Cadmium removal from water using thiolactic acid-modified titanium dioxide nanoparticles

L.R. Skubal [a,*], N.K. Meshkov [a], T. Rajh [b], M. Thurnauer [b]

[a] *Energy Systems Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA*
[b] *Chemistry Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA*

Abstract

This study investigated the use of titanium dioxide (TiO_2) nanoparticles to remove aqueous cadmium from simulated wastewaters. Nanosized (45 Å) colloids of anatase TiO_2 were synthesized through the controlled hydrolysis of $TiCl_4$ and their surfaces modified with the bidental chelating agent thiolactic acid (TLA). Colloids were introduced into 65 ppm cadmium-laden waters, and the suspensions were purged aerobically, anoxically with an inert gas, or by a sequential aerobic/anoxic purge. Suspensions were illuminated with 253.7 nm light. In each experiment, samples were taken from the reactor, filtered, and the filtrates analyzed by atomic absorption spectroscopy for residual cadmium. Results from the aerobic experiments exhibited minimal (approximately 10%) removal of the cadmium from solution and no reduction of the metal on either the modified or the unmodified colloid. Anoxic results were more promising, showing no cadmium reduction on the unmodified colloid but a 40% adsorption and reduction (from a +2 valence state to elemental cadmium as determined by methyl viologen tests) of cadmium on TLA-modified colloid in the presence of light. Results from the mixed atmospheric conditions fared the best and demonstrated that in the absence of light, approximately 20% of aqueous cadmium was sorbed to the modified colloid via a Freundlich adsorption isotherm. Upon illumination, greater than 90% of cadmium was removed by both adsorption and reduction processes onto the TLA-modified TiO_2. These removal and reduction processes were catalytic in nature. Results from this study are significant because to date, no other research in the literature has been able to accomplish cadmium removal and reduction using TiO_2. © 2002 Elsevier Science B.V. All rights reserved.
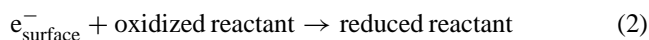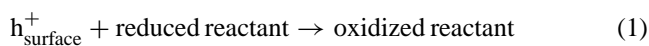
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1. Introduction

A variety of wastewater treatment processes including precipitation, adsorption, ion exchange, electrolytic techniques, and evaporation exist for removing soluble metals from industrial waste streams [1–3]. Most of these technologies have limitations that restrict the applications in which they can be used. Some of these technologies are pH sensitive, they cannot target specific metals, they cannot remove extremely low or high concentrations of metals, and most create sludges that must be disposed as hazardous waste. Of these technologies only one, electrolytic recovery, allows for the transformation of a metal from an aqueous phase into a solid phase and for its recovery in a pure (elemental) form [4,5].

This study relies upon our previous work that focused upon the removal of lead and copper from waste streams [6–15]. Our approach relies upon the photocatalytic properties of titanium dioxide (TiO_2) to reduce sorbed metals. TiO_2, a non-toxic semiconductor that is stable over a pH range 2–14, possesses unique physical properties enabling it to harvest solar energy and propagate energy transfer, including oxidative hole transfer and reductive electron transfer as indicated in Eqs. (1) and (2) [16].

$$h^+_{surface} + \text{reduced reactant} \rightarrow \text{oxidized reactant} \tag{1}$$

$$e^-_{surface} + \text{oxidized reactant} \rightarrow \text{reduced reactant} \tag{2}$$

As TiO_2 is illuminated, electrons and holes are produced. Electrons are promoted from the valence band into the conduction band leaving behind holes in the valence band. If electrons and holes do not recombine producing heat, they can be used to target specific oxidation or reduction reactions at the particle surface.

In this study, the surfaces of nanosized TiO_2 have been modified with thiolactic acid (TLA). The purpose of surface modification is to promote the adsorption of cadmium

* Corresponding author. Tel.: +1-630-252-0931; fax: +1-630-252-6407.
E-mail address: lskubal@anl.gov (L.R. Skubal).

to the TiO_2 surfaces, to more effectively separate photo-generated electrons and holes, and to provide a pathway for the electrons to transfer to the physisorbed cadmium ions. Specific objectives of our research are to characterize the synthesized/modified colloids, to determine the extent and mechanism of cadmium sorption (dark) and sorption/reduction (illumination) onto the modified colloids, and to determine the effect of a hole scavenger upon cadmium removal/reduction processes. These objectives will be accomplished by using a batch reactor with the TiO_2 in a slurry form.

2. Experimental

Nanosized TiO_2 colloids were prepared by the controlled hydrolysis of titanium tetrachloride ($TiCl_4$). This procedure is described elsewhere [17] and produces TiO_2 particles that are approximately 40–60 Å in diameter, allowing 40% of the titanium atoms to be located on the particle surface [8]. Once the particles are synthesized, they are modified with TLA ($C_3H_6O_2S$) an organic modifier that binds to the TiO_2 through the carboxyl functional group. The other functional groups of TLA attract cadmium ions to the modified TiO_2 surface [18].

Three types of reactions were performed using the TLA-modified and unmodified TiO_2: aerobic, anoxic and aerobic/anoxic. In aerobic experiments, 20 ml of a stock TLA-modified TiO_2 or unmodified TiO_2 solution were added to approximately 400 ml of deionized water. Aliquots of a stock cadmium perchlorate solution were added to the TiO_2 suspension and the solution was diluted to 500 ml in a quartz flask. The resulting mixture was allowed to equilibrate for 10 min in darkness. A stopwatch was then begun and the solution either continued to mix in the dark or under illumination using 253.7 nm light in an eight-light Rayonet Photochemical Chamber Reactor (RMR Model 600). Samples were periodically withdrawn and filtered through 0.05 μm millipore membranes. Filtrate was collected and analyzed by atomic absorption spectroscopy (Buck Scientific 200A) to determine residual cadmium concentrations; aliquots of the suspension were taken and combined with methyl viologen to determine the valence state of cadmium.

In anoxic reactions, 20 ml of stock TLA–TiO_2 or unmodified TiO_2 were added to approximately 475 ml of distilled water in a quartz flask. The flask was stoppered with septa and two needles were inserted through the septa. The TiO_2 suspension was purged with reagent-grade nitrogen gas (AGA, 99.995%) for 2 h (at approximately 20 ml per minute). After 2 h, the purge line was removed and stock solutions of cadmium (and methanol [Aldrich] if desired) were injected anoxically through the septa. The sample at this time was also diluted to 500 ml with N_2-purged deionized water if it had not reached the 500 ml capacity. A timer was begun and the suspension was either illuminated or it remained in the dark. Samples periodically were taken anox-

ically via syringe and filtered anoxically through an Amicon Diaflo pressure filter equipped with Amicon YM100 membranes. The filtrates were collected and analyzed for residual cadmium concentrations. Portions of the collected suspension were tested with methyl viologen for the presence of elemental cadmium according to Eq. (3) [18]:

$$2MV^{2+} \text{ (white)} + Cd^0 \rightarrow 2MV^+ \text{ (blue)} + Cd^{2+} \qquad (3)$$

Cadmium present in an elemental state will react with methyl viologen and turn the solution blue in color.

In the aerobic/anoxic reactions, suspensions of TiO_2/TLA/ cadmium were purged with air for 2 h in a quartz flask. The 500 ml quartz flask was then stoppered with septa and purged with nitrogen (AGA, 99.995%) for another 2 h via two syringes injected through the septa. After the anoxic purge was terminated the suspension was illuminated (light reaction) or kept in darkness (dark reaction). Methanol, a hole scavenger, was injected at this point in some experiments. As either the dark or light reaction progressed, samples were periodically taken from the reactor anoxically with a syringe purged with nitrogen gas and filtered anoxically through Amicon Diaflo pressure filters equipped with YM100 filter membranes. Aliquots of the samples were tested for the presence of elemental cadmium with methyl viologen, and residual cadmium concentrations in filtrates were determined by atomic absorption spectroscopy.

3. Results and discussion

Table 1 summarizes the results from all aerobic, anoxic, and aerobic/anoxic experiments performed. In Table 1, the concentrations of initial cadmium, and methanol are listed along with the initial pH of the system, the final pH of the system, the percentage of cadmium removed, and the detection of elemental cadmium. As the table reveals, no cadmium was reduced in any of the aerobic experiments.

Both the removal and the reduction of cadmium occurred in the illuminated anoxic experiments using TLA-modified TiO_2, whereas only removal (sorption) of cadmium occurred in the dark anoxic reactions. The same amount of modified colloid (2.94×10^{-3} M TLA-modified 5.00×10^{-3} M TiO_2) removed a greater mass of cadmium in solutions with higher initial concentrations of cadmium (65 ppm) than in those with lower (20 ppm) concentrations in both light and dark reactions.

In the illuminated reactions the efficiency of cadmium removal and reduction was improved by the addition of methanol in low concentrations (0.0246 M) but not in higher concentrations (0.246 M). For higher Cd concentrations (65 ppm) in anoxic dark reactions methanol seemed to interfere with the colloid's ability to sorb Cd as evidenced by the decrease in Cd sorption as the concentration of methanol increased. This suggests that methanol competes with TLA for sorption sites on the modified TiO_2. For lower Cd concentrations (20 ppm) methanol seemed to have little effect on the sorption of Cd to the modified TiO_2.
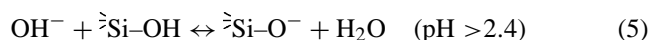
Table 1
Summary of cadmium removal by titanium dioxide (5.00×10^{-3} M) and TLA (2.94×10^{-3} M unless stated otherwise). Sorption of cadmium in dark reactions followed a Freundlich adsorption isotherm ($K = 9.70$, $1/n = 0.907$, $R^2 = 0.99$)

$[Cd]_{total}$	[MeOH]	Representative pH initial/final		% Cd removed after 210 min (unless otherwise indicated)		Reduced Cd	
		Light	Dark	Light	Dark	Light	Dark
Aerobic reactions							
5.78×10^{-4} M (65 ppm) Cd	None (no TLA)			9 (128 min)	15 (128 min)	No	No
	None			60 (128 min)	32 (128 min)	No	No
Anoxic reactions							
5.78×10^{-4} M (65 ppm) Cd	None (no TLA)	3.42/3.41	3.63/3.59	3	5	No	No
	None	3.13/2.97	3.13/3.15	44	44	Yes	No
	0.0246 M	2.88/2.79	2.96/2.95	52	35	Yes	No
	0.246 M	3.06/2.93	3.01/2.68	36	27	Yes	No
1.78×10^{-4} M (20 ppm) Cd	None	3.08/3.09	3.09/3.06	64	46	Yes	No
	0.00494 M	3.06/3.02	3.19/3.17	67	51	Yes	No
Aerobic/anoxic reactions							
5.78×10^{-4} M (65 ppm) Cd	None	2.95/2.73	2.85/2.84	76	12	Yes	No
	0.00494 M	–/2.76	2.85/2.84	73 (300 min)	19 (300 min)	Yes	No
		2.95/2.73	2.78/2.80	91 (300 min)	20 (300 min)	Yes	No

Generally, no change of pH occurred in anoxic dark (sorption) reactions. The pH of illuminated anoxic suspensions decreased over time in the reactions where cadmium was reduced; this pH drop was indicative that hydrogen ions were released as a result of oxidation of the TLA and/or methanol.

The amount of cadmium removed/reduced in the illuminated reactions purged aerobically then anoxically was much greater than the amount of cadmium removed/reduced in a strict anoxic environment. The converse was true in the dark reaction; the amount of cadmium removed by sorption processes in an anoxic environment was larger than the amount sorbed in an aerobic/anoxic environment. A possible explanation for the increase in the amount of cadmium removed in the illuminated aerobic/anoxic environment over that in the illuminated anoxic environment is as follows. Reduced cadmium metal did not adhere to the quartz reactor walls in any illuminated aerobic/anoxic reaction. In all TLA-modified TiO$_2$ illuminated anoxic reactions, reduced cadmium adherence to the reactor walls was highly visible during and at the termination of each reaction. The lack of reduced cadmium adherence to the quartz reactor walls in illuminated aerobic/anoxic reactions allowed more light to penetrate into the reactor, hence more cadmium could be reduced than in the corresponding illuminated anoxic reactions. In the dark reaction, O$_2$ seemed to inhibit the cadmium from being sorbed to the modified TiO$_2$.

The presence of organic molecules, especially amino acids (which contain carboxyl functional groups) has been shown to greatly enhance the dissolution of silica, including quartz [19]. Studies show three types of surfaces complexes are thought to exist on edge quartz silicate structures. These are represented in Eqs. (4) and (5)

$$\gtreqless Si{-}OH_2^+ \leftrightarrow \, \gtreqless Si{-}OH + H^+ \quad (pH < 2.4) \tag{4}$$

$$OH^- + \gtreqless Si{-}OH \leftrightarrow \, \gtreqless Si{-}O^- + H_2O \quad (pH > 2.4) \tag{5}$$

where $\gtreqless$Si– represents a Si surface site connected to the surface by one, two, or three oxygen bonds [20]. Our experiments are run at a pH greater than the pH$_{zpc}$ ($\sim$2.4 for quartz at 25 °C) and lower than a pH of 5. In this pH range, most surface quartz molecules have the configuration $\gtreqless$Si–OH [20]. An aerobic purge followed by an anoxic purge maximizes the amount of oxygen hydrogen bonded to the $\gtreqless$Si–OH complex and limits any compounds less electronegative than oxygen from being hydrogen bonded to $\gtreqless$Si–OH. Further studies will be conducted to confirm this hypothesis.

Fig. 1 graphically compares dark and light results of the anoxic reactions using unmodified TiO$_2$, the anoxic reactions using TLA-modified TiO$_2$, and the aerobic/anoxic reactions using TLA-modified TiO$_2$.

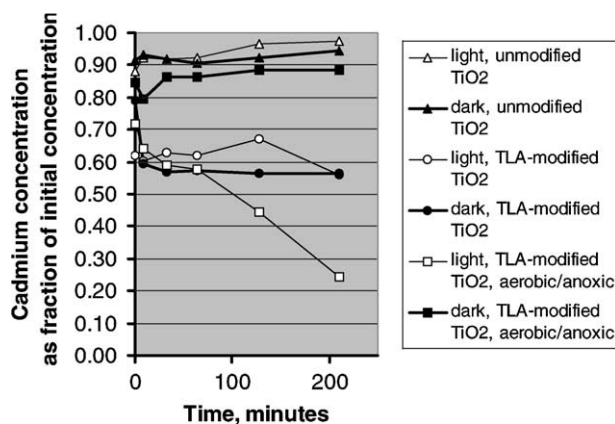As Fig. 1 shows, 44% of the cadmium initially present in solution was removed and reduced by TLA-modified TiO$_2$

Fig. 1. Removal of 65 ppm cadmium using unmodified TiO$_2$ in an anoxic environment, TLA-modified TiO$_2$ in an anoxic environment, and TLA-modified TiO$_2$ in an aerobic/anoxic environment. Both light and dark reactions are presented. Initial concentrations of TiO$_2$ and TLA used are 5.00×10^{-3} and 2.94×10^{-3} M, respectively.
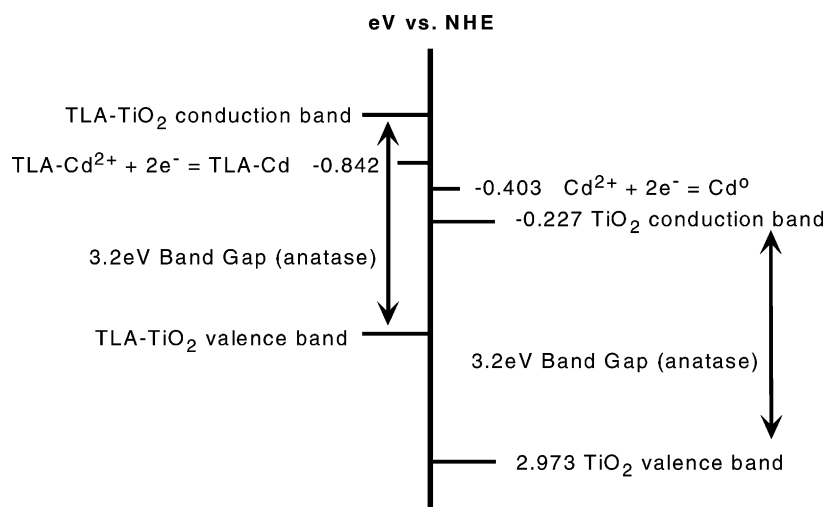
Fig. 2. Electrochemical potential modifications of TiO$_2$ and cadmium before (right side) and after (left side) surface enhancement with TLA [21]. Electrochemical potentials were determined by cyclic voltammetry and by pulse radiolysis [18].

in an illuminated anoxic environment within 210 min. This amount was much greater than the 4% removed by either the light or dark anoxic, unmodified TiO$_2$ reaction where no reduction occurred. For cadmium removal, the light aerobic/anoxic reaction using TLA-modified TiO$_2$ fared the best, removing and reducing 76% of the initial cadmium in solution within 210 min of illumination. Removal/reduction of cadmium continued (up to 96% removal) in this illuminated experiment until the experiment was terminated at 375 min. The increase in the removal/reduction of cadmium as a function of time in illuminated aerobic/anoxic reactions suggests that the process is catalytic.

The mechanism of cadmium reduction has been described elsewhere and is reiterated here. Cadmium sorbs to the modified colloid through the functional groups of the surface modifiers. As electrons and holes are photogenerated, the charges are separated spatially through the modifier. Electrons transfer to the sorbed metal while holes either oxidize the modifier or any hole scavenger present in solution. Electron transfer occurs via a two-electron transfer process and reduces the metal from a +2 valence state into an elemental state [10].

Surface modification of the colloid caused two changes to occur in the photocatalytic system. As Table 1 and Fig. 1 have shown, the presence of TLA greatly enhances the sorption of ionic metal to the colloidal surface. Surface modification also causes electrochemical changes in the colloidal TiO$_2$ and in the cadmium ions. These changes are shown in Fig. 2.

As shown in Fig. 2 the conduction band of unmodified TiO$_2$ is not sufficiently negative to reduce cadmium ions. As TLA is chemisorbed to the TiO$_2$, new trapping sites are created that shift the position of the TiO$_2$ conduction and valence bands to more negative values. (The Fermi level of TLA-modified TiO$_2$, measured by pulse radiolysis, could not be exactly quantified, but did shift to a more negative

potential.) This was confirmed by failure of a monovalent zwitterion radical of methyl viologen to inject a charge into TLA-modified TiO$_2$ [18]. The cadmium redox potential is also shifted to more negative values but by a lesser amount at a value less negative than the conduction band as measured by cyclic voltammetry [18]. This shift in energy levels occurs only in nanosized TiO$_2$ particles. It does not occur when TiO$_2$ particle size exceeds 150 Å because the bonding of the TLA to TiO$_2$ changes with increasing colloid size [7].

4. Conclusions

With the exception of electrowinning operations, little work has been done to develop successful methods for removing aqueous metallic constituents from a waste stream and converting them into an elemental (non-toxic) state. Our work with modified TiO$_2$ colloids has shown that cadmium can be removed from water and reduced to metallic form using a new photocatalytic process. Cadmium reduction has been made possible by using nanosized (4.5 nm) TiO$_2$ particles and modifying their surface with TLA. TiO$_2$ modification not only allows for the reduction of cadmium to occur, but it also enhances the sorption of cadmium onto its surfaces, it physically separates the electrons and holes from recombining and producing heat, and it forms a bridge for charge transfer to occur from the TiO$_2$ to the sorbed metal. Results from this study demonstrated that simple Cd sorption upon the TLA-modified colloid occurs in anoxic environments better than in aerobic or aerobic/anoxic environments. Methanol acts as a hole scavenger increasing the rate of cadmium reduction if it is not used in excessive concentrations. Illuminated systems purged aerobically then anoxically are able to remove and reduce cadmium more effectively than systems purged anoxically. This may be attributed to the

absence of reduced cadmium metal adhering to the walls of the quartz reactor.

Acknowledgements

References

[1] N. Nemerow, Liquid Waste of Industry: Theory, Practices, and Treatment, Addison-Wesley, Reading, MA, 1971, pp. 397–422.

[2] F.W. Pontius (Ed.), Water Quality and Treatment: A Handbook of Community Water Supplies, McGraw-Hill, New York, 1990.

[3] R.W. Peters, B.M. Kim (Eds.), Separation of Heavy Metals and Other Trace Contaminants, AIChE Symposium Series, Vol. 243, 1985, pp. 165–203.

[4] H.F. Freeman, Standard Handbook of Hazardous Waste Treatment and Disposal, McGraw-Hill, New York, 1989.

[5] L.K. Wang, M.H.S. Wang, Handbook of Industrial Waste Treatment, Marcel Dekker, New York, 1992, pp. 127–227, 293–306.

[6] L.X. Chen, T. Rajh, O. Micic, Z. Wang, D.M. Tiede, Nucl. Instrum. Meth. Phys. Res. Sec. B 133 (1997) 8.

[7] L.X. Chen, T. Rajh, Z. Wang, M.C. Thurnauer, J. Phys. Chem. 101 (1997) 10688.

[8] N.K. Meshkov, T. Rajh, Novel Biomimetic TiO_2 Photo-catalysts for Selective Heavy Metals Removal, Field Proposal, Argonne National Laboratory, ES Division, November 15, 1995.

[9] N.K. Meshkov, L.R. Skubal, T. Rajh, in: Proceedings of the Third International Conference on TiO_2 Photocatalytic Purification and Treatment of Water and Air, Radisson Twin Towers Hotel, Orlando, FL, September 23–26, 1997.

[10] O.I. Micic, A.E. Ostafin, T. Rajh, J.J. Sabelko, M.C. Thurnauer, D.M. Tiede, Y. Zhang, in: Proceedings of the Fifth International Symposium on Chemical Oxidation Technology for the Nineties, Vanderbilt University, Nashville, TN, 1995.

[11] O.I. Micic, T. Rajh, J. Nedeljkovic, M. Comor, Isr. J. Chem. 33 (1993) 59.

[12] O.I. Micic, Y. Zhang, K.R. Cromack, A.D. Trifunac, M.C. Thurnauer, J. Phys. Chem. 97 (1993) 7277.

[13] T. Rajh, J. Nedeljkovic, L.X. Chen, D.M. Tiede, M.C. Thurnauer, Removal of heavy metals from aqueous waste streams using surface-modified nanosized TiO_2 photocatalysts, in: Third International Conference on TiO_2 Photocatalytic Purification and Treatment of Water and Air, Radisson Twin Towers Hotel, Orlando, FL, September 23–26, 1997.

[14] T. Rajh, D.M. Tiede, M.C. Thurnauer, J. Non-Cryst. Solids 205–207 (1996) 815.

[15] T. Rajh, A.E. Ostafin, O.I. Micic, D.M. Tiede, M.C. Thurnauer, J. Phys. Chem. 100 (1996) 4538.

[16] N. Serpone, E. Pelizzetti, Photocatalysis: Fundamentals and Applications, Wiley, New York, 1989, pp. 123–157.

[17] C. Kormann, D.W. Bahnemann, M.R. Hoffman, J. Phys. Chem. 92 (1988) 5196.

[18] M.C. Thurnauer, T. Rajh, D.M. Tiede, Acta Chem. Scand. 51 (1997) 610.

[19] J.B. Dixon, S.B. Weed (Eds.), Minerals in Soil Environments, Soil Science Society of America, Madison, 1989, pp. 913–974.

[20] P.V. Brady, J.V. Walther, Geochim. Cosmmochim. Acta 53 (1989) 2823.

[21] L.R. Skubal, Removal of lead, copper, and cadmium from water using surface-enhanced titanium dioxide colloids, Ph.D. Thesis, The Pennsylvania State University, May 1999.