negative potential.
- Adsorption of zinc(II) plays a major role in zinc(II) removal in the direct photocatalysis process.
- Addition of hole scavengers (e.g., formate and acetate ions), drastically increases zinc(II) removal efficiency. This finding suggests the most effective conditions to remove zinc(II) from the studied wastewater.
- The different reactor materials, glass and quartz, do not effect the decreased amount of the zinc(II) removal. Both types of reactors can achieve the same efficiency in different periods.

Acknowledgement

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