

Arsenic Removal and Recovery from Copper Smelting Wastewater Using TiO₂

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Removal and recovery of high levels of arsenic (As) in copper smelting wastewater present a great environmental challenge. A novel approach was investigated for the first time using TiO₂ for As adsorptive removal from wastewater and subsequent spent adsorbent regeneration and As recovery using NaOH. EXAFS results demonstrate that As(III), as the only As species present in the raw water, does not form an aqueous complex with other metal ions. An average of 3890 ± 142 mg/L As(III) at pH 1.4 in the wastewater was reduced to 59 ± 79 µg/L in the effluent with final pH at 7 in the 21 successive treatment cycles using regenerated TiO₂. Coexisting heavy metals including Cd, Cu, and Pb with concentrations at 369 mg/L, 24 mg/L, and 5 mg/L, respectively, were reduced to less than 0.02 mg/L. As(III) adsorption followed pseudosecond-order rate kinetics, and the adsorption behavior was described with the charge distribution multisite surface complexation model. Approximately 60% As(III) in the waste solution after the TiO₂ regeneration process was recovered by thermo vaporization and subsequent precipitation of sodium arsenite, as suggested by the EDX and XPS analysis. This “zero” sludge process sheds new light on successful As remediation technology for acidic metallurgical industry wastewater.

Introduction

Smelting and mining are major industrial processes that lead to anthropogenic heavy metal contamination of air, water, and soil (1). Among various heavy metal contaminations, arsenic (As) from copper smelters has caused increasing public concern because of its high concentrations and apparent carcinogenicity (2, 3). Developing innovative treatment technologies for As-containing metallurgical industry wastewater is currently of great urgency and high priority in many countries including Chile, China, and India. The efficient removal and, more importantly, the recovery of As from the smelter wastewater present a challenge, because of the ultrahigh As concentrations at several grams per liter level and extremely low pH around 1.

Extensive research has been conducted for decades to remove As from metallurgical industry wastewater, and the findings suggest that neutralization and precipitation is the most widely used technology (4–6). Since the solubility of metal sulfides is generally several orders of magnitude less than that of metal hydroxides, sulfide precipitation could result in a better metal removal (7). However, due to the high cost and the noxious H₂S evolution from the system, the application of sulfide precipitation is limited to site specific conditions. Recently, some copper smelters in China have upgraded from the sulfide process to a metal hydroxide process, e.g. iron precipitation of a high density sludge (HDS). The iron precipitation approach requires increasing the pH with an alkaline reagent such as hydrated lime and subsequently coprecipitating As with amorphous ferric oxyhydroxide (8–10). HDS is a benchmark procedure in acidic mine drainage treatment (11) and widely used in China. Instead of adding lime directly to the acidic wastewater, HDS recycles a portion of sludge with the lime slurry for acid neutralization. The precipitates are primarily formed onto recycled particles, creating larger particles and a denser sludge that can settle and compress better than conventional iron precipitates. However, HDS has its own disadvantages. The calcium arsenate precipitate formed as a result of lime addition is not stable, because it could decompose to calcium carbonate and release As under the attack of atmospheric carbon dioxide (12). In addition, HDS generates a large volume of sludge (4), which requires further treatment. Recently, TiO₂ has been demonstrated as a high capacity adsorbent for As removal from groundwater (13–15). However, to the best of our knowledge, no attempt to use TiO₂ in the remediation and subsequent recovery of As from copper smelters has been reported.

The objective of this study was to investigate an innovative As removal and recovery technology from copper smelting wastewater using TiO₂. To investigate the hypothesis that TiO₂ could be regenerated and reused, As was extracted from the spent TiO₂ with NaOH and subsequently recovered by thermo evaporation and precipitation of sodium arsenite under oversaturated conditions.

Materials and Methods

Materials. The raw water containing an average concentration of 3310 mg/L As(III), 24 mg/L Cu, 5 mg/L Pb, and 369 mg/L Cd at pH 1.4 was obtained from a copper smelting company in China. The copper ore used by the company contains As as an impurity. Volatile As in smelter gas emissions reached a sulfuric acid plant where SO₂ in the effluent gas stream was treated and recovered. Hence, wastewater with elevated As concentration was produced in the gas washing step. The HDS process has been employed for the wastewater treatment with limited success, as shown in Table S1 and Figure S1 in the Supporting Information (SI). The TiO₂ used in this study was prepared by hydrolysis of titanyl sulfate at 4 °C (16). The details of the TiO₂ synthesis and the comparison of its As adsorption capacity with some commercial TiO₂ materials are shown in the SI. The BET surface area was 196 m²/g, and the point of zero charge was 5.8.

Arsenic Treatment and Recovery. The flowchart of the As treatability experiments is shown in SI Figure S3. In a typical treatment chain, three successive adsorption reactions were employed. Suspensions containing 1 L raw water and 30 g/L TiO₂ were prepared in a 2 L beaker covered with aluminum foil to prevent light exposure. The pH was adjusted to 7.0 using NaOH and H₂SO₄ solutions. Suspensions were

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agitated using a mechanical mixer for 1 h before filtering through a 0.45- μm membrane filter. The second and third adsorption reactions were started by adding 30 g/L TiO_2 to the filtrate from the previous step.

The spent TiO_2 adsorbent was regenerated by mixing the above filter cake with 100 mL 5 M NaOH for 1 h. The solid was separated from the extraction solution by centrifugation at 8000 rpm for 15 min. The TiO_2 adsorbent after regeneration was reused in adsorption steps to remove As from raw water. The extraction solution was then utilized in the following As recovery process.

The As recovery was realized by heating the extraction solution containing high concentrations of sodium and As after TiO_2 regeneration. The extraction solution was heated on an electric hot plate at 70 $^\circ\text{C}$ for approximately 7.5 h until the volume of the residual liquid was approximately one-tenth of the initial solution. Precipitation occurred when the solution cooled to room temperature. The solid was recovered by a 0.45- μm membrane filtration. The residual liquid was then mixed with raw water as feeding solution for the adsorption treatment chain in the next treatment cycle.

Batch Experiments. Batch kinetic experiments were carried out by reacting 1 L of raw water in a 2 L beaker with 30 g of the TiO_2 adsorbent. The suspension was agitated mechanically for 24 h in the dark at pH 7.0, and batch solution samples were taken at designed time intervals for dissolved As measurement.

Adsorption isotherm experiments were conducted by transferring 50 mL of raw water to each tube containing varying amounts of TiO_2 adsorbent and then mixing the samples on a rotator for 24 h. The isotherm experiments were performed at pH 1.4, 6, and 7.

Adsorption envelope experiments were performed to determine the adsorption edge, which is the percentage of As adsorbed as a function of the final solution pH. Suspension samples containing raw water and 30 g/L TiO_2 were adjusted to desired pH values in the range of 3 to 12 with NaOH and H_2SO_4 . After the samples were mixed on a rotator for 24 h, the final pH was measured, and the suspension was filtered through a 0.45- μm membrane filter for dissolved As analysis.

Analysis. The concentrations of dissolved metals and As were determined using a furnace atomic absorption spectrometer (FAAS) (Perkin-Elmer AAS-800). The As speciation determination was performed using HPLC-AFS. Separation of As compounds was carried out in a Hamilton PRP-X100 anion exchange column, using 10 mM phosphate buffer at pH 5.8 as mobile phase at 1.0 mL/min flow rate. Details of EXAFS, XPS, SEM-EDX, and charge distribution multisite complexation (CD-MUSIC) modeling are reported in the SI.

Results and Discussion

Local Coordination of As(III) in Raw Water. EXAFS spectroscopy was employed to determine the local coordination environment of aqueous As(III) in raw water, given the complexity of the smelter wastewater with a conductivity as high as 0.2 S/cm. If aqueous As(III) complexes with other ions, this will have a direct impact on As(III) adsorption behavior. The k^3 -weighted As K-edge EXAFS spectra are shown in Figure 1-A for raw water and reference standards, and the corresponding Fourier transforms of EXAFS are depicted in Figure 1-B. Based on the fit of the theoretical to the experimental spectrum, the first shell was composed of three oxygen atoms at a distance of 1.78 \AA . The As(III)-O coordination number and distance are in agreement with previous EXAFS results (17). The first shell single scattering path is the dominant contribution to the total signal, whereas negligible additional peaks at distance regions may derive from multiple scattering components within the first coordination shell. In contrast, EXAFS spectra of solid NaAsO_2 and As_2O_3 revealed a second peak (Figure 1-B). The absence

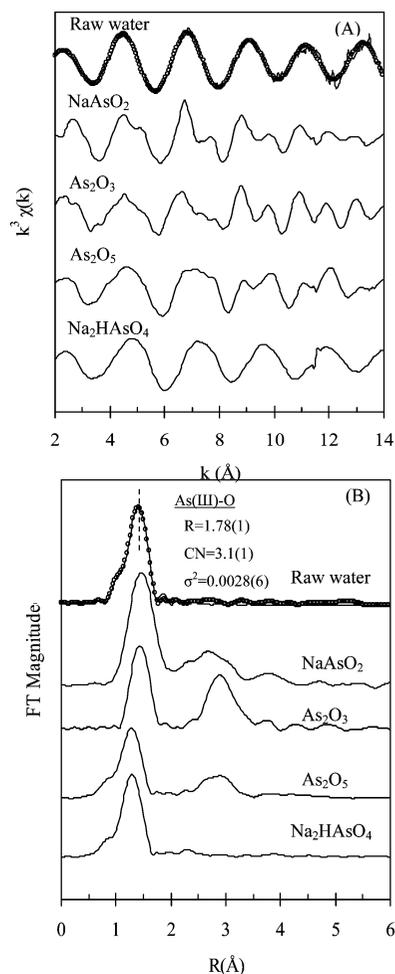


FIGURE 1. Normalized k^3 -weighted observed (solid line) and model calculated (dotted line) As K-edge EXAFS spectra (A) and Fourier transform magnitude (B) for As reference compounds and raw water. Numerical fit results (inset) are true interatomic distances (R) corrected for backscatterer phase shifts; CN is the average coordination number of backscatterers, and σ^2 is the Debye–Waller disorder parameter.

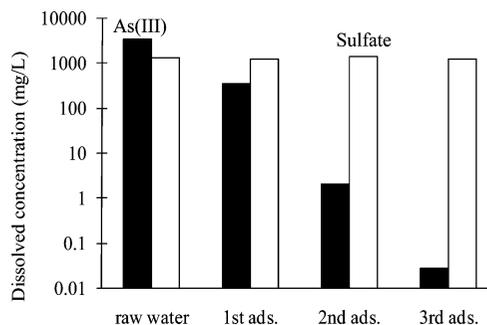


FIGURE 2. Concentrations of As(III) and sulfate in raw water and in three consecutive adsorption reactions. Initial As concentration was 3310 mg/L in raw water; $\text{TiO}_2 = 30$ g/L in each adsorption; pH = 7.

of this apparent second peak in raw water sample indicates that As(III) was not associated with other metals at the g/L concentration level at low pH. Therefore, H_3AsO_3 is the only As form in the following adsorption study.

As(III) Removal Using TiO_2 . The results of As(III) removal from raw water using TiO_2 are shown in Figure 2. The initial As(III) concentration at 3310 mg/L was decreased to 27 $\mu\text{g/L}$ after three consecutive adsorption reactions. Our results demonstrate for the first time that TiO_2 is an effective

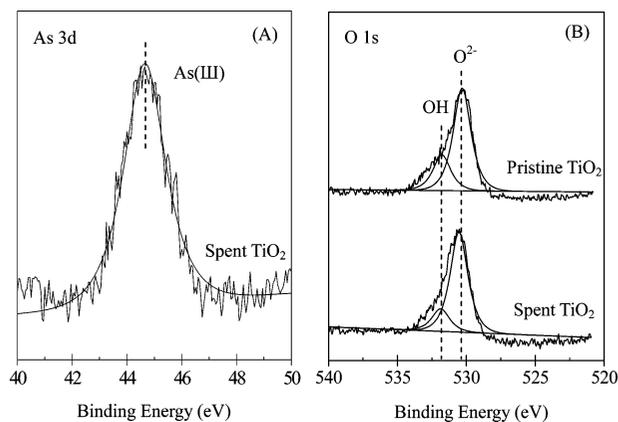


FIGURE 3. High-resolution XPS survey of As 3d (A) and O 1s (B) for spent TiO₂. Vertical lines indicate As(III), O²⁻, and OH binding energies at 44.6 ± 0.1, 530.4 ± 0.1, and 531.7 ± 0.1, respectively.

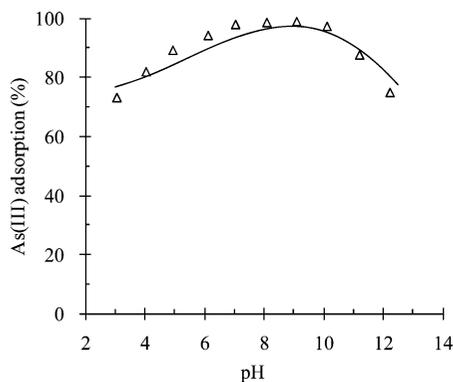


FIGURE 4. Experimental results (open triangles) and CD-MUSIC modeling (solid line) of As(III) adsorption as a function of pH at equilibrium conditions. Initial As(III) concentration was 3310 mg/L in raw water. TiO₂ = 30 g/L.

adsorbent that could be used in the remediation of acidic metallurgical wastewater with As(III) concentration at the g/L level.

Sulfate was approximately 1 g/L and remained unchanged in the treatment chain (Figure 2). The results suggest that sulfate has a weaker affinity to TiO₂ surface than As(III). For example, approximately 90% As(III) was adsorbed, whereas only 7% sulfate was removed in the first reactor. It has been reported that sulfate forms both outer-sphere and inner-sphere surface complexes (18), while As(III) forms inner-sphere bidentate binuclear complexes (13). Therefore, As(III) should exhibit a stronger binding to surface sites than sulfate.

The As 3d and O 1s XPS spectra are shown in Figure 3 for pristine and spent TiO₂ samples. The binding energy of the As 3d peak at 44.6 eV is in agreement with reported value for As(III) (19). Conversely, no As(V) 3d peak at 45.6 ± 0.2 eV (20) was observed, indicating that As(III) is the only As species on spent TiO₂. Changes in the ratio of O²⁻ at 530.4 eV and OH at 531.7 eV in the O 1s spectra show that As(III) mainly occupies OH surface sites on the TiO₂.

Surface Complexation Modeling. The results of the As(III) adsorption edge experiments, which determined the percentage of As(III) adsorbed as a function of equilibrium pH, and CD-MUSIC model calculations are shown in Figure 4. The experimental observations show that the As(III) adsorption increased from 78.8% to 98.2% when pH was increased from 3 to 9. With the constraint of As(III) bidentate binuclear surface configurations obtained from a previous EXAFS study of As(III) adsorption on TiO₂ (13), the CD-MUSIC model described the As(III) adsorption behavior reasonably well. Adsorption of As(III) apparently involves the replacement of

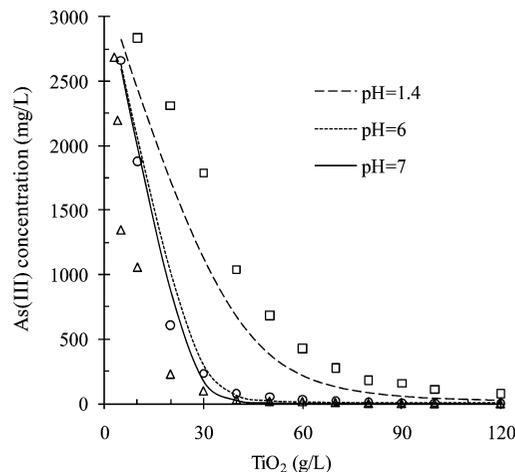


FIGURE 5. Adsorption of As(III) from raw water as a function of TiO₂ concentration at pH values of 7 (Δ), 6 (○), and 1.4 (□). Symbols are the experimental data, and lines represent CD-MUSIC model results. Initial As concentration was 3310 mg/L in raw water.

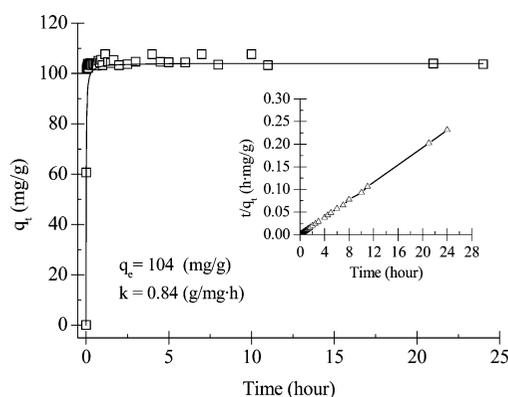


FIGURE 6. Adsorption kinetics of As(III) in raw water on TiO₂. Symbols are experimental data, and the solid lines represent the pseudosecond-order kinetic model simulation. Inset shows the linear regression ($R > 0.999$) and the best-fit parameters. Initial As concentration was 3310 mg/L in raw water; TiO₂ = 30 g/L; pH = 7.

surface OH groups (Figure 3-B). At high As(III) concentrations, bidentate surface configuration is preferable where each As atom is bonded to two oxygens, each of which is bonded to a Ti atom. This structure preference introduces less charge into the surface and results in a more stable configuration than a monodentate configuration (21). Additional batch adsorption experiments were performed by adding increasing amounts of TiO₂ into raw water at various pH values, and the observed and CD-MUSIC calculated results are shown in Figure 5. The experimental and model results suggest that a minimum dosage of 30 g/L TiO₂ was required to achieve more than 90% As(III) removal at pH 6–7.

Kinetics Study. The adsorption kinetics results in Figure 6 show that the adsorption rate of As(III) was rapid during the initial 2 min, and As(III) concentration kept relatively constant thereafter. A pseudosecond-order kinetic model has been applied previously to describe As(III) adsorption on TiO₂ (22) and was used in the present study. The equation is expressed as $t/q_t = t/q_e + 1/k \cdot q_e^2$, where q_t and q_e are the amounts (mg/g) of As(III) adsorbed at time t and at equilibrium, respectively, and k (g/mg·h) is the equilibrium rate constant of pseudosecond-order adsorption. The model parameters inserted in Figure 6 were obtained by linear regression of the integrated rate equation ($R > 0.999$). The adsorption capacity q_e (104 mg/g) is an order of magnitude higher than that of a previous report (7.1 mg/g) in which a

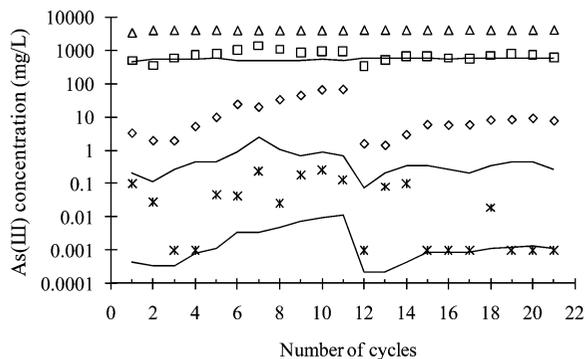


FIGURE 7. As(III) concentrations in raw water (Δ), after the first adsorption (\square), after the second adsorption (\circ), and after the third adsorption ($*$) as a function of TiO_2 recycle times. Solid lines are results of CD-MUSIC simulations.

synthetic groundwater with 2 mg/L As(III) was adsorbed using 0.2 g/L TiO_2 (22). The higher As adsorption capacity might be due to the higher mass ratio of As: TiO_2 (1:10) in the present study than that in the previous report (1:100) (22). The higher As loading (1.7 mmol/g) than that in the previous report (0.13 mmol/g) could be able to occupy more surface sites on TiO_2 (6 mmol/g), which resulted in a higher adsorption capacity. This observation is in agreement with a previous report (23).

TiO_2 Regeneration and Reuse. Spent TiO_2 was regenerated using NaOH extraction and then reused in the adsorption treatment. Our results demonstrate that 5 M NaOH could extract more than 60% adsorbed As(III) at a 100 mL NaOH to 30 g spent TiO_2 ratio (Figure S4). The incomplete extraction of As(III) may be attributed to the strong binding of As(III) on TiO_2 and possible formation of As(III) coprecipitates with cations at high pH. The extraction of As(III) occurred almost immediately when spent TiO_2 was added to the NaOH solution, and the aqueous As(III) concentration remained constant during the extraction with sonication and mechanical mixing for an hour. Because no difference in the As(III) extraction ratio was observed with sonication and mechanical mixing, spent TiO_2 was regenerated with 5 M NaOH under mechanical mixing for an hour in the following adsorption-regeneration-reuse treatment cycle. The As(III) desorption ratio in the 21 treatment cycles was in the range of 55–87% (Figure S5). The regenerated TiO_2 was then reused to remediate a mixed solution of raw water and As recovery waste with an average As(III) concentration of 3890 ± 142 mg/L, as detailed in the following section. The treatment process resulted in an average residual As concentration of 59 ± 79 $\mu\text{g/L}$ (Figure 7), which is far less than the Chinese regulatory discharge limit of 500 $\mu\text{g/L}$. However, the As concentration in the effluent is far above the drinking water standard at 10 $\mu\text{g/L}$. The effluent As concentration could be further reduced to less than 10 $\mu\text{g/L}$ with the inclusion of one more adsorption reaction in the treatment chain. Removal of As from levels of hundreds of $\mu\text{g/L}$ to drinking water standard has been previously demonstrated using TiO_2 (13, 14, 22). The experimental and CD-MUSIC model results in Figure 7 suggest that the As(III) removal percentage was $81 \pm 6\%$ in the first TiO_2 adsorption step, $98 \pm 2\%$ in the second step, and $99 \pm 1\%$ in the third step. The slightly reduced As(III) adsorption percentage in the first step may be attributed to the complicated composition of the raw water, with other species competing for the available surface sites.

Besides the As(III) removal, heavy metals can be effectively removed in each cycle of the 21 treatment cycles, and the effluent Cu, Pb, and Cd concentrations were less than 0.02 mg/L (Table S3). The association of As, Cu, Pb, and Cd with TiO_2 was demonstrated by the EDX spectrum (Figure S6 in

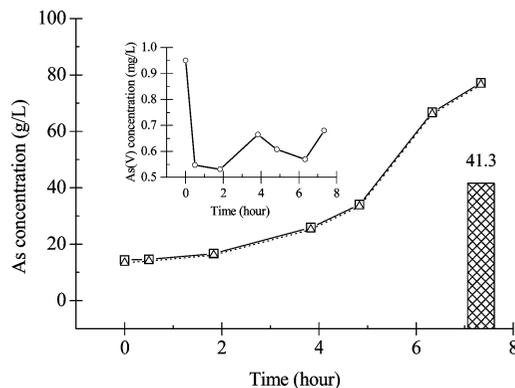


FIGURE 8. Concentrations of total As (\square), As(III) (Δ), and As(V) (\circ) in the recovery process. The column shows the As(III) concentration in the residual liquid after recovery.

the SI). The results suggest that TiO_2 can be used as an effective adsorbent for heavy metal removal from highly contaminated copper smelting wastewater.

As(III) Recovery. As(III) in the waste solution from the TiO_2 regeneration process was concentrated by heating at 70 $^\circ\text{C}$ and subsequently recovered by precipitation. Figure 8 shows the change of As(III) and As(V) concentrations as a function of heating time during the recovery process. The results indicate that As(III) was the predominate As species, and little As(III) was oxidized during the recovery process. When the solution was cooling down to room temperature, 60–62% As(III) was recovered as precipitate based on the mass balance calculation. The EDX analysis indicates that the dominant elements in the recovered solid were As, Na, and O (Figure S7). The As 3d XPS spectrum reveals a peak around 44.3 eV binding energy (Figure S7), which is in good agreement with the peak of As 3d in NaAsO_2 at 44.2–44.3 (24, 25), suggesting the precipitation of sodium arsenite precipitates. The precipitate could be used as an intermediate for sodium arsenite chemical refinement. The residual liquid after recovery was recycled and mixed with raw water as influent in the TiO_2 adsorption process, and its contribution to the total As(III) concentration was less than 20%.

Implications for Copper Smelting Wastewater Treatment. Extrapolations from our laboratory experimental results to full-scale implementation suffer from some limitations that should be addressed. The TiO_2 employed in this study was prepared chemically and was more expensive than the iron salts and lime used in the HDS process. Therefore, the initial capital cost might be a consideration. However, the advantages of adsorbent regeneration and minimum sludge generation should reduce the operating and maintenance costs and, more importantly, the adverse environmental impact. Second, our process involved three successive adsorption reactions and TiO_2 regeneration, which require sophisticated solid/liquid separation systems such as filtration and centrifugation. Furthermore, only about 60% of the adsorbed As(III) was extracted using 5 M NaOH. Further study is needed to maximize the desorption ratio of As(III) from TiO_2 . In addition, recovery of As(III) required evaporation of the NaOH extract to 10% of the initial volume, but only about 60% As(III) was recovered. Although the alkali was recycled, most of it would have been consumed in neutralizing the sulfuric acid in raw water from pH 1. The resultant extract would have very high concentrations of Na_2SO_4 , which would limit the number of times it could be recycled.

Despite such shortcomings, our innovative process could achieve adsorbent regeneration and arsenic recovery and has the advantage of producing “zero” amount of sludge. It resolves a difficult environmental problem about the secondary pollution from the huge volumes of sludge, which

prevails in the smelting industry and causes a significant proportion of overall treatment costs. For example, the average amount of sludge produced from the HDS process in the studied copper smelting company is approximately 70 t/d with a wastewater flow rate of 500 m³/d. The conventional neutralization and precipitation process generates 10–18 g sludge per liter of synthetic acid mine drainage treated using various laboratory batch tests (4). The results in this study show that low metal concentrations in the effluent and no sludge generation could be accomplished by taking advantage of the high adsorption capacity and chemical stability of TiO₂. The results are generally applicable to copper smelting industries worldwide.

Acknowledgments

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Supporting Information Available

Description of TiO₂ synthesis, SEM-EDX, XPS, EXAFS, and CD-MUSIC modeling; tables showing arsenic concentrations in a copper smelter wastewater, metal concentrations in 21 treatment cycles, and CD-MUSIC model parameters; figures showing metal concentrations in a copper smelter wastewater, the schematic diagram of proposed treatment processes, As(III) desorption in 21 treatment cycles, EDX spectrum of spent TiO₂, and EDX and XPS spectrum of recovered sodium arsenite. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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