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TECHNICAL ARTICLE

Prospect for Treating Antimony-Laden Mine Wastewater Using Local Materials

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Abstract The wastewater from the world's largest antimony mine (Hunan, China) contains high level of metal and metalloid contaminants (As, Cd, Hg, Pb, Se, and Sb). We tested the effectiveness of low-cost local industrial by-products [coal fly ash (CFA) and Ca–Si slag from the metals industry] and traditional agents [limestone, diatomaceous earth (DE), and zeolite] to treat the wastewater. Their relative effectiveness ranked: CFA > Ca–Si slag > DE > limestone > zeolite. CFA and Ca–Si slag removed 9.9–85.5% of the As, Cd, Hg, Pb, Se, and Sb from the wastewater. The CFA and Ca–Si slag could be used as commercial filters or biogeochemical barriers to protect surface water and groundwater. A similar approach could be used at other mines.

Keywords Arsenic · Cadmium · Mercury · Lead · Selenium · Sb · Ca–Si slag · Fly ash

Introduction

The mining process, including flotation, ore washing and tailings disposal, can release trace elements formerly locked up in the ore, causing water and soil pollution (Younger et al. 2002). In China, some of the wastewater is reused in the mine or concentrator, but surplus mine wastewater is often discharged untreated into natural ecosystems (Lingyun 2010).

As new technologies are developed to make it more profitable to mine low grade ore, even more waste will be generated. This trend requires the mining industry to adopt and consistently apply practices that minimize the environmental impacts of waste production (Lingyun 2010). The use of treatment methods such as commercial filtration systems can dramatically reduce mine profitability. It is therefore very important to find alternative low-cost adsorbents for removing pollutants from contaminated mine water (Ungureanu et al. 2014).

Low-cost materials with potential to be used for purification of wastewater are often located near mine sites. These include industrial by-products, e.g. slag, coal fly ash (CFA), or natural minerals, e.g. limestone, dolomite, vollastonite, and diatomaceous earth (Dong et al. 2013; Godimchyk and Il'in 2003; Madzivire et al. 2013).

Zeolites and diatomaceous earth are highly porous Si-rich minerals with useful physicochemical properties, such as cation exchange, molecular sieving, catalysis, and sorption (Lin et al. 2013; Panagiotis 2011; Rios et al. 2008; Wang and Peng 2009). Local industrial by-products like CFA or slag from the metals industry also can be used to remove mine water contaminants (Beh et al. 2012; Rios et al. 2008). Most of the literature on this theme refers to metal contaminants, but metals and non-metals can both be present at problematic concentrations in many types of mine wastewater (Gray and Eppinger 2012; Liu et al. 2009, 2010). Identifying a low-cost local materail that can remove metal and non-metal contaminants from mine wastewater would be advantageous.

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Study Area

The Xikuangshan mine near Lengshuijiang City has the largest antimony (Sb) deposit in the world. It is located between 27.7°N and 111.4°E in the northern part of the Xiangzhong Basin of Hunan Province (Liu et al. 2010). The deposit covers an area of about 16 km^2 and comprises four ore bodies: Feishuiyan, Tongjiayuan, Laokuangshan, and Wuhua (Peng et al. 2003). The annual production capacity of the mine is 40,000 metric tons (t) of Sb products, and 40,000 t of Zn ingots (He 2007; Wang et al. 2010). The environmental impact includes water and soil pollution by metals (Pb, Hg, Ni, Cd) and metalloids (Sb, As, Se) (He 2007; Liu et al. 2010; She et al. 2010; Zeng et al. 2006).

The As, Sb, and Hg in the Xikuangshan mine wastewater poses a high risk for environmental contamination and uptake of the pollutants by cultivated plants in this region (Liu et al. 2009). The aim of this study was to examine the effectiveness of various substances (limestone, zeolite, diatomaceous earth, Ca-Si slag, and CFA) in removing As, Cd, Hg, Pb, Se, and Sb from the mine wastewater.

Materials and Methods

Wastewater was collected from a concrete drainage channel near the tailings of the antimony mine (South Mine), where contaminated water collects and flows to the Lianxi River (a tributary of the Zijiang and Yangtze Rivers). After collection in polypropylene bottles, the wastewater samples were stored at 4 °C.

The following materials (Table 1) were used: limestone (chemically pure $CaCO_3$, Fisher Chemicals), Si-rich zeolite (clinoptilolite, $(Na,K,Ca)_{2-3}Al_3(Al,Si)_2Si_{13}O_{36}\cdot 12(H_2O)$ from the Orlov region, Russia), Si-rich diatomaceous earth (DE), (natural silica, Synergy Fertilizers Pty Ltd, North Queensland, Australia), Ca–Si iron slag (locally obtained from the Lengshuijiang Iron and Steel Co. Ltd.), and CFA (from a local electrical power station).

To prepare the materials and to determine if they would contribute pollutants, each material type was ground to 0.1–0.5 mm and tested. To determine pH, 6 g of each was agitated in 30 mL of water for 1 h and then tested for pH. To determine the total Si content, the material was dissolved in a $NaOH–H_2O_2$ matrix for microwave digestion. For determination of As, Cd, Hg, Pb, Se, and Sb, a HNO_3–HCl–HF matrix was used for microwave digestion (Lambre and Hill 1998). After digestion, the element concentration was measured using an ICP-OES Perkin Elmer Optima 5300 DV. Each material was analysed four times.

Adsorption tests were conducted in plastic columns with a diameter of 1.5 cm and a total volume of 10 cm^3. 10 g of the test material were placed in each column; the control column was filled with pure quartz sand (0.2–0.5 mm size). Columns were run in triplicate and the results were averaged. Mine wastewater was added to each column at 6–8 mL h^{-1} using a peristaltic pump. The percolate was collected at 10 mL intervals. A total of 50 mL of wastewater solution were applied to each column. Analyses of As, Cd, Hg, Pb, Se, and Sb in the collected percolate were done using an ICP-OES Perkin Elmer Optima 5300 DV. The amounts of adsorbed contaminants were calculated for each material. The monosilicic acid content in the percolated solution was also measured using the same ICP-OES unit. A 95% LSD (least significant difference) analysis of variance was performed with Statgraphics Plus 5.1 software to determine whether there was a significant difference in the mean between treatments at the ($p \leq 0.05$) level.

Results

The use of an industry by-product for water treatment has a risk of environmental contamination if these substances contain pollutants (Dung et al. 2014). Therefore, it was important to verify that these low-cost adsorbents were environmentally safe. All materials used to pack the columns were determined to have very low concentrations of pollutants, and therefore would not contaminate the percolate (Table 1). The slag from the Lengshuijiang Iron and Steel Co. Ltd. contained only trace amounts of Pb and the

Table 1 Selected property of the Si-rich materials

Material	pH	Total (%)					As	Cd	Hg	Pb	Se
		Si	Fe	Ca	Mg	Na	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
$CaCO_3$	8.8 ± 0.01	N/D	N/D	25.4 ± 1.4	N/D	N/D	N/D	N/D	N/D	N/D	N/D
DE	7.2 ± 0.01	32.1 ± 2.1	4.0 ± 0.1	1.0 ± 0.1	0.6 ± 0.1	0.7 ± 0.1	N/D	N/D	N/D	N/D	N/D
Zeolite	7.6 ± 0.01	30.7 ± 2.0	0.6 ± 0.1	0.5 ± 0.1	0.5 ± 0.1	2.1 ± 0.2	N/D	N/D	N/D	N/D	N/D
Ca–Si slag	8.5 ± 0.01	19.3 ± 1.8	2.6 ± 0.2	20.5 ± 1.3	4.1 ± 0.2	N/D	N/D	N/D	N/D	0.2 ± 0.1	N/D
CFA	8.2 ± 0.01	17.8 ± 1.5	3.1 ± 0.2	4.5 ± 0.3	0.6 ± 0.1	0.1 ± 0.1	0.02 ± 0.01	0.01 ± 0.01	N/D	0.1 ± 0.1	0.03 ± 0.01

N/D not detected

Table 2 The content of As, Cd, Hg, Pb, and Se in the original wastewater and final volume of the percolated solution, ppm

Materials	pH	As	Cd	Hg	Pb	Se	Sb	Si
Wastewater	8.21 ± 0.03	7.90 ± 0.20	0.26 ± 0.03	0.14 ± 0.03	1.43 ± 0.04	13.42 ± 0.10	14.52 ± 0.45	5.91 ± 0.05
Sand	8.20 ± 0.01	7.92 ± 0.18	0.25 ± 0.03	0.14 ± 0.03	1.42 ± 0.03	13.45 ± 0.10	14.50 ± 0.35	5.23 ± 0.05
$CaCO_3$	8.34 ± 0.02	4.83 ± 0.14	0.13 ± 0.02	0.12 ± 0.02	0.50 ± 0.04	6.92 ± 0.05	5.76 ± 0.25	4.28 ± 0.06
Zeolite	8.17 ± 0.02	7.12 ± 0.20	0.11 ± 0.02	0.07 ± 0.01	0.53 ± 0.04	4.51 ± 0.05	2.13 ± 0.15	40.53 ± 0.20
DE	8.15 ± 0.01	5.84 ± 0.14	0.15 ± 0.02	0.08 ± 0.02	0.47 ± 0.04	7.64 ± 0.06	8.43 ± 0.20	41.33 ± 0.25
Ca–Si Slag	8.20 ± 0.01	2.54 ± 0.10	0.10 ± 0.02	0.04 ± 0.01	0.31 ± 0.03	5.44 ± 0.05	2.15 ± 0.15	21.55 ± 0.14
CFA	8.21 ± 0.02	3.83 ± 0.12	0.07 ± 0.02	0.09 ± 0.03	0.30 ± 0.03	2.20 ± 0.02	2.11 ± 0.12	15.46 ± 0.12

Table 3 The ranks of tested pollutants adsorption

Element	Rank of adsorption with content of adsorbed pollutants
As	CFA > Ca–Si slag > DE > Limestone > Zeolite
Cd	CFA = Ca–Si slag > Zeolite > Limestone > DE
Hg	Ca–Si slag > CFA > Zeolite = DE
Pb	CFA > Ca–Si slag > DE > Zeolite > $CaCO_3$
Se	CFA > Zeolite > Ca–Si slag > $CaCO_3$ > DE
Sb	Zeolite > CFA > Ca–Si slag > $CaCO_3$ > DE

CFA contained low amounts of As, Cd, Pb, and Se. These low levels are not considered to have had an impact.

The mine wastewater had extremely high concentrations of As (7.90 ppm), Se (13.42 ppm), and Sb (14.52 ppm) (Table 2), which corresponds to the literature data (He 2007; Liu et al. 2009) and is typical of mine wastewater. The concentration of soluble Pb was more than 1 ppm. The Cd and Hg concentrations were not high. The concentration of the soluble Si was extremely low at 5.91 ppm.

The quartz sand had very low adsorption capacity, compared to all of the other tested substances. For As and Hg, the slag was the best sorbent (the concentrations were reduced by 65.1% and 71.4%, respectively). For other elements the highest adsorption capacity was provided by CFA. It is important to note that the slag adsorbed the tested contaminants better or the same as zeolite, lime, or DE (Table 3).

The Si-rich substances (except quartz sand) increased the concentration of dissolved Si in the percolated solution from 5.91 ppm in the original wastewater to 15.46 ppm for CFA and to 41.53 ppm for DE. The column test enabled us to determine of the dynamics of the contaminants adsorption by each substance. From the adsorption curve, the smallest maximum adsorption capacity of As was obtained for the quartz sand (8.8 mg kg^{-1}) and zeolite (20.0 mg kg^{-1}) (Fig. 1). For the other substances, the maximum adsorption capacity was not reached. However the following amounts of pollutants were adsorbed: 23.0, 23.3, 30.1, and 33.1 mg kg^{-1} for the DE, lime, CFA, and slag, respectively. Complete saturation of Cd was only achieved by the quartz sand (0.26 mg kg^{-1}) (Fig. 2). For all of the other tested substances adsorption saturation was not achieved. The following rank for Cd adsorption was obtained: CFA (1.09 mg kg^{-1}) = slag > zeolite (1.06 mg kg^{-1}) > limestone (1.01 mg kg^{-1}) > DE (0.95 mg kg^{-1}). The Hg concentration

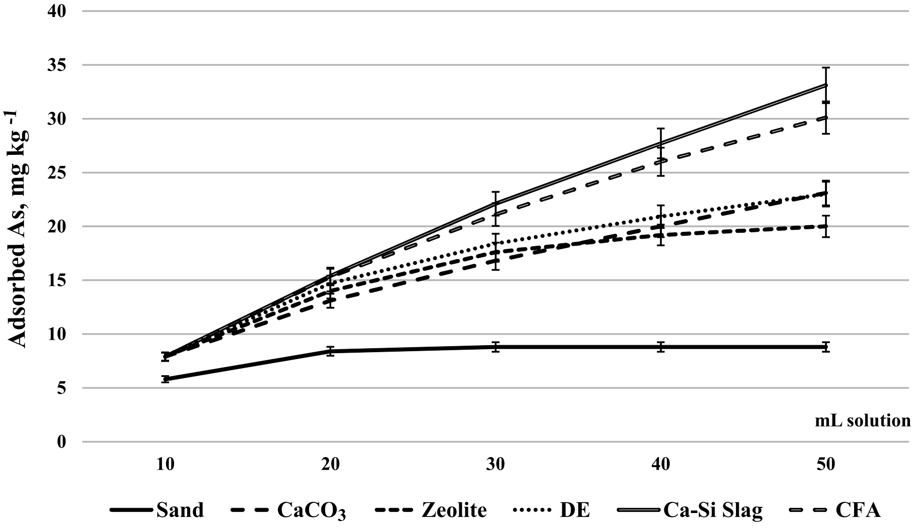
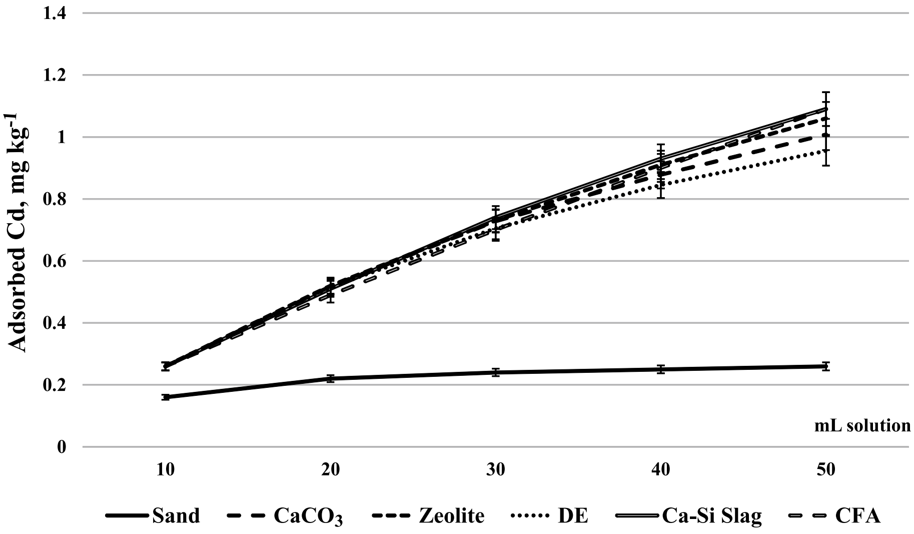


Fig. 1 The dynamics of As adsorption on tested substances, mg kg^{-1}

Fig. 2 The dynamics of Cd adsorption on tested substances, mg kg^{-1}



in the original wastewater was low (0.14 ppm), but for quartz sand and $CaCO_3$, the adsorption reached their maximum adsorption capacity of 0.21 and 0.36 mg kg^{-1}, respectively (Fig. 3).

The following rank for Hg adsorption was determined: slag (0.58 mg kg^{-1}) >CFA (0.48 mg kg^{-1}) > zeolite (0.51 mg kg^{-1}) = DE (0.51 mg kg^{-1}). The lead content in the original mine waste water was about 1 mg L^{-1}. Quartz sand adsorbed 1.5 mg kg^{-1}of Pb (Fig. 4). The Pb adsorption of the other tested substances was similar and ranged from 5.83 to 6.50 for the limestone and CFA, respectively.

The mine wastewater was characterized by very high concentrations of Se and Sb. Adsorption of these elements by the tested substances was also high. Quartz sand adsorbed 21.40 mg kg^{-1} of the Se, which according to the dynamics of adsorption can be classified as the sand's maximum adsorption capacity (Fig. 5). The following rank for Se adsorption was determined: CFA (61.79 mg kg^{-1}) > zeolite (55.89 mg kg^{-1}) > slag (53.70 mg kg^{-1}) > $CaCO_3$ (49.30 mg kg^{-1}) > DE (45.89 mg kg^{-1}).

Quartz sand adsorbed 17.79 mg kg^{-1} of the Sb (Fig. 6). Complete saturation of the sand by Se and Sb was obtained with 30 mL of the wastewater. Other substances were not saturated by Se or Sb; however, the following rank for Sb adsorption was determined: zeolite (68.66 mg kg^{-1}) > CFA (68.28 mg kg^{-1}) > slag (67.85 mg kg^{-1}) > $CaCO_3$ (60.04 mg kg^{-1}) > DE (56.46 mg kg^{-1}).

Discussion

Our previous study demonstrated that application of the Si-rich materials to soil resulted in Cd, Cu, Ni, and Pb immobilization and reduced leaching (Matichenkov et al.

Fig. 3 The dynamics of Hg adsorption on tested substances, mg kg^{-1}

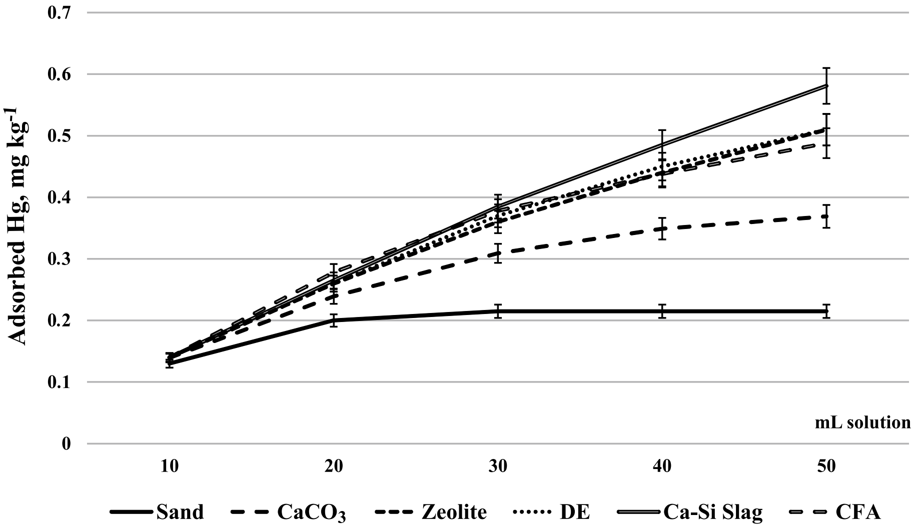


Fig. 4 The dynamics of Pb adsorption on tested substances, mg kg^{-1}

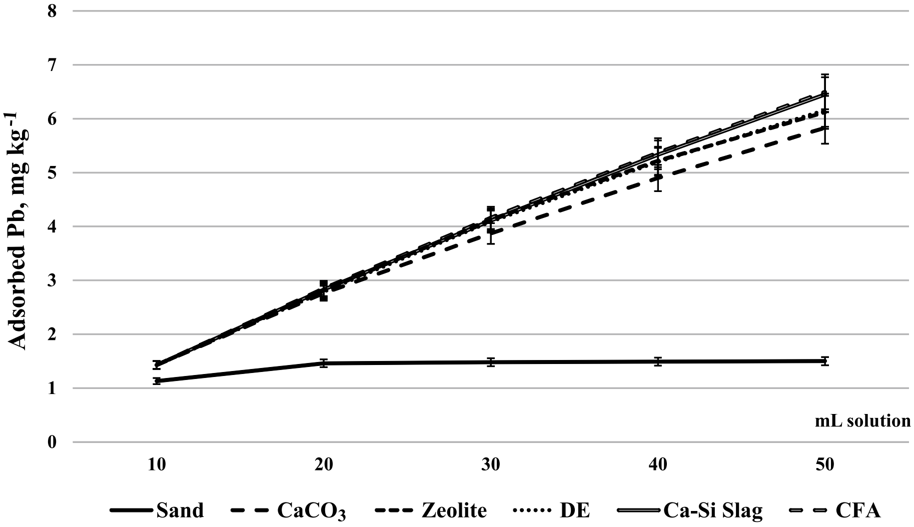


Fig. 5 The dynamics of Se adsorption on tested substances, mg kg^{-1}

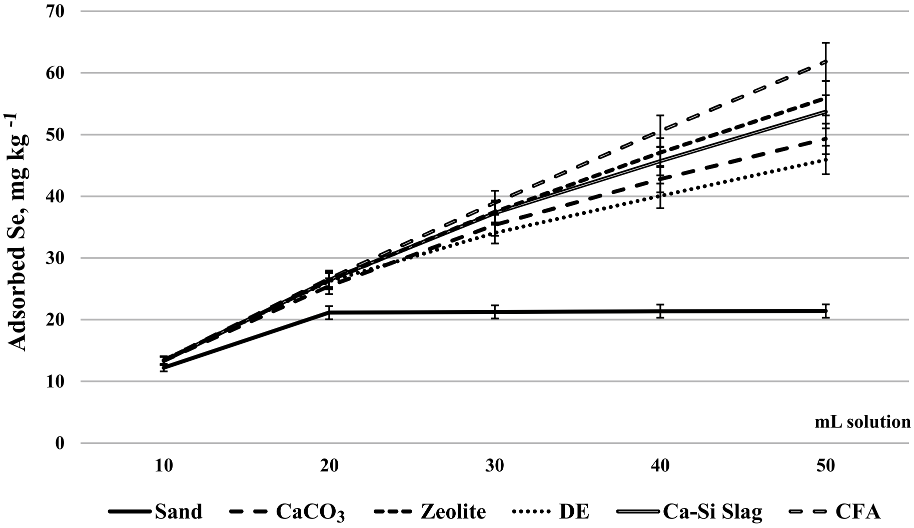
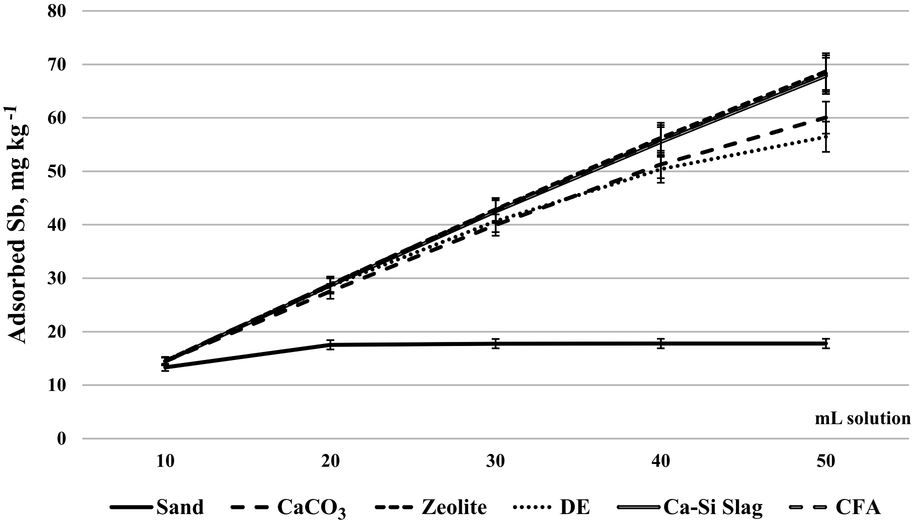


Fig. 6 The dynamics of Sb adsorption on tested substances, mg kg^{-1}



2016). Zeolite and DE were tested in this investigation. Both Si-rich minerals dramatically reduced the mobility of the metals via chemical sorption and silicates formation. In the more recent investigation, relatively low-cost materials were compared to the previously tested minerals. The CFA and slag had much higher adsorption capacities than the DE, lime, and zeolite for both metals and non-metals. Another benefit is that both of these local by-products are cheaper than natural minerals or lime.

The high level of contaminant removal by the local industrial wastes can be explained by the chemical composition of the by-products and their chemical properties. First, the CFA and slag are both more alkaline than the DE and zeolite, which can cause contaminants to precipitate (Godimchyk and Il'in 2003; Houben et al. 2013). Second, both by-products contain Fe and Al oxides, which provide additional mechanisms for metal and non-metal adsorption (Mahapatra et al. 2013). Third, the metals can react with monosilicic acid or chemically react with the Si-rich surface by the formation of slightly soluble silicates (Lindsay 1979; Matichenkov 2008; Matichenkov et al. 2016). This reaction efficiency depends on surface area and the solubility of the Si compound. Taken together, this gives the slag and CFA an advantage over the other materials tested.

Metalloids (As, Se, and Sb) can be adsorbed by Si-rich materials, where several mechanisms can be realized, including direct reaction with silicic anions, physical–chemical adsorption, and encapsulation by polysilicic acid (Mahmood et al. 2012; Matichenkov 2008; Matichenkov et al. 2016). The main mechanism that lowers the contaminant concentrations in the wastewater is very difficult to determine because the efficiency of the processes depends on numerous factors, including surface area, pH, temperature, electrical conductivity, and concentration of soluble elements. However, it is clear that larger-scale tests should be conducted using the slag and CFA to reduce pollution to the Zijiang River.

Conclusions

The wastewater from the Xikuangshan antimony mine contains high level of metal and metalloid contaminants (As, Cd, Hg, Pb, Se, and Sb). This study examined potential low-cost local industrial by-products (CFA and Ca-Si slag) and traditional materials (limestone, DE, and zeolite) for wastewater purification. The following rank of removal was determined: CFA > Ca-Si slag > DE > limestone > zeolite. The CFA and slag removed 9.9–85.5% of the As, Cd, Hg, Pb, Se, and Sb from the wastewater. The CFA and slag could be used as commercial filters or geochemical barriers to protect natural surface and underground water. A pilot-scale study is recommended.

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