

Enhanced Photocatalytic Reduction of Hg(II) in Aqueous Medium by 2-Aminothiazole-Modified TiO₂ Particles

Valtair M. Cristante,^a Adriana B. Araujo,^a Sônia M. A. Jorge,^b Ariovaldo O. Florentino,^b José P. S. Valente^{*,b} and Pedro M. Padilha^b

^aInstituto de Química, Universidade Estadual Paulista, 14800-900 Araraquara-SP, Brazil

^bInstituto de Biociências, Universidade Estadual Paulista, 18618-000 Botucatu-SP, Brazil

Este trabalho descreve a síntese e caracterização da titânia modificada pelo ligante 2-aminotiazol e sua aplicação na foto-redução de íons Hg (II) em meio aquoso. Espectros obtidos na região do infravermelho confirmaram a modificação química da matriz de titânia. A quantidade de grupos 2-aminotiazol ligados à superfície da titânia foi determinada por meio da análise de nitrogênio, utilizando-se o método de Kjeldahl. Todos os experimentos de foto-redução foram feitos em um foto-reator cilíndrico termostatizado a 298 K. O catalisador modificado, 2-aminotiazol titânia (TiAT), apresentou maior capacidade de foto-redução dos íons Hg(II) nos valores de pH estudados (3, 7 e 9). Além disso, os estudos de sorção mostraram que o TiAT apresentou um menor tempo de equilíbrio e uma maior capacidade de sorção dos íons Hg(II), demonstrando que o processo de sorção desempenha um papel fundamental no mecanismo de foto-redução.

This work describes the synthesis and characterization of 2-aminothiazole-modified titania and its application on Hg (II) photoreduction in aqueous medium. Infrared spectroscopy confirmed the chemical modification of the titania matrix. The number of 2-aminothiazole groups attached to the titania was determined by Kjeldahl's method. The photocatalytic experiments were carried out in a cylindrical photoreactor thermostatted at 298 K. The resulting modified photocatalyst 2-aminothiazole titania (TiAT) revealed an enhance in the Hg (II) photoreduction capacity at studied pH values (3, 7 and 9). In addition, sorption studies showed that the photocatalyst TiAT presented a lower equilibrium time and a higher sorption capacity of Hg(II) ion, demonstrating that sorption plays a fundamental role in the photoreduction mechanism.

Keywords: TiO₂, 2-aminothiazole, photocatalysis, 3-chloropropyltrimethoxysilane

Introduction

For the past few decades, growing interest has been demonstrated in mercury treatment in aqueous medium due to its toxic, bioaccumulative properties and because of its resistance to biological or chemical degradation in the environment, as is the case of many organic pollutants (e.g. phenol and its derivatives).^{1,2} Mercury and its compounds are often converted by bacteria to more toxic species, such as methylmercury, representing a potential risk to human health and to fish-consuming animals.³ The major source of mercury pollution in aquatic environments is industrial and consists of products such as chloralkali,

paint, catalysts used in the metallurgical, pharmaceutical, chemical and petrochemical industries, in electronics, cosmetics, thermometers, gauges, and batteries, as well as agricultural products such as pesticides, fungicides, herbicides, insecticides and bactericides.⁴

Various physical and chemical methods have been used in the removal of mercury from water and wastewater streams. However, these processes are inefficient, generating secondary wastes in the form of by-products that must often be disposed of as hazardous. The most promising methods of treatment include sorption, ion exchange, precipitation, liquid emulsion membranes and photoreduction.⁵

Photocatalysis using TiO₂ as photocatalyst appears very promising for complete wastewater treatment. This

* e-mail: padilha@ibb.unesp.br

semiconductor has been widely used due to its nontoxicity, high stability under irradiation and the possibility of using natural UV-light in the photoreduction of mercuric ions to metallic Hg, calomel or HgO, depending on the nature and concentration of the starting salt, which may be recycled.⁶⁻⁸

However, as the concentration and number of contaminants increase, the process becomes increasingly complex, leading to catalyst deactivation, slow kinetics and low photoefficiencies. Thus, the use of compounds that increase the efficiency of the excitation process is essential to optimize the photocatalytic process.⁹

Surface modification of TiO₂ with carboxylic acids and arginine has shown enhanced photoreduction of mercury (II).^{10,11} This is attributed to the replacement of surface OH groups and the coordination of surface titanium atoms with a carboxyl group, generating new trapping sites that localize photogenerated holes and electrons outside the semiconductor. The modifier increases the distance between trapped electrons and holes, preventing the occurrence of recombinations. This modification also leads to the accumulation of trapped electrons and holes, permitting the injection of multielectrons into the sorbed metal, which is advantageous since multielectron transfers usually require lower reduction potentials than single electron transfers.¹⁰⁻¹² Another important factor is the enhanced sorption of mercury on the TiO₂ surface, which facilitates charge transfers from the TiO₂ to the sorbed mercury.¹⁰

The present paper describes the preparation of titania chemically modified with 2-aminothiazole groups, its characterization, sorption studies and photocatalytic reduction of mercury (II) in aqueous medium. The principal objective was to demonstrate the direct correlation between the enhanced photocatalytic properties of modified TiO₂ and the effectiveness of mercury (II) sorption onto the modified TiO₂ surface and its photoreduction.

Experimental

Reagents

The specifications that accompanied the titania samples (Degussa P25) indicated an average particle size of ~ 5 μm. Anhydrous dimethylformamide and anhydrous ethanol were supplied by Aldrich and treated with molecular sieves before use. 2-aminothiazole and 3-chloropropyltrimethoxysilane were purchased from Aldrich and Merck and used as received. Mercuric chloride of highest purity, produced by Merck, was used. NaOH and HCl solutions supplied by Merck were used in the pH adjustments.

Characterization

Diffuse reflectance infrared Fourier Transform (DRIFT) spectra were obtained with a Nicolet spectrometer model Nexus 670; the spectra were taken with 200 scans and a resolution of 8 cm⁻¹.

The specific surface area was determined by the BET method¹³ on a Micromeritics Flow Sorb 300 equipment of Micromeritics Instrument Corporation.

The number of 2-aminothiazole groups attached to the titania was determined by a nitrogen analysis based on the Kjeldahl method.¹⁴

Organofunctionalization of TiO₂

Titania (Degussa P25) was activated at 420 K under vacuum (10⁻³ Torr). About 50 g of titania (0.02 mol of active OH groups)¹⁵ were immersed in 400 mL of dried dimethylformamide, and 7.40 mL of chloropropyltrimethoxysilane (0.04 mol) were added. The mixture was refluxed in a nitrogen atmosphere for 36 h, centrifuged, washed with dimethylformamide, ethanol, and water and heated to 343 K under vacuum to eliminate all the solvent. The resulting solid (TiSA) was immersed in 200 mL of dried dimethylformamide and 4 g of 2-aminothiazole (0.04 mol) were added. The mixture was stirred for 48 h at 380 K in a nitrogen atmosphere. The resulting modified titania (TiAT) was centrifuged off, washed with dimethylformamide, ethanol, and water and heated for 8 h at 343 K under vacuum.

Photocatalytic experiments

The photoreduction experiments were performed in a Quimis cylindrical photoreactor thermostatted at 298K with luminous intensity of 3.81 mW cm⁻². Nitrogen was bubbled into the mercury solution before conducting the experiment to remove excess oxygen. A Solar Light Company Inc. model PMA 2100 radiometer was used to measure the luminous intensity. A mass of 125 mg of TiO₂ was suspended in 250 mL of HgCl₂ solution (20 mg L⁻¹). Experiments without the presence of light but with the catalysts were conducted to measure the sorption of mercury (II) on the matrices. The photocatalytic reaction was conducted with the reactor open to the air. Samples were periodically taken and filtered through 0.22 μm Millipore filters. Triplicate runs were carried out for each condition to ensure reproducibility, showing a standard deviation lower of 5%. The mercury in the solutions and adsorbed in the surface of TiO₂ and TiAT, after the photocatalytic experiments, were determined

by cold vapor atomic absorption spectroscopy, using a Shimadzu AA6800 spectrometer. Standard mercury solutions ($5\text{--}50\text{ mg L}^{-1}$) were prepared by stepwise dilution from 1000 mg L^{-1} stock solution (Merck - Titrisol) with Milli-Q water, acidified with HCl solution to pH 2.

Results and Discussion

Characterization of TiAT

Figure 1 shows the infrared spectra of bare titania, 3-chloropropyltrimethoxysilane titania (TiSA) and 2-aminothiazole titania (TiAT) in the region of $4000\text{--}400\text{ cm}^{-1}$. A broad absorption band between $2500\text{ and }4000\text{ cm}^{-1}$, characteristic of the stretching vibration of hydroxyl groups and resulting from the chemisorption of molecular H_2O , covers the -NH stretching vibration regions of the 2-aminothiazole molecule and the stretching bands of the hydroxyl groups chemically bonded to the various titania sites.¹⁶ However, a low intensity band may be seen at 3688 cm^{-1} in the titania matrix, which has been attributed to hydroxyl groups with weak Lewis and Bronsted sites.¹⁷ The disappearance of this band in the spectrum of the modified materials is an indication of the functionality of the titania matrix. The asymmetric and symmetric stretch of -CH_2 groups characteristic of a chloropropyl agent are visible in the TiSA and TiAT spectra at 2961 and 2935 cm^{-1} , respectively.¹⁸ Other modes at 1338 , 1386 , and 1471 cm^{-1} can be attributed to the deformation mode $\delta(\text{CH}_2)$ of the propyl bridging group.¹⁹ The small absorption band

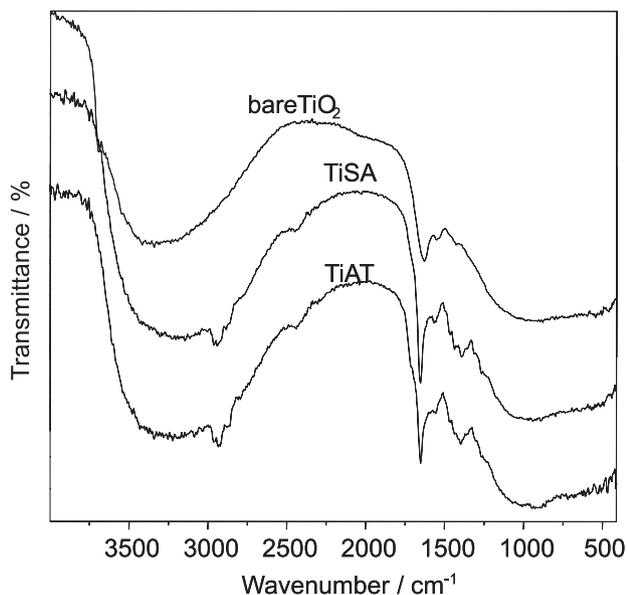


Figure 1. FTIR spectra showing the presence of 3-chloropropyltrimethoxysilane (TiSA) and 2-aminothiazole (TiAT) groups on the TiO_2 particles.

observed at 2858 cm^{-1} is due to the -CH stretching of aromatic olefins, confirming the anchorage of the 2-aminothiazole group.²⁰

The chemical analysis of nitrogen in TiAT yielded a content of $0.43 \pm 0.01\text{ mmol g}^{-1}$ for the quantity of the functional groups attached to TiO_2 surface. The specific surface assessed was $36 \pm 0.4\text{ m}^2\text{ g}^{-1}$ to TiAT and $50 \pm 0.6\text{ m}^2\text{ g}^{-1}$ to TiO_2 . The decrease of specific surface area observed in the modified titania, occurred due to covering of pores of adsorbent by anchorage of 2-aminothiazole groups, decreasing the adsorption of N_2 molecules used in the process of S_{BET} measure.²¹

Adsorption of Hg(II) onto TiO_2

Experiments in the dark with the photocatalysts bare titania and titania-2-aminothiazole (TiAT) were carried out with varying pHs to investigate Hg(II) sorption. The time required to achieve equilibrium was 60 min for titania and 15 min for titania-2-aminothiazole (TiAT). Table 1 summarizes the percentage of sorption onto the photocatalysts as a function of pH and the percentage of mercury sorbed after the photocatalytic experiments.

Table 1. Percentage of Hg(II) adsorbed on the two TiO_2 catalysts

pH	Quantity of Hg sorbed (%)	
	Degussa P25	TiAT
3.0	$3 \pm 0.15^*$ 11 ± 0.44	$2 \pm 0.05^*$ 37 ± 1.45
7.0	$2 \pm 0.08^*$ 17 ± 0.68	$1 \pm 0.04^*$ 54 ± 2.10
9.0	$2 \pm 0.06^*$ 21 ± 0.84	$1 \pm 0.03^*$ 58 ± 2.30

*Percentage of mercury sorbed after the photocatalytic experiments.

The sorption capacity of TiAT is easily explained by the presence of 2-aminothiazole groups anchored on the titania surface. The presence of the heteroatoms, sulfur and nitrogen, with free electron pairs, allows for coordination with metallic ions, particularly with Hg.²² The electronic clouds of sulfur and its cation are very strongly overlap, rendering the bond extremely stable and resulting in an increased number of Hg(II) ions sorbed in a shorter period of time.²³ The decrease observed in the sorption values in pH 3 is due to the protonation of the nitrogen and sulfur atoms responsible for coordinating the ions Hg(II). In pH 7, the number of organofunctional groups per mass of TiAT was saturated. Thus, the 4% enhancement in pH 9 is attributable to physisorption by the TiO_2 matrices. This is a reasonable assumption, considering that the coordination of metal could occur with the nitrogen atoms and the thiazole sulfur atom, yielding a relation of the type metal/ligand = 1.²²

Bare titania showed an increase in mercury adsorption with the enhanced pH. Because the isoelectric point of titania is approximately 6.2, TiO_2 powders are positively charged when the pH is lower than 6.2.²⁴ This leads to repulsion between the Hg(II) ions and the positively charged photocatalyst surface in lower pH. With HgCl_2 salts there is a high stabilization of positively charged Hg(II) and Hg(I) ions at high pH values due some hydrolytic effects, such as the formation of the complex Hg(OH)Cl .⁴ Thus, since the surface of the photocatalyst appears in negative form, there is greater electrostatic interaction between the species and the catalyst, causing an increase in the adsorption process.

The percentage of mercury sorbed onto the photocatalysts determined after the photocatalytic experiments (Table 1) presents very small values, indicating that the reduction process removed practically the whole mercury sorbed onto the photocatalysts.

Photocatalytic experiments

The Figures 2, 3 and 4 show the percentage of reduction as a function of time. It should be noted that no variation in mercury concentrations occurs in systems in which a photocatalyzer is not interposed between the mercury-containing material and the light source.

Mercury conversion increased with increasing pH values in the photocatalysts studied, being that the faster transformation occurred at pH 9. The conversions obtained in pH 3 were around 30% (in relation to TiAT) and 26% (in relation to TiO_2) lowers, indicating that sorption and acidity medium play a crucial role in the photoreduction process.

TiAT was found to consistently promote higher Hg(II) photoreduction than bare titania throughout the photocatalytic process. As an example, in a 60 min time, the percentage of photoreduction in pH 3, 7 and 9 was 65%, 95% and 99% in TiAT, respectively, versus 46%, 66% and 72% in titania. The modifier enhances sorption of Hg(II) ions onto the TiO_2 surface, facilitating the charge transfer from the valence band of titania to sorbed Hg(II) , resulting in a decrease in the electron-hole recombination process. Dark deposits were visually observed on the recovered photocatalysts, mainly in pH 9. Previous investigations utilizing HgCl_2 as the starting salt made chemical and XRD analyses of the product formed, attributing these deposits to Hg^0 , HgO and/or calomel (Hg_2Cl_2), indicating the complexity of the system. In acid and neutral pH, XRD revealed the presence of a mixture of Hg and calomel, the former in smaller amounts, while a mixture of Hg and HgO was detected in alkaline media.^{4,24-26}

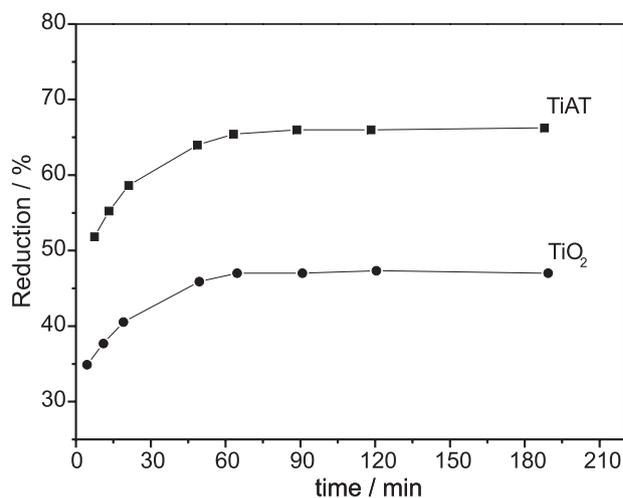


Figure 2. Comparison of the percentage of reduction in titania-2-aminothiazole (TiAT) and bare TiO_2 in pH 3.

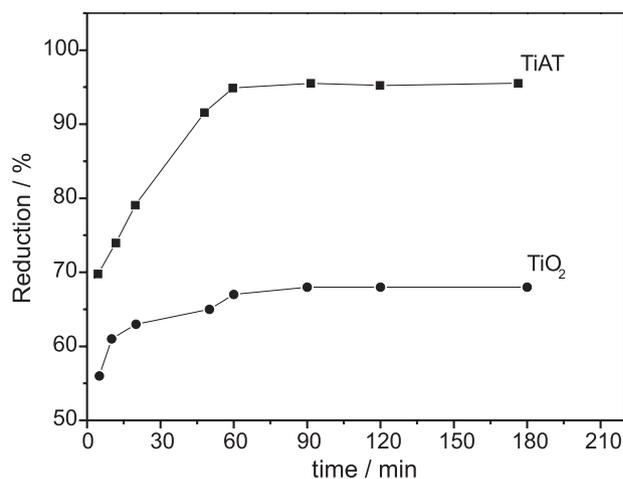


Figure 3. Comparison of the percentage of reduction in titania-2-aminothiazole (TiAT) and bare TiO_2 in pH 7.

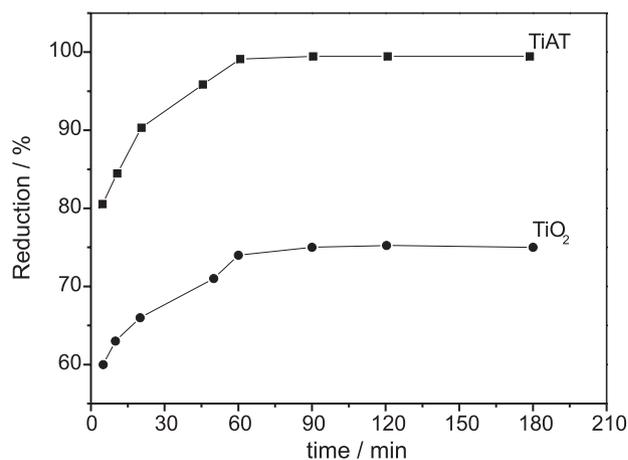


Figure 4. Comparison of the percentage of reduction in titania-2-aminothiazole (TiAT) and bare TiO_2 in pH 9.

Conclusions

The chemical modification on titania (Degussa P25) surface was successfully obtained via silyl linkage with 3-chloropropylmethoxylane and further anchorage of 2-aminothiazole ligand. The organofunctionalization of photocatalyst was checked by nitrogen analysis, determination of surface area and infrared spectroscopy. Sorption experiments of Hg(II) showed that the functionalized titania (TiAT) presents higher sorption capacity of these ions rather than bare titania, explained by the great affinity of 2-aminothiazole, a soft base, with Hg(II) ions, a soft acid. The anchorage made the charge transfer easier from semiconductor valence bond to Hg(II) ions decreasing the electron-hole recombination, thus improving the capacity of Hg (II) photoreduction. Our findings indicate that this new material can be used in the remediation of aquatic systems contaminated by mercury species, what could be developed in further studies.

Acknowledgments

The authors thank FAPESP (Brazil), FUNDIBIO (Brazil) for granting a fellowship (Process 03/03846-6) and for its financial support of this work (Processes 99/12916-0 and 00/08859-0).

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Received: August 9, 2005

Published on the web: March 3, 2006

FAPESP helped in meeting the publication costs of this article.