Simultaneous As(III) and Cd removal from copper smelting wastewater using granular TiO$_2$ columns

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**Abstract**

Remediation of metallurgical industry wastewater has presented a great environmental challenge for decades. In this study, a complete remediation technology was proposed for simultaneous As(III) and Cd adsorptive removal, adsorbent regeneration, and recovery of As and Cd. Using three granular TiO$_2$ columns in series, As(III) and Cd in the raw water at $2590 \pm 295$ and $12 \pm 2$ mg/L, respectively, could be reduced to $0.16 \pm 0.11$ and $0.0133 \pm 0.0134$ mg/L, well below the wastewater discharge limit. Spent TiO$_2$ media could be regenerated using H$_2$SO$_4$ and NaOH, and the regenerated adsorbent could be re-used for at least 10 treatment cycles and 770 bed volumes with no decrease in its adsorption capacity. Remediation of 1 L wastewater generated 0.89–1.5 g solid residue which could be used as an intermediate for the As and Cd chemical refinement. The waste solution can be further treated after mixing with raw water to adjust the raw pH from 1.4 to 7. This adsorption, regeneration, and reuse process provides an innovative technology for metallurgical industry wastewater remediation that is promising for practical application.

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**1. Introduction**

Mining and smelting are major industrial processes that are associated with multiple toxic metal contaminants (Bian et al., 2012). In these industrial wastewaters, coexistence of As(III) and Cd is a great public concern because of their carcinogenicity (Barrett, 2012; Lubin et al., 2008). Thus, developing effective and robust wastewater treatment technology for simultaneous As(III) and Cd removal has motivated extensive research (Allende et al., 2012; Deschamps et al., 2005; Dey et al., 2009; Jiang et al., 2014; Johnson and Hallberg, 2005).

Many efforts have been made to solve this problem over past decades, with the result that neutralization-precipitation has been adopted as a commonly used method for removal of heavy metals, including As(III) and Cd, from mining and smelting wastewaters (Dong et al., 2011; McDonald et al., 2006; Wang et al., 2003). For example, an approach using iron precipitation and high density sludge (HDS) recycling has become a benchmark procedure in acid mine drainage treatment (Dey et al., 2009). This HDS process requires increasing the pH with hydrated lime and subsequently adding iron salts to form precipitates with As. However, HDS generates large volumes of sludge with low chemical stability (Dey et al., 2009; McDonald et al., 2006), which may release As under the attack of carbon dioxide (Nishimura and Robins, 1998; Pantuzzo and Ciminelli, 2010).
Recent studies have employed various adsorbents to remove As from wastewater (Adra et al., 2013; Dou et al., 2013; Luo et al., 2010; Mohan and Pittman Jr, 2007; Mueller et al., 2010), and the results indicate that TiO₂ is a promising material for As removal due to its high adsorption affinity and chemical stability (Guan et al., 2012). Our previous study demonstrated that regenerable and reusable nanocrystalline TiO₂ can remediate acidic metallurgical wastewater with As(III) concentrations at the g/L levels (Luo et al., 2010). However, the use of nanocrystalline TiO₂ requires laborious solid/liquid separation in the treatment chain, and the possible leakage of As-adsorbed nano TiO₂ presents an environmental risk if not safely disposed of (Luo et al., 2013). To prevent the potential loss of nanomaterials, granular adsorbents based such as iron dust, bone char, and micrite have been evaluated for the treatment of synthetic acid mine drainage with 5 mg/L As(V) (Liu et al., 2013). However, these granular media have low As adsorption capacity (2.7–6.6 mg/g) and are unsuitable for remediation of industrial wastewaters with As concentrations at the g/L levels. In addition, these granular media are generally designed for one time use only, and the disposal of spent media involves additional economic and environmental concerns. Our approach to solve this problem is to use regenerable granular TiO₂ in a fixed-bed column. Granular TiO₂ based As removal from groundwater has been investigated in previous study (Bang et al., 2005). However, no attempt to use granular TiO₂ in the remediation of metallurgical wastewater has been reported. As a proof-of-concept study herein, we implemented a granular TiO₂ based complete treatment chain to remediate copper smelting wastewater with 2590 mg/L As(III) and 12 mg/L Cd. This adsorption-regeneration-reuse treatment process results in successful remediation and “zero” residue, and can avoid the possibility of secondary pollution and reduce the post-treatment cost.

2. Materials and methods

2.1. Materials

The raw water was obtained from a copper smelting company in China (Luo et al., 2010). The stock solutions of As(III) and Cd were prepared by dissolving NaAsO₂ and Cd(NO₃)₂ in deionized (DI) water solution. The TiO₂ used in this study was prepared by hydrolysis of titanyl sulfate as detailed in the supplementary materials (SM) (Jing and Cui, 2011). Granular TiO₂ of 40–60 mesh (250–380 μm) with BET of 196 m²/g was used in this study.

2.2. Adsorption isotherm

Adsorption isotherm experiments were performed to determine the As(III) and Cd adsorption capacity on granular TiO₂ in 0.04 M NaClO₄ solution. Suspension samples containing 0.39–2460 mg/L As(III) or 0.05–1470 mg/L Cd and 2.5 g/L TiO₂ were adjusted to pH 5 and 7 with NaOH and HClO₄. The solutions were purged with nitrogen for an hour to remove O₂ and CO₂. After the samples were mixed on a rotator for 72 h in the dark, the final pH was measured and the suspensions were filtered through a 0.45-μm membrane filter for soluble arsenic and cadmium measurements.

2.3. As(III) and Cd removal using granular TiO₂ columns

The flowchart of the wastewater treatment is shown in Fig. 1. The pH of the raw water was adjusted from 1.4 to 4 using 10 wt % lime, and then to pH 7 using industrial grade NaOH. The water contained an average concentration of 2590 ± 295 mg/L As(III) and 12 ± 2 mg/L Cd, which was treated using three TiO₂ columns in series. When granular TiO₂ in the first column was saturated, the spent media in this column was transferred into a 100 mL Teflon container for regeneration. The regenerated granular TiO₂ was reused as the last column in the next cycle, and the other two columns were shifted forward in sequence. In this way, the first column always has the highest adsorption loading and the last column has the highest available adsorption capacity, to safeguard the effluent quality.

The column parameters are summarized in Table 1. In a typical setting, granular TiO₂ (20 g) was packed in a 1.2 cm inner diameter glass column, resulting in 16 cm height and 18 mL volume. The columns were covered with aluminum foil to prevent light exposure. The upflow rate was designed at 0.6 mL/min with an empty bed contact time (EBCT) of 30 min for each column.

2.4. Granular TiO₂ regeneration

The spent granular TiO₂ (20 g) was regenerated in the following procedure. First, acid regeneration was employed to
extract cations by reacting with 70 mL 0.5 M H2SO4 on a rotator for 2 h. Then, the media was rinsed with 70 mL tap water. The media was then mixed with 70 mL 5 M NaOH solution for 2 h, and rinsed with 70 mL tap water. This alkali wash was repeated three times to maximize the desorption of As(III) from TiO2. Finally, 70 mL 0.5 M H2SO4 solution was applied to adjust pH to neutral.

2.5. Recovery of As and Cd from regeneration solution

The above acid and alkali regeneration solutions were mixed and precipitates were formed. After solid/liquid separation by centrifugation at 8000 rpm for 15 min, the solids were freeze-dried before characterization using X-ray absorption near edge structure (XANES), X-ray diffraction (XRD), scanning electron microscopy and energy dispersive X-ray (SEM-EDX). The residue liquid after recovery was recycled and mixed with raw wastewater as influent in the next adsorption-regeneration-reuse cycle.

2.6. Characterization

X-ray powder diffraction (XRD) data were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA using a Cu-target tube and a graphite monochromator. Scans were performed in the 2θ range of 5°—90° with a step size of 0.01° and a count time of 2 s per step. The PDF-2 reference database from the international center for diffraction database was used to analyze the XRD patterns. A Hitachi S-3000N scanning electron microscope and energy dispersive X-ray (SEM-EDX) analyzer was used for qualitative analysis of the solid residue from adsorbent regeneration. EDX mapping was used to examine the dominant elements in the solid residue. The solid residue was analyzed using XANES on beamline BL14W1 at the Shanghai Synchrotron Radiation Facility (SSRF), China. XANES spectra were acquired from —150 to 300 eV relative to the As K-edge of 11,867 eV. Elemental arsenic (As0) was used to calibrate the energy at 11,867 eV. The spectra were collected in fluorescence mode. Na2HAsO4 · 7H2O and NaAsO2 spectra were also collected and analyzed as standard references. The XANES spectra were analyzed using a linear combination fit in the Athena program in the IFEFFIT package (Ravel and Newville, 2005).

2.7. Sample analysis

A furnace atomic absorption spectrometer (FAAS, Perkin—Elmer AAS-800) was used to measure the total concentration of As and Cd. The As speciation was determined by a high performance liquid chromatography atomic fluorescence spectrometer (HPLC-AFS, Jitian, China). 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. The quality assurance/quality control procedure followed that of our previous studies (Cui et al., 2013; Luo et al., 2010). Extended X-ray absorption fine structure (EXAFS) spectroscopy was used to explore the adsorption mechanism of wastewater As(III) on granular TiO2, and the information is detailed in the SM.

3. Results and discussion

3.1. Granular TiO2 adsorption capacities for As(III) and Cd

The adsorption isotherms of As(III) and Cd conformed to Langmuir model (Fig. 2), and the fitting parameters were presented in Table S1. Neutrally charged As(III) and cationic Cd exhibited different adsorption behaviors on granular TiO2. Specifically, the adsorption capacity for As(III) ranged from 145 to 160 mg/g when pH increased from 5 to 7 (Fig. 2-I). On the other hand, the Cd adsorption capacity substantially increased from 57 mg/g at pH 5 to 380 mg/g at pH 7 (Fig. 2-II). Compared with As(III) adsorption capacity of 2.2—10.23 mg/g on powder (hydrous) or granular TiO2 found in previous

| Parameter          | Column parameters |
|--------------------|-------------------|
| Mass of granular TiO2 (g) | 20                |
| TiO2 particle size   | 40—60 mesh (250—380 μm) |
| Column diameter (cm) | 1.2               |
| Bed depth (cm)       | 16                |
| EBCT (min)           | 30                |
| Flow rate (mL/min)   | 0.6               |
| Hydraulic loading rate (cm/min) | 0.53           |
| Initial As(III) concentration (mg/L) | 2590 ± 295       |
| Initial Cd concentration (mg/L) | 12 ± 2            |

Fig. 2 — Adsorption of (I) As(III) and (II) Cd (point) on TiO2 and Langmuir modeling (line) at pH 5 and 7.
studies at pH 4–9 (Bang et al., 2005; Guan et al., 2012; Xu et al., 2010), our granular TiO$_2$ exhibited a higher value (145–160 mg/g). Meanwhile, the Cd adsorption capacity has been reported to be in the range 3.9–56.0 mg/g TiO$_2$ with different particle size at pH 6.1 (Gao et al., 2004), an order of magnitude smaller than the present granular TiO$_2$. The high adsorption capacity of granular TiO$_2$ in this study may be attributed to the high As(III) and Cd initial concentrations, which ensures its utility to treat real industrial wastewaters.

### 3.2. As(III) and Cd removal using granular TiO$_2$ columns

Simultaneous As(III) and Cd removal was achieved using three consecutive granular TiO$_2$ columns, and the effluent concentrations were below the regulatory requirements (Figs. 3 and 4). For instance, the influent As(III) concentration at 2590 ± 295 mg/L was decreased to 0.16 ± 0.11 mg/L, and Cd was reduced from 12 ± 2 mg/L to 0.0133 ± 0.0134 mg/L. The effluent concentrations were well below the Chinese industrial wastewater discharge limit, 0.5 mg/L for As and 0.1 mg/L for Cd. Although in some cycles, the effluent Cd concentration from the 3rd columns was higher than that in other two, the effluent Cd concentrations were all below the discharge limit of industrial wastewater in each treatment cycle (Fig. 4). Our results suggest that over 98% As(III) and nearly 100% Cd in wastewater can be removed in the treatment chain. The As speciation analysis indicated that no As(V) was detected in the treatment chain.

During the column experiments, the pH of the influent was decreased from 7.0 to 5.9 ± 0.8 in the effluent (Fig. S1), within the range for industrial wastewater discharge permits (6–9). This pH decrease can be attributed to surface complexation reactions of As(III) and Cd that resulted in the net release of one and two protons, respectively. The surface complexation reactions evidenced by EXAFS studies are descried as follows (Collins et al., 1999; Janusz and Matysek, 2006; Pena et al., 2006; Randall et al., 1999):

\[
\begin{align*}
\text{H}_3\text{AsO}_3 + 2(>\text{TiOH}) &= (>\text{TiO}_2\text{AsO}^- + \text{H}^+ + 2\text{H}_2\text{O}) \\
\text{Cd(H}_2\text{O})_6^{2+} + 2(>\text{TiOH}) &= (>\text{TiO}_2\text{Cd(H}_2\text{O})_4 + 2\text{H}^+ + 2\text{H}_2\text{O})
\end{align*}
\]

Our As K-edge EXAFS analysis for spent TiO$_2$ (Fig. S2 and S3, Table S2) indicates that As(III) formed a bidentate binuclear inner-sphere complex on the TiO$_2$ surface without Cd-As(III)-TiO$_2$ ternary surface complex or surface precipitate existed in this study.

### 3.3. Granular TiO$_2$ regeneration and reuse

Extraction using 0.5 M H$_2$SO$_4$ followed by 5 M NaOH could release 97% of adsorbed As(III) and 66% of adsorbed Cd.
The desorption kinetics indicated that the aqueous As concentration reached equilibrium after mixing with H₂SO₄ and NaOH for 2 h (Fig. S5). Therefore, the spent granular TiO₂ was regenerated by mixing with 0.5 M H₂SO₄ and subsequently 5 M NaOH for 2 h. Under this optimized condition, the total desorption ratio was in the range 76–93% for As(III) in 10 treatment cycles, and 62–89% for Cd (Fig. S6 and S7). The regenerated granular TiO₂ was then reused to treat the mixture of raw water and waste solution from TiO₂ regeneration with average As and Cd concentrations of 2590 ± 295 and 12 ± 2 mg/L, respectively (Fig. 1).

The 60-g granular TiO₂ in three consecutive columns was effective in As(III) and Cd removal for more than 10 treatment cycles in 770 bed volumes (BV) (Figs. 3 and 4). Here, it is noteworthy that considering the recycle of residual liquid (about 40% of the treated water), about 462 BVs (8316 mL raw water) were actually treated. The mass balance calculation indicates that the average concentration of As(III) and Cd loaded on the first TiO₂ column in each treatment cycle was 162 ± 20 and 1.00 ± 0.16 mg/g, respectively (Fig. 5). This As(III) adsorption capacity was in line with the adsorption isotherm results (145–160 mg/g, Fig. 2-I), indicating that the first TiO₂ column reached its maximum As(III) adsorption capacity in each cycle. Compared with the adsorption capacity of reported granular adsorbents (0.16–32.4 mg/g) (Badruzzaman et al., 2004; Bang et al., 2005; Dou et al., 2013; Gibbons and Gagnon, 2010; Liu et al., 2013), the granular TiO₂ in this study

Fig. 4 – Effluent Cd concentrations from three columns in series as a function of bed volume. Diamonds: column A, Circles: column B, Triangles: column C. The numbers after the A, B, and C column represent the number of times that the column was regenerated and reused.

Fig. 5 – TiO₂ adsorption capacity for As(III) and Cd in 10 treatment cycles.
exhibited high As(III) adsorption capacity (145–160 mg/g). The reason may be ascribed to higher initial As(III) concentration (2590 mg/L) and longer EBCT (30 min) than that in previous studies with As concentration in range 0.04³–5 mg/L and EBCT of 2–15 min. Nevertheless, the Cd loading on the first TiO₂ column (1.00 ± 0.16 mg/g) was appreciably lower than its adsorption capacity (57–380 mg/g, Fig. 2-II). The significant difference can be attributed to the relatively low Cd concentration in the raw water (12 mg/L).

The XRD patterns of pristine and spent TiO₂ shown in Fig. S8 exhibit no change in crystalline structure and TiO₂ remained in the anatase form (PDF #21-1272). The chemical stability of TiO₂ ensures its high effectiveness after regeneration, which enables its reuse in the following cycle.

### 3.4 Recovery of As and Cd from regeneration solution

Precipitation occurred when the acid and alkali regeneration solutions were mixed (Fig. S9). Remediation of 1 L wastewater could produce 0.89–1.5 g solid residue (dry weight), and 35–46% desorbed As(III) (553–897 mg) and >99.8% desorbed Cd (10.7 ± 1.4 mg) were in the precipitate based on mass balance calculation. The SEM-EDX results show the dominant elements in solid residue were O (39.9%), Na (27.3%), As (11.1%), and Ca (6.4%), with trace amounts of S (2.0%), Ti (1.9%) and Cd (0.57%) (Fig. S10). Furthermore, the As in the solid residue was composed of 25.2% As(V) and 74.8% As(III), as evidenced by our XANES analysis (Fig. S11). The existence of As(V) indicated that the strong alkali condition during the regeneration process may facilitate the oxidation of As(III). Our XRD analysis demonstrates the presence of NaAsO₂ (PDF #07-0009), NaCaAsO₄ (PDF #27-0664), and Na₂CdO₂ (PDF #36-1199) (Fig. S12), which could be used as a raw material for the production of As and Cd chemicals.

The volume of residual liquid was about 40% of the treated water. The As concentration in the residue liquid was approximately 2500 mg/L, which was comparable to that in the influent (2590 ± 295 mg/L). The As speciation analysis showed that an average of 14.9% As was in the As(V) form. Conversely, only μg/L level Cd was detected in the residue liquid. The residual liquid was then mixed with raw water at a volume ratio of 2:5 to adjust the influent pH to 7, resulting in about 4.1% As(V) in the influent. Thus, the residual liquid was recycled and its alkalinity was used to neutralize the acidity in the raw water.

### 3.5 Evaluation of small column tests

Accurate prediction of As(III) breakthrough curves from the fixed-bed system is important in facility design and operation. A close examination of the As(III) breakthrough profile in Fig 6 shows its similarity in the three consecutive columns, with a substantial steep curve for the first column. The three small columns in series can be considered as three sections of one large column with sampling ports placed at the top (i.e., after 30 min EBCT), middle (i.e., after 60 min EBCT), and bottom (i.e., after 90 min EBCT) (Westerhoff et al., 2006). Incorporating sampling ports in one large column helps to understand the effect of EBCT. For example, the As(III) concentration from the top sampling port reached 0.5 mg/L at about 32 bed volumes, whereas the effluent (i.e., the bottom sampling port) was below 0.03 mg/L up to 90 bed volumes (Fig. 6). The results clearly demonstrate that enhanced As(III) removal can be achieved with extended EBCT (Westerhoff et al., 2005; Zeng et al., 2008).

Individual column port data provide the opportunity to evaluate the efficiency of the treatment chain. The As(III) adsorption density (q_column) in the first and second TiO₂ column was 80.9 and 11.5 mg/g, respectively, when their effluent As(III) concentration reached 0.5 mg/L, whereas the effluent As(III) concentration from the third TiO₂ column never reached 0.5 mg/L, the discharge limit. At 90 bed volumes, the As(III) concentration from the first column port reached 2220 mg/L (i.e., 86% of raw water at 2590 mg/L), and the second column port was only 5.3 mg/L (i.e., 0.2% of raw water at 2590 mg/L) (Fig. 6). Based on the mass balance calculation, when TiO₂ in the first column was saturated, 55–73% of TiO₂ in the second column would be available for adsorption. Therefore, the column operation in a series configuration would be beneficial to take advantage of the TiO₂ adsorption capacity in the second and third column after forwarding the columns in sequence in the next treatment cycle as shown in Fig. 1 (Kanematsu et al., 2012; Westerhoff et al., 2006).

As a proof-of-concept study herein, the results obtained with laboratory small columns packed with granular TiO₂ can be used to simulate the performance of pilot or full-scale systems. The breakthrough curves of small and large columns are expected to be analogous because of the similarity in mass transfer and hydrodynamic characteristics (Crittenden and Weber, 1978a, b; Kanematsu et al., 2012). Thus, the proportional diffusion (PD) scaling approach could be used to design a full-scale column because of its successful performance prediction of such systems (Kanematsu et al., 2012; Westerhoff et al., 2006, 2005). In the PD scaling approach, the relationships among empty bed contact time (EBCT), particle diameter (dₚ), operating duration (t), hydraulic loading rate (V), Reynolds number (Re), Schmidt number (Sc) are related together according to the following equations:

\[
\frac{EBCT_{SC}}{EBCT_{LC}} = \frac{d_p^{0.4} \cdot CE}{d_p^{0.4} \cdot LC} \cdot \frac{t_{SC}}{t_{LC}}
\]
The subscript LC and SC in the above equations indicated large-scale and small-scale column, respectively. The magnitude of ReLC × Sc was set to 2000 in this study to minimize axial dispersion, and this value is generally used to scale up granular iron oxide columns for As(V) removal (Kanematsu et al., 2012; Westerhoff et al., 2006, 2005). The detailed calculation and list of large column design parameters are presented in the SM.

According to the parameters of the full-scale column (Table S5), three columns of 2.6 m in diameter and 3.8 m in height with granular TiO₂ (20–40 mesh) weighted 22,222 kg in each column should be implemented to remediate 500 m³ wastewater per day. The average solid waste in this proposed system is about 600 kg, much less than the 70 t/d sludge from the traditional HDS process (Luo et al., 2010).

4. Conclusions

Our laboratory experimental results provide a novel treatment process for metallurgical industry wastewater, which includes As and Cd adsorptive removal, adsorbent regeneration, and recovery of As and Cd. The granular TiO₂ used in this study has unique advantages over nanocrystalline TiO₂ powder because of its greater particle size. Thus, granular TiO₂ can be readily installed with column-based treatment chains and the TiO₂ regeneration is operationally feasible. Using this triple fixed-bed continuous process, the arsenic and coexisting heavy metals in the acidic wastewater can be removed in an on-line system. In addition, our treatment technology could achieve adsorbent regeneration and has the advantage of producing “zero” amount of sludge. This heavy metal treatment system should be applicable to smelting industries worldwide.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2014.10.042.

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