

Antimony Immobilization in Primary Explosives Contaminated Soils by Fe-Al Based Amendments

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Abstract

The soil in primary explosives sites have been contaminated by high concentrations of antimony(Sb) and co-occurring heavy metals (Cu and Zn), but which is largely overlooked and neglected. In this study, we investigated the concentrations and species of Sb and studied the effect of Fe based, Fe-Al based sorbents combined application on the mobility of Sb and co-occurring metals. The content of Sb in soil samples was from 26.7 to 4255.0 mg/kg, occurring predominantly as Sb(V) (65.57 ~ 95.46%). In batch experiments, FeSO_4 showed ideal sorption of Sb (up to 97% sorption with 10% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), while sorption rates of 10% Fe^0 and 10% goethite were 72% and 41% respectively. However, Fe-based sorbents enhanced the mobility of co-occurring Cu and Zn in varying levels, especially $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. $\text{Al}(\text{OH})_3$ was necessary to prevent mobilization of Cu and Zn. In this study, 5% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 4% $\text{Al}(\text{OH})_3$ mixed with soil was the optimal choice to solve this problem with stabilization effect of Sb, Zn, Cu being 94.6%~~74.2%~~ and 82.2% respectively. Column tests spiked with 5% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 4% $\text{Al}(\text{OH})_3$ showed significant retention of Sb (85.85%), Zn (83.9%), Cu (94.8%). pH regulated results indicated that acid condition was more beneficial for retention of Sb than alkaline condition. However, there was no significant difference between sets of acidification and sets without pH regulation. Overall, the experimental results showed that 5% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ + 4% $\text{Al}(\text{OH})_3$ without pH regulation could be effective for the stabilization of Sb and co-occurring metals in primary explosives soils.

1. Introduction

Antimony (Sb) is an element of growing environmental concern due to the widespread use and uncontrolled release of Sb compounds into the environment (Filella et al. 2002b, He et al. 2019, Hu et al. 2014, Kong et al. 2015). In general, background concentrations of Sb in soil are lower than 1 mg/kg (Filella et al. 2002b). However, the massive smelting and utilization of Sb lead to severe contamination near the sites, posing a great risk to the local environment (Wang et al. 2018a, Wang et al. 2019, Wang et al. 2010a) and residents (Wu et al. 2011). More and more studies have shown that antimony pollution is a global issue (Amarasiriwardena & Wu 2011, Filella et al. 2009a) because of its toxicity to humans and its role in causing diseased of liver, skin, and respiratory and cardiovascular systems (Wu et al. 2011). Soil is an important medium for concentration and migration of Sb. In recent years, more attention has been paid to Sb contaminated soil in mining area and shooting ranges (Ahmad et al. 2014, Okkenhaug et al. 2013, Wang et al. 2018b, Wang et al. 2010b, Wu et al. 2011). However, there are little study on Sb contaminated soils caused by primary explosives due to the confidentiality and sensitivity. A significant input of Sb into the environment occurs through the production and utilization of primary explosives due to Sb used as combustible agent for classical primary explosives in history, which contain 33.4% Sb_2S_3 (Matyáš 2013). Weathering and corrosion of combustion residue lead to mobilization of metalloid Sb in anionic form (Hu et al. 2015). In addition, primary explosives sites, often characterized by critical concentrations of co-occurring copper (Cu), zinc (Zn) (Brede et al. 1996, Huynh et al. 2006, Jiang et al. 2020), can be of particular environmental concern since they represent hazardous multi-element contamination sources for sites zones. Leaching of Sb and co-occurring metals from primary explosives production and utilization areas pose a serious long-term threat to the environment and human health. Thus, immobilizing or reducing the mobility and bioavailability of Sb and co-occurring metals in primary explosives sites are crucial.

In the natural environment, the mobility, bioavailability and toxicity of Sb are primarily dependent on its chemical speciation (Filella et al. 2002b, a). Antimony is reported to exist in a variety of oxidation states (-III, 0, III, V), with oxidation states III and V being predominant in aqueous environment across a wide pH wide (4–10) (Ilgen et al. 2014). In the natural environment, Sb(III) primarily occurs as $\text{Sb}(\text{OH})_3$ under anaerobic conditions between pH 2 and 10 (Filella et al. 2002b, a), while Sb(V) is the predominant species existing as $\text{Sb}(\text{OH})_6^-$ in aerated environment (Filella et al. 2009b) and displays a high affinity to amorphous and crystalline Fe-(hydr)oxides with which it can form stable bidentate inner-sphere complexes (Guo et al. 2014b). These interactions are particularly favored by goethite in the pH range of 7.5–9.0, by hematite at pH of 8.5, by ferrihydrite in the pH range of 7.0–7.9, by akaganeite in the pH range of 9.5–10 (Garau et al. 2017). However, Sb with different valence states has different properties, in instance, Sb(III) can strongly adsorb on goethite over a wide pH range from 3 to 12, whereas the maximum adsorption of Sb(V) only occurs below pH 7 (Leuz et al. 2006). In addition, these Fe-based metals not only can adsorb Sb strongly but also acting as oxidants in transforming Sb(III) to Sb(V) (Kong & He 2016). Laboratory-scale testing indicated that $\text{Fe}_2(\text{SO}_4)_3$ is potentially applicable to Sb immobilization in soils (Okkenhaug et al. 2013). The sorption effects is based on the reaction of Sb(V) with surface hydroxyl group of Fe-based materials. However, the mobility of co-occurring Cu and Zn was enhanced after the addition of Fe-based sorbent (Okkenhaug et al. 2013). In the pH rang of 5–9, co-occurring metals behave quite differently, being commonly present in the soil solution as cations at acidic and circumneutral pH or as soluble SOM-metal(II) complexes at higher pH values (Garau et al. 2017). Moreover, at neutral and alkaline pH, substantial amounts of heavy metals are immobilized as Me-hydroxides, Me-carbonates or Me-hydroxycarbonates. Soluble heavy metals show limited affinity for hydroxyl groups due to their cationic nature but interact more strongly with negatively charged components (Garau et al. 2017). Thus, the different speciation, mobility and bioavailability

between Sb and co-occurring metals make the identification of suitable amendments a very challenging task. Aluminum (hydr)oxides show important sorption properties for Pb, Cd and Zn (Wang et al. 2013), At the same time, Aluminum (hydr)oxides can be protonated, making the surface positively charged and thereby generating electrostatic interactive forces with negatively charged Sb(V) (Garau et al. 2014). To date, only a few amendments, mostly based on Fe- and Al-containing materials, have been tested with variable success as Sb-immobilizing agents. There limited number of studies highlight the need to deepen our knowledge on the mobility of Sb and co-occurring metals in soil and to select ideal sorbents to immobilize them.

Focusing on soil contaminated with Sb in primary explosives production site, the main goals of this work were to (i) investigate the mobility and speciation of Sb in primary explosive sites, (ii) evaluate the effects of combined application of Fe-Al mixed amendments for primary explosives sites using batch tests and column tests, (iii) investigate pH effect on Sb immobilization.

2. Materials And Methods

2.1 Sb-Contaminated Soils and adsorbents

Sb-contaminated soils was collected from primary explosives production workshops of primary explosives site in Heilongjiang province of China. The specific coordinates were not elaborated due to the confidentiality and sensitivity of military enterprise. This site has been produced primary explosives for more than 60 years and is still in production now. The soil samples (S1-S9) were collected at the surface (0–20 cm depth), air-dried at room temperature, crushed with a wooden roller and sieved through a 150 µm mesh, which size fraction is thought to better estimate human exposure than bulk soil (James et al. 2011). Then fully mixed and prepared for soil analysis.

The soil sample with highest concentration of Sb was used for soil immobilization studies. Four different amendments used in the study as follows: (i) ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, powder), (ii) goethite (HFeO_2 , powder), (iii) Fe^0 grit (powder); (iv) aluminum hydroxide ($\text{Al}(\text{OH})_3$, powder).

2.2 Soil analysis

Soil physicochemical properties were measured on triplicate samples. Cation exchange capacity (CEC) was calculated by measuring the spectrophotometry of the supernatant of the leachate with a UV-1800 ultraviolet spectrophotometer (Stewart & Hossner 2001). The soil pH was determined in a 1:5 (w/v) soil/deionized soil suspension by pH meter after 1 h of equilibration according to ISO10390:2005. Soil organic matter content (OM) was determined by the acid dichromate oxidation method (Yin et al. 2015). Soil particle size was obtained using a laser particle size analyzer. Following microwave-assisted digestion with $\text{HCl} + \text{HNO}_3 + \text{HClO}_4$ (3:1:1) at 190 °C for 15min, cooled, filtered (< 0.45 µm) and diluted with ultrapure deionized water, total Sb (Sb_{tot}) concentrations were determined by hydride generation atomic fluorescence spectrometry (HG-AFS) (Kong et al. 2015). The total contents of Fe, Mn, Zn, and Cu were determined using inductively coupled plasma atomic emission spectrometer (ICP-AES) (Zhang et al. 2018). For Sb speciation analysis in soil samples, 0.2 g soil samples accurately weighed were extracted with 10ml of 0.1mol/L citric acid in 10g/L ascorbic acid medium pH 2 in an ultrasonic bath for 2 h, followed by centrifugation (30min, 3000rpm). Then filtered through a 0.45 µm membrane filter and prepared for analysis by HG-AFS (Potin-Gautier et al. 2005). The modified European Community Bureau of Reference (BCR) sequential extraction method (Rauret et al. 1999) is used as a sequential extraction process for Sb.

2.3 Immobilization experiment

2.3.1 Batch experiments

The soil (S9) mostly contaminated with Sb were used for batch experiment. Four grams of untreated soil or soil amendment mix (0%, 2%, 5%, 10% iron-based adsorbent, and 0%, 2%, 4% aluminum-based adsorbent) was weighed into a 50mL centrifuge tube and add the corresponding volume of deionized water in a liquid to solid ratio of 10 (L/S) with a horizontal shaker (100 rpm/min) for 10 days at room temperature ($25 \pm 1^\circ\text{C}$). All experiments were performed in triplicate. The samples were centrifuged, and filtered at 0.45 µm filter membrane for analysis.

2.3.2 Column leaching experiments

Column leaching experiments were carried out in triplicate with untreated soil and in quintuplicate with 5% FeSO_4 and 4% $\text{Al}(\text{OH})_3$ stabilized soil without or with pH regulators (i) 4% sodium bisulfate and (ii) 4% sodium carbonate. Column leaching experiments were carried out in polyethylene columns (length 300 mm × internal diameter 22 mm) packed with 160g thoroughly mixed soil material of

untreated soil (Group A), stabilized soil + 4% NaHSO₄ (Group B), stabilized soil (Group C), stabilized soil + 4% Na₂CO₃ (Group D), respectively.

Double filter papers (0.45µm) and 50mm-long quartz sands was installed at top and bottom of the column for particle retention. Deionised water was then added to the columns in an upward flow direction at a rate of approximately 0.38 mL/min via peristaltic pump over a 18 day period. The pore volume (PV) in the soil column was calculated to be 0.043 L based on an assumed soil porosity of 0.4 (total 550 – 600 PV) (Okkenhaug et al. 2013). In the course of the column experiment, samples were collected regularly and filtered for analysis.

3. Results And Discussions

3.1 Soil characteristics and risk

The major soil physicochemical properties are summarized in Table 1. All the nine soil samples were alkaline with pH values varying from 7.69 to 8.37, that was consistent with local soil pH range (Gao et al. 2018). Soil samples had a high CEC (45.82 ~ 144.39 cmol/kg) and covered a wide range of OM (12.3 ~ 101.0 g/kg). According to particle-size analysis, the soil texture in the primary explosives site varied greatly with sand 5.76%~93.53%, silt 5.77%~78.29%, clay 0.69%~12.47%. The mass fraction of Fe and Mn in the soil are 20000 ~ 32200 mg/kg and 396 ~ 719 mg/kg, respectively. Total concentration of Sb, Cu, and Zn in the studied area were varying from 26.73 ~ 4255.03 mg/kg, 24.29 ~ 312.30 mg/kg and 67.62 ~ 1330.05 mg/kg respectively. Antimony was the main contaminant in this primary explosives site, which is 0.34 ~ 211.75 times higher than Chinese screening value of the first land use category (20 mg/kg), based on the document of “Soil Environmental Quality Risk Control Standard for Soil Contamination of Development Land” issued by Ministry of Ecology and Environment of China (MEEC., 2018). The highest concentration of Sb was found in the soil sample S9 (4255 mg/kg), which was 211.75 times and 105.38 times higher than the corresponding risk screening value (20 mg/kg) and control value (40 mg/kg) respectively. Otherwise, Sb(V) was the major part of soil Sb, which occupied 65.57–95.46% of the total Sb. This result answered the transformation processes of Sb that most Sb was emitted in nature as Sb(III) (Hu et al. 2014), but Sb(V) was the predominant species by oxidation (Kong et al. 2015).

Table 1
Main physico-chemical characteristics of the soils (mean ± standard deviation; n = 3)

Soil	pH	OM (g/kg)	CEC (cmol/kg)	Texture ^a			Concentrations (mg/kg)						
				Clay (%)	Silt (%)	Sand (%)	Mn	Fe	Cu	Zn	Sb _{tot}	Sb ³⁺	Sb ⁵⁺
S1	8.37	23.5	88.42	0.69	5.77	93.54	499	32200	25.37	71.19	26.73	2.53	24.2
S2	7.8	19.5	144.39	12.47	81.77	5.76	573	30000	24.29	67.62	61.32	5.39	56.01
S3	8.11	12.3	90.12	9.34	76.92	13.74	545	28900	33.55	83.80	108.01	9.65	98.49
S4	7.96	47.8	134.52	10.48	73.22	16.3	413	24200	232.85	402.75	216.60	37.34	179.36
S5	7.69	73.8	89.62	5.29	55.37	39.34	628	31200	186.74	868.02	267.26	12.16	255.13
S6	7.93	49.2	46.44	1.35	11.81	86.84	396	23000	103.76	331.36	512.09	115.92	396.14
S7	8.15	101.0	45.82	10.63	29.54	59.83	513	25000	312.30	981.60	719.36	150.24	569.17
S8	7.91	84.8	76.99	6.37	45.77	47.86	554	23600	35.26	215.88	953.91	160.01	793.90
S9	8.25	28.9	50.52	12.08	78.29	9.63	719	20000	80.16	1330.05	4255.03	160.74	4094.33

^a Clay, silt and sand are defined as soils with particle size of 0–2, 2–20, 20–200, respectively.

The BCR method is extensively used as a sequential extraction process for heavy metal (Zhang et al. 2018), thus BCR sequential analysis was used for main contaminant (Sb). The speciation of Sb in primary explosives site soil is divided into soluble/exchangeable fraction (F1), reducible fraction (F2), oxidizable fraction (F3) and residual fraction (F4) based on the BCR technique (Weng et al. 2014). The fraction of Sb in primary explosives contaminated soil listed in Fig. 2 followed the order (average values): residual (38.05%~94.22%) > reducible fraction (0.01%~31.80%) > oxidizable fraction (0.32%~21.55%) > acid extractable fraction (0.76%~12.92%). F4 is considered to be strongly bound to the crystalline matrix with the lowest mobility (Weng et al. 2014), thus, Sb in S2 soil sample was the most stable, as a result, S2 may be with least risk. The residual fraction of Sb had minor difference in S1, S2, S3 while decreased significantly in the other

soils especially in S9 (only 38.05 %). The Sb of F1 and F2 can be combined as directly available fractions (Shen et al. 2017) with direct toxicity (Chen et al. 2008), because Sb in these two fractions is highly mobile when environmental conditions (pH, Eh, etc.) change. F3 of Sb is easily mobilized and transformed into F1 and F2, potential eco-toxicity should not be ignored (Chen et al. 2008). The total concentration of F1, F2 and F3 can be recognized as bioavailable fraction due to their direct and potential eco-toxicity (Weng et al. 2014). Figure 2 showed that Sb has highest proportion of F1 + F2 + F3 phase (61.95 %) in S9, indicating that S9 has a high migration potential and most biological impact (Garau et al. 2014). The amount of exchangeable Sb is negatively correlated with soil CEC ($r = -0.682$; $P < 0.05$) (Hailegnaw et al. 2020, Huang et al. 2020) and concentration of Fe ($r = -0.867$, $P < 0.01$) for all soil samples.

3.2 Batch experiments

3.2.1 The changes of pH and Sb fractions

In this study we evaluated the application of ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), goethite (HFeO_2), Fe^0 grit, at three different rates (2%, 5% and 10%), as potential amendments for the remediation of Sb and co-occurring metals contaminated soil. Then, to get better stabilizing results, $\text{Al}(\text{OH})_3$ was applied (0%, 2% and 4%) as combined amendments with Fe-based amendments. As shown in Fig. 3, after the equilibration period of 10 d, addition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ significantly decreased pH values of water extracts (21%, 24%, and 28% decreased at 2%, 5% and 10% amendment rates, respectively) compared to control, while HFeO_2 and Fe^0 grit had little effect on pH of water extracts. This largely due to the hydrolysis reaction of FeSO_4 ($\text{Fe}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_2 + 2\text{H}^+$) in pore-water of soil (Tresintsi et al. 2012, Zhang et al. 2019). The application of $\text{Al}(\text{OH})_3$ clearly increased pH values of water extracts in a small range (less than one unit) no matter combined application with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, HFeO_2 , or Fe^0 . This slight increase of pH mainly attributed to weak alkalinity of $\text{Al}(\text{OH})_3$ and partial dissolution of amendments and adsorption/precipitation (Jang et al. 2007).

Sequential extraction procedures of BCR were used for 5%Fe + 4%Al based modified soils (with the best modified result) and presented in Fig. 4. The Sb proportion of F1, F2, F3, and F4 in control soil were 8.7%, 4.5%, 27.0% and 59.7% respectively. F1 (Weng et al. 2014) decreased significantly in modified soils compared to control. Approximately 66.67%, 44.44% and 66.67% reductions (vs. control) were observed for $\text{FeSO}_4 + \text{Al}(\text{OH})_3$, goethite + $\text{Al}(\text{OH})_3$, $\text{Fe}^0 + \text{Al}(\text{OH})_3$ modified soil respectively. This is very important because this fraction of Sb has the most biological impact with direct toxicity (Chen et al. 2008). Together with F1, F2 is considered the most available to soil biota and the most easily leached to groundwater (Shen et al. 2017). However, only $\text{FeSO}_4 + \text{Al}(\text{OH})_3$ addition significantly reduced the F2 from 5–1%, despite with an decrease of soil pH. It is likely that the decrease of soil pH caused increase of exchange sites (Fe/Al oxides and oxyhydroxides), which has great affinity for Sb (Garau et al. 2011). Fe–Al based amendments additions induced a shift of F1, F2 and F3 towards to F4, which was more strongly retained by the Fe and Al (hydr) oxides (Filella et al. 2009b, Wilson et al. 2010) by adsorption. The concentration drop of F1, F2 and F3 fractions resulted in a subsequent low bioavailability and eco-toxicity (Weng et al. 2014). However, this was not obvious for the goethite and $\text{Al}(\text{OH})_3$ modified soil with only 2% bioavailable fraction shift to stable residual fraction. $\text{FeSO}_4 + \text{Al}(\text{OH})_3$ addition had significant increase of F4 (71%) compared to Goethite + $\text{Al}(\text{OH})_3$ and $\text{Fe}^0 + \text{Al}(\text{OH})_3$ groups, this could explained its high sorption capacity of Sb (Manzano et al. 2016). Overall, the BCR extract results showed that combined addition of 5% FeSO_4 and 4% $\text{Al}(\text{OH})_3$ induced a significant redistribution of Sb with a reduction of its more labile and bioavailable fraction and an increase of the residual fraction.

3.2.2 The effects of Fe and Al based sorbents on Sb

The results of batch experiments (Fig. 3) showed that leaching concentration of Sb in control groups was more than 14 mg/l, far exceeding the fifth category water limit (0.01mg/L) of the "Standard for groundwater quality issued by General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China (AQSIQ., 2017). This result proved high liquidity of antimony in primary explosives contaminated soils. This mainly due to a high percentage of soluble fraction (11.03%) and reducible fraction (30.12%) of Sb in S9 (Fig. 2). Thus, immobilizing or reducing the mobility and bioavailability of Sb in explosives contaminated soils with the aim of reducing plant and human bioavailability and reducing leaching of Sb to groundwater is necessary (Palansooriya et al. 2020). Chemical speciation analysis showed that almost all the Sb existed as Sb(V) with the concentration of Sb(III) being less than detection limit in water extracts. This is in accordance with thermodynamically that Sb(V) should be the main form in oxic environments (Okkenhaug et al. 2013, Serafimovska et al. 2013). In addition, widely distributed dissolved iron in the environment plays a significant role in rapid oxidation of Sb(III) (Kong et al. 2016). Ferric ion and iron oxyhydroxides in the environment are strong adsorbents of Sb (Guo et al. 2014a). Sb(III) can be simultaneously oxidized into Sb(V) once adsorbed on the surface of iron oxyhydroxides (Kong et al. 2016).

The amendment additions did not change the total concentrations of Sb. However, Fe-based amendments effectively prevented Sb mobility and reduced Sb's bioavailability by a strong preference of Sb binding to Fe hydroxides (Scheinost et al. 2006). $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

possessed the strongest sorption properties for Sb with 85.64%, 97.21%, 98.50% sorption at the addition rate 2%, 5% and 10% respectively (Fig. 3a). The sorption property was greatly enhanced by adding various concentrations of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. The sorption rate increased gradually with increasing $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentration from 0–10%, but which was growing modest with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentration from 5–10%. Furthermore, amendments of Fe^0 and HFeO_2 displayed lower sorption property of Sb compared with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Although, the sorption rate increased gradually with increasing Fe^0 or HFeO_2 concentration from 0–10%, 10% Fe^0 retained up to ~72.34% of Sb (Fig. 3c), whereas the HFeO_2 only retained up to ~41.05% of Sb (Fig. 3e). In the severely Sb contaminated primary explosives site, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is more effective for Sb immobilization than Fe^0 or HFeO_2 . The results are consistent with immobilization rate of Fe-based amendments for Sb in shooting range soil (Okkenhaug et al. 2013). So far, the immobilization mechanism of iron oxide for Sb(V) were summarized as direct precipitation, co-precipitation and adsorption (Guo et al. 2009, Wu et al. 2010). Direct precipitation mechanism could lead to the secondary Fe-Sb mineral tripuyite (FeSbO_4) formation, which was an important and ultimate sink for Sb in environment with very low solution ($\log K_{\text{so}} = -13.41$) (Leverett et al. 2012). Adsorption of Sb(V) was predominant mechanism and co-precipitation also played an important role in $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ modified soil (Liu et al. 2019). Adsorption by FeOOH , hydrolysis product of Fe(II) and Fe(III), rather than co-precipitation was predominant in the coagulation mechanism (Guo et al. 2014b). In addition, the Fe(II) in the solution was quickly oxidized to Fe(III) which significantly improved the efficiency of antimony removal (Zhang et al. 2019). Meanwhile, Fe(II) oxidation and ferric hydroxide formation may also lead to increase of adsorption between ferric flocs and Sb (Dehghani et al. 2016, Jarvis et al. 2012). The addition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ can clearly reduce the pH of soil solution, and only at the $\text{pH} < 7$ conditions, iron oxide shows strong affinity to Sb. When the $\text{pH} < 3$, too much $[\text{H}^+]$ could inhibit the hydrolysis extent of Fe (II) and Fe(III), which will limited the Sb(V) immobilization efficiency. In the pH of 3–6 range, the isoelectric point of FeSO_4 -produced iron flocs were at 7.5. Iron flocs with positive charge had better capture negative charged $\text{Sb}(\text{OH})_6^-$ at weak acid condition within pH 5 to 6 (Liu et al. 2019). As a result, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ amendment could further promote Sb(V) immobilization by reducing pH of soil solution. The maximum Sb(V) adsorption on HFeO_2 is found below pH 7 (Leuz et al. 2006) and is considered as pH dependence (Essington & Stewart 2015). In this study, the pH of soil extract solution was higher than 7, thus, HFeO_2 immobilize Sb in this primary explosives contaminated soils to a certain degree. When contact with oxygenated water, Fe^0 will convert to activated Fe^0 containing both ferrihydrite and goethite distributed on the surface (He et al. 2019). The big surface coverage makes activated Fe^0 recognized as a suitable adsorbent for the adsorption and immobilization of Sb (Mishra et al. 2016). However, the immobilization efficiency of Fe^0 for Sb was lower than $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. According to batch experiments of Fe-based amendments, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was most appropriate for high concentration of Sb contaminated soil.

The addition of $\text{Al}(\text{OH})_3$ slightly increased the mobility of Sb no matter in FeSO_4 , goethite or Fe^0 modified soils by raising soil pH (Liu et al. 2019). The sorption rate of Sb in FeSO_4 and $\text{Al}(\text{OH})_3$ modified soil reduced slightly from 85.82–67.77% in 2% FeSO_4 sets, from 97.09–94.69% in 5% FeSO_4 sets, from 98.60–93.88% in 10% FeSO_4 sets with the addition rate of $\text{Al}(\text{OH})_3$ from 0–4%. Approximately 2.47–21.03% reductions were observed for $\text{Al}(\text{OH})_3$ addition. The sorption rate of Sb in goethite and $\text{Al}(\text{OH})_3$ modified soil reduced slightly from 14.09–10.68% in 2% goethite sets, from 15.91–11.02% in 5% goethite sets, from 41.04–24.55% in 10% goethite sets with the addition rate of $\text{Al}(\text{OH})_3$ from 0–4%. Approximately 24.19–40.20% reductions were observed. However, change of sorption rate was not obvious for Fe^0 and $\text{Al}(\text{OH})_3$ modified soil even with substantial amounts of $\text{Al}(\text{OH})_3$ (Garau et al. 2011). In the Fe-Al mixed addition cases, a possible reduction reason of sorption rate was the change of pH (Dai et al. 2014). In addition, $\text{Al}(\text{OH})_3$ owns less adsorption efficient than iron oxides especially in neutral and alkaline environments (Daoyong et al. 2008). However, FeSO_4 and $\text{Al}(\text{OH})_3$ modified soil still showed an more efficient sorption rate which attributing to the ion exchange ability of Fe-Al double hydroxide and adsorption of SbO_3^- on the $\text{FeO}(\text{OH})$ surface (Kameda et al. 2009).

3.2.3 The effects of Fe and Al based sorbents on Zn and Cu

Adding $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ amendments to the soil resulted in a great concentration drop of Sb, however, higher concentrations of Zn and Cu were detected in soil extract solution especially for Zn (Fig. 3). In addition, release rate of Zn increased gradually with increasing $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentration from 0–10%. After adding $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, the highest leaching concentration of Zn was 34.57mg/L, which were 181.94 times of the original soil leaching concentration (0.19 mg/L). The similar promotion leaching effects of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was found for Cu. Leaching concentration of Cu was 0.84 mg/L with 10% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ addition, which were 21 times as leaching concentration as original soil (0.04 mg/L). Addition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ significantly decreased pH values of water extracts by largely hydrolysis reaction of FeSO_4 (Tresintsi et al. 2012, Zhang et al. 2019). The acid environment significantly promoted release of Zn and Cu, thus resulting in the high leaching concentration of Zn and Cu (Hai-ying et al. 2010, Li et al. 2013). In contrast to FeSO_4 , the application of goethite and Fe^0 significantly reduced the concentration of Zn and Cu. There was no further reduction with adding rate of goethite and Fe^0 . As shown in

Fig. 3, the maximum adsorption efficiency of Zn and Cu were 72.60% and 68.05% respectively in goethite treated soil. The maximum adsorption efficiency of Zn and Cu were 61.29% and 63.31% respectively in Fe⁰ modified soil. Zn and Cu fixation by goethite could be mainly attributed to the diffusion of metal into the structural lattice of goethite by the following reactions: $\equiv\text{Fe-OH} + \text{Me}^{2+} + \text{H}_2\text{O} \rightleftharpoons \equiv\text{Fe-O-MeOH}_2^+$; $\equiv\text{Fe-O-MeOH}_2^+ + \text{Me}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe-O-MeOH}_2^+ + \text{Me(OH)}_2(\text{s}) + 2\text{H}^+$ (Cui et al. 2017).

With the addition of Al(OH)₃, Zn and Cu concentration in leachate significantly reduced, especially in FeSO₄·7H₂O treated soil. 4% Al(OH)₃ reduced extractable Zn by 99.72%, 83.47% and 96.26% in FeSO₄·7H₂O, goethite, Fe⁰ modified soil, respectively (Fig. 3), while 4% Al(OH)₃ addition reduced extractable Cu by 96.11%, 83.61% and 93.21% in FeSO₄·7H₂O, goethite, Fe⁰ modified soil, respectively. The reduction of extractable Zn and Cu in Fe-Al based modified soil may indicate Al(OH)₃ played a key role to the immobilization of Zn and Cu. These results substantially was similar to those report earlier (Garau et al. 2014). This was somewhat expected in Fe-Al based modified soil where a substantial amount of the Sb and co-occurring metals were likely to form stable surface complexes or precipitated with iron and aluminum hydroxide (Garau et al. 2014). In soil amended with 5% ferrous sulfate and 4% aluminum hydroxide, the leaching concentration of Sb, Zn and Cu decreased significantly and the maximum stabilization efficiencies were 94.69%, 74.17%, and 82.15%, respectively. 10% goethite and 2% aluminum hydroxide (pH = 8.36±) addition showed 32.60% stabilization efficiency of Sb and 87.45% and 93.73% decrease of Zn and Cu, respectively. The mixture of 10% Fe⁰ and 2% aluminum hydroxide (pH = 8.74±) also had the valid stabilization effect on Sb, Zn and Cu in soil, and the stabilization efficiencies were 75.00%, 94.01% and 94.14%, respectively. Considering the serious contamination of Sb and light pollution of Zn and Cu in studied area, 5% FeSO₄·7H₂O and 4% Al(OH)₃ was the most suitable amendment course.

3.3 Column experiments

3.3.1 Column experiments on Sb immobilization

In column experiments, the initial Sb concentration in leachate of untreated soil was 16.5mg/L, exceeding the GB/T 14848–2017 □Standard for Groundwater Quality□ type V leaching limit value (0.01mg/L) (AQSIQ., 2017) (Fig. 5 (a)). When the pore volume was up to 3.7, the concentration of Sb in leachate increased substantially to a peak of 17.73 mg/L. The similar leachate results were found in shooting ranges soil (Okkenhaug et al. 2013). Okkenhaug et al. (2013) thought this initial increase of Sb possible due to the depletion of H⁺ in the soil during leaching process, which induced the decrease of positive surface charge of minerals such as iron oxyhydroxides. Consequently, the sorption capacity for negatively charged anions decreased. But in this study, there was no significant pH increase captured. In addition, Sb increased mobilization in the untreated soil could occurred through organic and inorganic components depletion, but also through partial dissolution of reducible and oxidizable fractions (Hu &He 2017, Hu et al. 2014). After initial increase, the Sb concentration decreased exponentially up to PV 74.4. In this stage, pH rapidly reduced until to 7.03. Subsequently the pH values stabilized around 7. As a result, the Sb concentration stabilized, remaining at 0.99 mg/L. The leaching concentration trend of Sb always keep a consistence with pH trend, as a result, Sb dissolution rate are affected by soil pH (Hu et al. 2016). Hockmann et al. (2015) also found a similar effect on Sb in large-range soil under large seepage conditions. The initial Sb concentration of leachate in 5% FeSO₄·7H₂O and 4% Al(OH)₃ modified column was 0.024mg/L, which was 675 times lower than that of untreated soil, and the stabilization efficiency was 99.86%. Adjust the pH to the range of 3–10 by adding pH regulators NaHSO₄ or Na₂CO₃. The leaching concentration of Sb in the stabilized soil is shown in Fig. 5(a). The results showed that the leaching concentration of Sb in descending order is as follows: Group A, Group D, Group B, Group C. Group D showed a high initial Sb concentration (16.82 mg/L) compared to Group B (0.29 mg/L) and Group C (0.02 mg/L). This was the result of rapid increase pH induced by large amounts of OH⁻, which would decrease the positive surface charge of iron and aluminium oxyhydroxide. Consequently, Group B decreased the retention capacity for negatively charged anions (Klitzke &Lang 2009, Li et al. 2013). The leaching concentration of Sb in Group B decreased to the levels similar to Group C as PV increase and pH decrease.

The calculation results of the cumulative leaching amount of Sb in the dynamic process of each group are shown in the Fig. 5(b). When the PV up to 223.3, the total leaching amount of Sb in Group A, Group B, Group C, and Group D is 577.61 mg/kg, 79.75 mg/kg, 81.71 mg/kg, and 101.01 mg/kg, respectively. It can be seen that the soils amended by FeSO₄·7H₂O mixed Al(OH)₃ have good stabilization effects of Sb (Garau et al. 2014), and the stabilization efficiencies are 86.19%, 85.85%, and 82.51% in Group B, Group C, and Group D respectively. Group B significantly decreased soil pH, but did not increase the retention effect of Sb. The pH of Group C was consistent with untreated soil when PV up to 37.2. Then 5% FeSO₄·7H₂O and 4% Al(OH)₃ mixed addition showed the best stabilization performance of Sb with less pH disturbance.

3.2.2 Column experiments on Zn and Cu immobilization

The initial Zn (0.056 mg/L) and Cu (0.067mg/L) concentration in the leachate of untreated soil showed in Fig. 5(c) and (e), exceeded the GB/T 14848—2017 Standard for Groundwater Quality (AQSIQ., 2017) type I and II leaching limit value, respectively. As shown in Fig. 6(c), (d), (e) and (f), the leaching concentration of Zn and Cu decreases more significantly when $PV < 74.4$, while decreases in a slower trend and tends to stable when $PV \geq 74.4$. The final leaching concentration of Zn and Cu stabilized at about 0.009mg/L and 0.0035mg/L, which was 6.2 and 19.1 times lower than that of initial concentration respectively. The initial Zn and Cu concentration in the leachate of soil amended by 5% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 4% $\text{Al}(\text{OH})_3$ was 7.83mg/L and 0.069mg/L, which was 139 and 1.04 times higher than that of untreated soil. After adding Fe-Al-based adsorbent, the soil becomes transitory acidic, which promotes the leaching of Zn and Cu (Hai-ying et al. 2010). Furthermore, significant increase of leaching concentration of Zn and Cu was observed in stabilized soil with acidification but significant decrease of leaching concentration of Zn and Cu was observed in stabilized soil with alkalization, which was the result of the surface charge variation of minerals induced by pH and positively charged property of Zn and Cu (Li et al. 2013). In the period of $PV \geq 74.4$, leaching concentration of Zn and Cu in three group modified soil was consistent with untreated soil as pH eventually even out.

The calculation results of the cumulative leaching amount of Zn and Cu in the dynamic process of each group are shown in the Fig. 5(d) and Fig. 5(f). The total leaching amount of Zn in Group A, Group B, Group C, and Group D is 2.88 mg/kg, 44.37 mg/kg, 11.34 mg/kg, and 1.19 mg/kg, respectively. The release amount of Zn increased slowly when $PV \geq 74.4$ and depends ultimately on soil pH (Ke et al. 2020). The total leaching amount of Cu in Group A, Group B, Group C, and Group D are 1.27 mg/kg, 2.02 mg/kg, 1.55 mg/kg, 1.23 mg/kg, respectively. The most release was found in Fe-Al stabilized soil with acidification group. In the four groups, even moderate change of pH can induce persistent release of Cu.

3.2.3 pH effects on Sb and co-occurring heavy metals immobilization

The initial pH in the leachate of 5% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ + 4% $\text{Al}(\text{OH})_3$ addition with or without pH regulator significantly differed from pH of control groups, however, pH differences between them were diminishing until pore volumes (PV) up to 55.4 (Fig. 5). The initial pH of Group A and Group D were 8.05 and 9.30, which decreased with the increase of PV and the pH value of column leachate was tending towards stability when PV up to 74.4. Quite the contrary, the initial pH in leachate of Group B and Group C were 3.70 and 3.30, which increased dramatically with the increase of PV until PV up to 37.2 and 74.4. The dynamic column experiment results show that pH of the leaching solution finally stabilized in the range of 6–8. And the addition of 5% FeSO_4 and 4% $\text{Al}(\text{OH})_3$ without pH regulator had less effect on the ultimate pH of column soil.

The change of pH with PV affects the stabilization of Sb, Zn and Cu in the soil. Sb could be amended by Fe-Al-based mixed amendments in a wide pH range (pH = 3 ~ 10) mainly by strongly binding to Fe oxyhydroxides as inner-sphere surface complex (Mitsunobu et al. 2010) and the optimization pH range for adsorption processes was less than 7. This result was in accordance with findings of Leuz et al. (2006), who found that H^+ can increase the positive surface charge of iron oxyhydroxides and then enhance the sorption capacity for $\text{Sb}(\text{OH})_6^-$. However, when pH values were more than 8, desorption of Sb(V) also was observed in the study of Leuz et al. (2006). This desorption reaction mainly because that surface electronegativity of alkaline soil is higher than that of acidic soil, and it has strong repulsive force to the anion $\text{Sb}(\text{OH})_6^-$, which is not conducive to adsorption (Ma et al. 2015). Therefore, the retention rate and stabilization efficiency of Sb decreased with pH increase. As opposed to Sb, the stabilization efficiency of Zn and Cu in soil increased significantly with pH increase. The stabilization effect of Zn and Cu under alkaline conditions is better than that of acidic conditions. This reduced retention effectiveness in acidic conditions could be caused by the following processes. First, H^+ will replace the Zn^{2+} and Cu^+ in the complex formed by the adsorption reaction and then induced Zn and Cu ions to migrate into the soil pore water (Du et al. 2021); Second, partial dissolution of the sorbent, especially $\text{Al}(\text{OH})_3$, in the soil will lead to reduced sorption sites and finally a possibly lower retention amount of Zn and Cu. However, because of limited sorption capacity for Sb, partial dissolution of $\text{Al}(\text{OH})_3$ had little effect on adsorption of Sb in acidic conditions (He et al. 2019). This pH contradiction of between stabilization of Sb and co-occurring metals was lightened FeSO_4 mixed $\text{Al}(\text{OH})_3$ addition.

4. Conclusions

This work shows that the studied iron-aluminium based amendments are suitable for simultaneous stabilization of Sb and co-occurring metals such as Cu, Zn in primary explosives sites soil contaminated with high concentration of Sb. Experimental results demonstrate that $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ had ideal retention of Sb and $\text{Al}(\text{OH})_3$ could effectively prevent mobilization of Cu and Zn. Both batch and column leaching results determined that 5% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ + 4% $\text{Al}(\text{OH})_3$ application mixed with soil was a feasible process for immobilization of Sb and significant retention of co-occurring metals at high contamination Sb contaminated soils. pH regulated column test results indicated that acid condition was more beneficial for retention of Sb. The amendments addition had a clear positive impact on retention of Sb and

reduced the labile fractions of the Sb. However, the retention behavior and mechanism, ion exchange mechanism involved in these processes, possible changes of remediation effect over time remain to be determined by further experiments. Furthermore, in this case, the selection of amendments for primary explosives contaminated soils is primarily based on its ability to reduce the concentration of labile Sb, Cu and Zn. By contrast, additional effects such as the impact of the amendments on the soil microbial abundance, community, diversity and soil functionality are often neglected. Sulfate accompanied into soil following $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, which likely had a substantial influence on the microbial community. All of these may affect soil key ecosystem processes and then result in ecological risk in the amended soil. Since soil ecological risk should be further investigated after adding these efficient chemical amendments.

Declarations

5.1 Ethics approval and consent to participate

Not applicable

5.2 Consent for publication

Not applicable

5.3 Availability of data and materials

Not applicable

5.4 Competing interests

The authors declare that they have no competing interests

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5.6 Authors' contributions

NN.W performed the histological examination of the batch and column experiments, and was a major contributor in writing the manuscript. JY.C performed the batch and column experiments. All authors read and approved the final manuscript.

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Figures

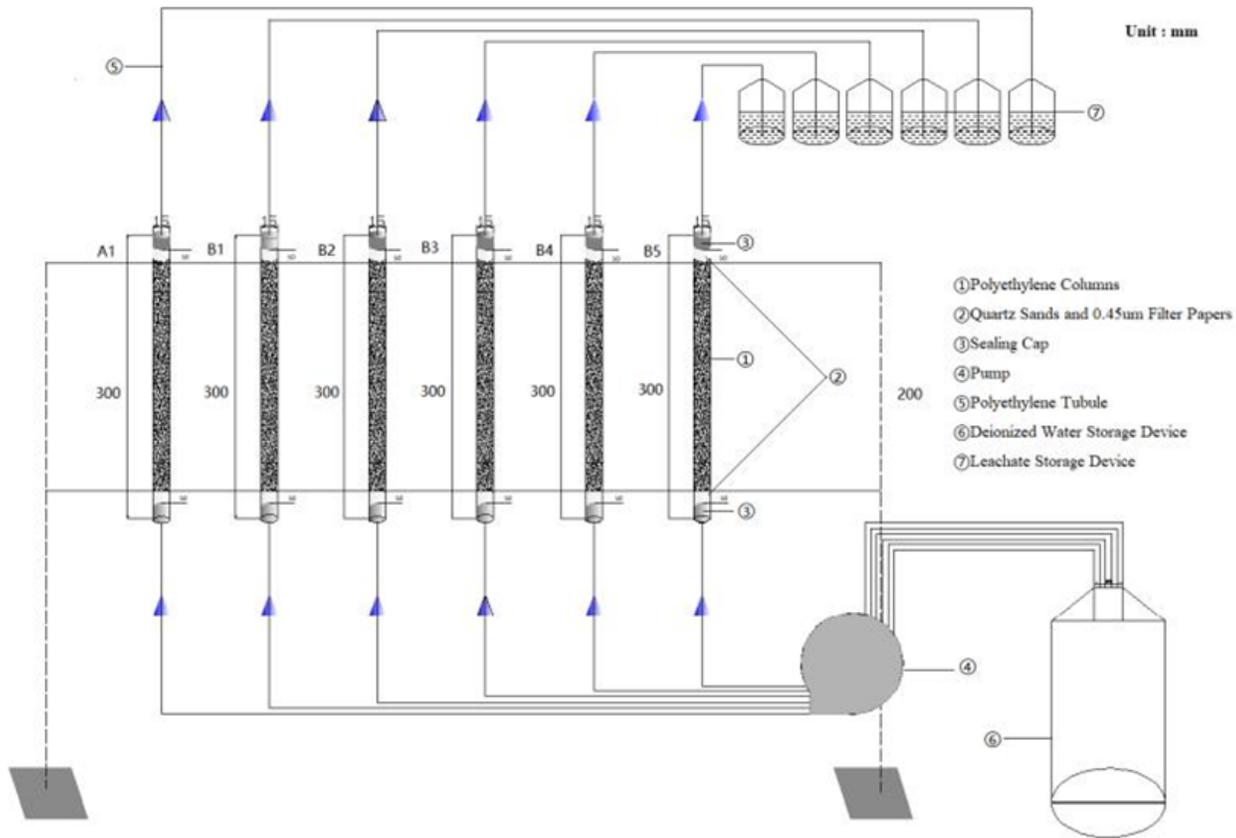


Figure 1

The structure of column experiments

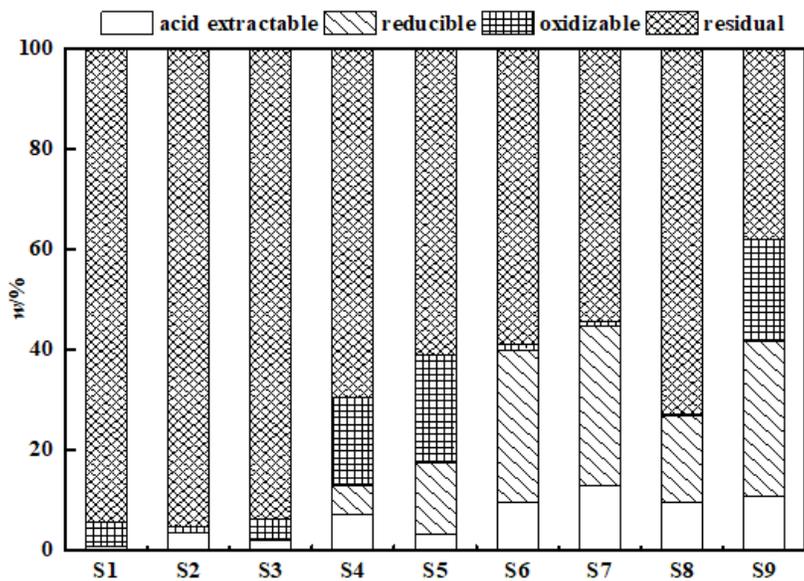


Figure 2

Sequential extraction of Sb from primary explosives contaminated soils

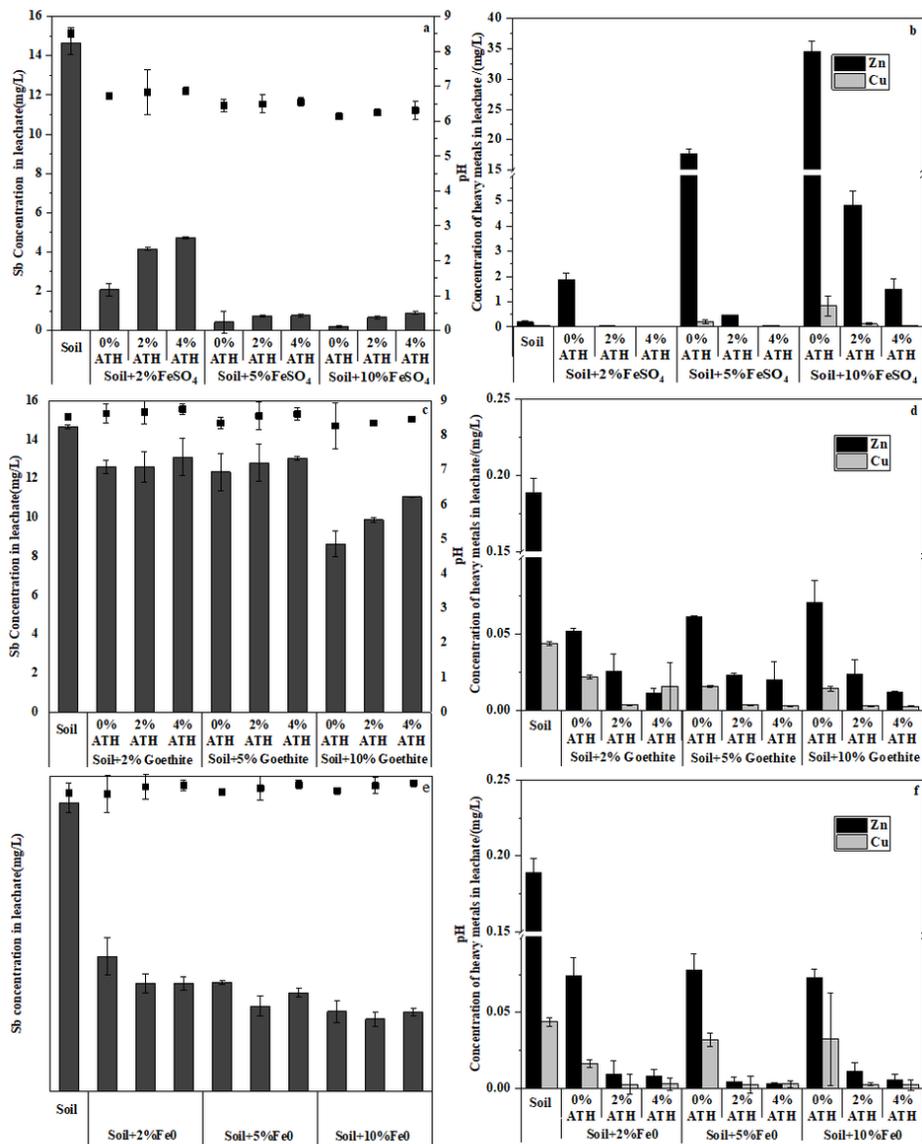


Figure 3

pH and Sb and co-occurring heavy metals concentration in water extracts

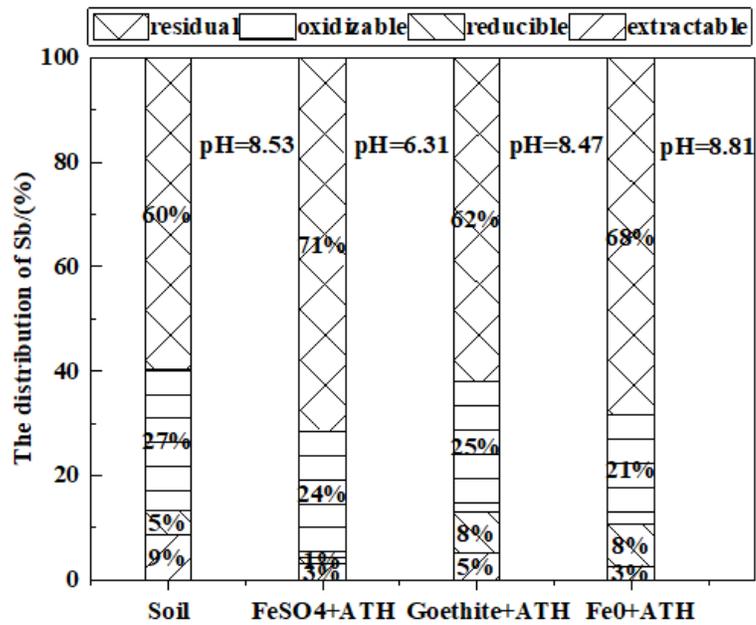


Figure 4

Sequential extraction of Sb in amended soil with Fe and Al mixed adsorbent

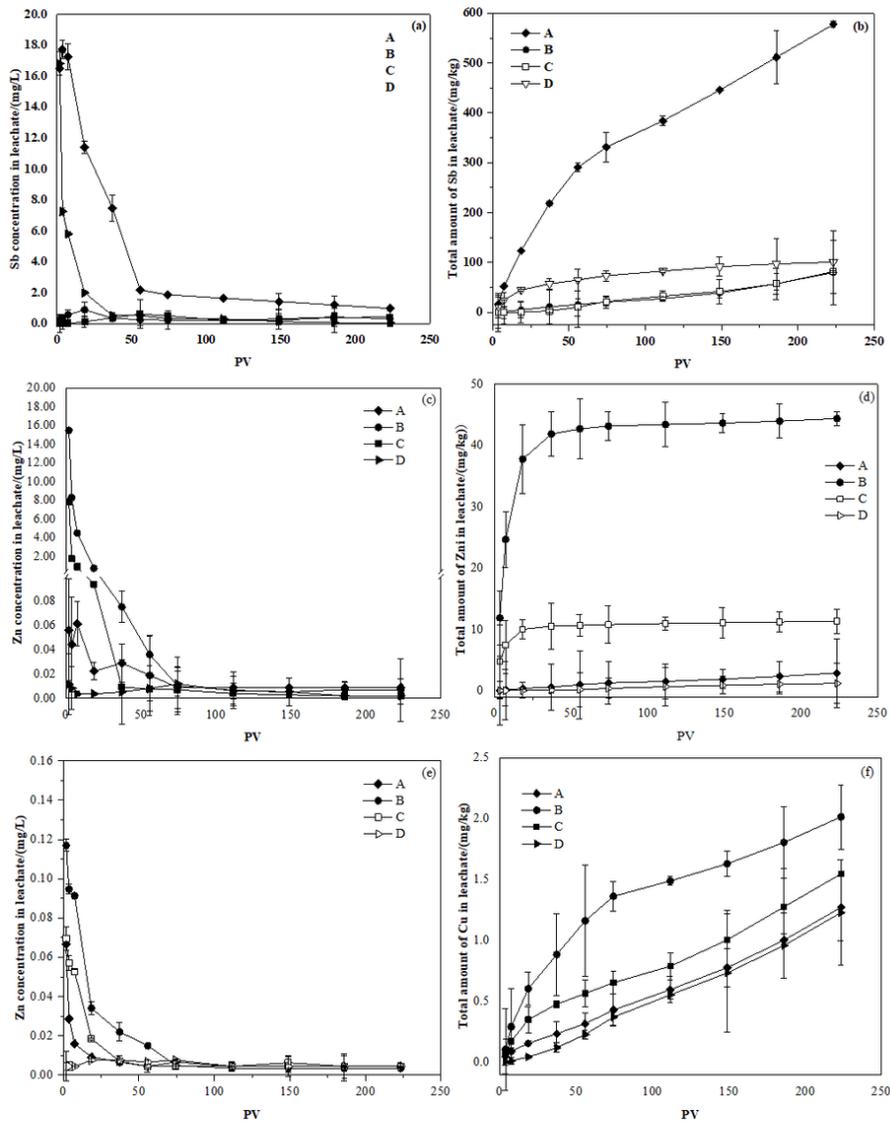


Figure 5

Changes of leaching concentration and accumulation of heavy metals in column experiment: (◻) untreated soil; (●) Fe-Al stabilized soil with acidification; (□) Fe-Al stabilized soil; (▷) Fe-Al stabilized soil with alkalization

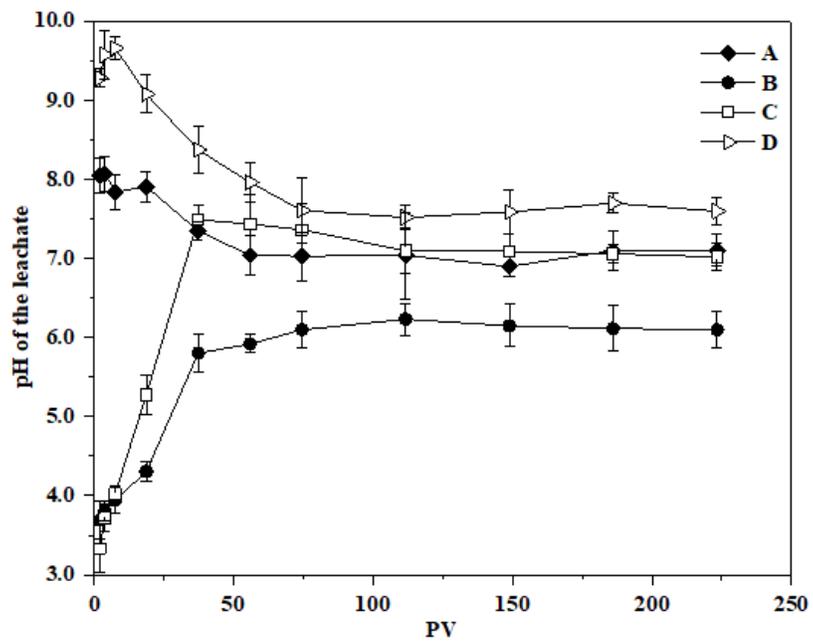


Figure 6

The pH value of leach solution with the change of PV