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A novel heavy metal chelating agent sixthio guanidine acid for in situ remediation of soils contaminated with multielements: its synthesis, solidification, biodegradability, and leachability

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Abstract

Purpose The main objectives of the study were to (1) develop a one-step facile procedure for synthesizing a new chemical amendment agent with three chelating groups for solidifying multiple heavy metals, called sixthio guanidine acid (SGA), using guanidine hydrochloride and carbon disulfide as raw reactants and (2) assess its biodegradability, solidification effectiveness, and leachability in remedying soils contaminated with multiple heavy metals of various concentrations compared with other traditional amendment agents.

Materials and methods Polluted soil samples were collected near a metalliferous mining site of Qixiashan in the southeast of Nanjing, China. Their concentrations were determined at 22.15–320 mg kg^{-1} for As, 3.30–29.31 mg kg^{-1} for Cd, 115.66–158.65 mg kg^{-1} for Ni, 165.04–1677.06 mg kg^{-1} for Pb, and 355.6–2426.91 mg kg^{-1} for Zn. Biodegradability of SGA was assessed in accordance with GB/T 21831-2008 and OECD-301D. Total concentration of heavy metals was determined according to ISO11466:1995. A modified three-step sequential Community Bureau of Reference (BCR) extraction procedure was used to examine speciation of heavy metals in the soil sample, and concentrations of heavy metals were measured by using inductively coupling plasma optical emission spectrometry (ICP-OES). Leachate extraction tests were carried out before and after the soil sample was solidified with different amendments in accordance with HJ/T 557-2009.

Results and discussion It is found that the optimal conditions for SGA synthesis are a molar ratio of 4:1, a reaction temperature of 40 °C, and a reaction time of 2 h. Under such conditions, SGA yield is achieved as high as 91.5 %. The bioavailability and mobility of As, Cd, Ni, Pb, and Zn in highly contaminated soils can be reduced via using SGA. Our results indicate that SGA is nonbiodegradative and much more effective than other traditional chemical amendment agents in that it is highly effective in comprehensively solidifying As, Cd, Ni, and Pb.

Conclusions SGA has the potential for comprehensive in situ remediation of soils contaminated with several heavy metal elements of various concentration levels, and such findings may be used as a guide to design new chemical amendment agents for rehabilitating soils contaminated with heavy metals.

Keywords Heavy metal · Remediation · Soil · Stabilization · Sixthio guanidine acid

1 Introduction

Heavy metal pollution in soil has worsened as a result of developments in local geochemistrical industries and human activities. High levels of heavy metals in soil are hazardous to

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plants, animals, and human health (Wu et al. 2010). According to a national survey jointly released by the Ministry of Environmental Protection and the Ministry of Land and Resources of China on April 17, 2014, 16.1 % of soil sample points have a concentration exceeding the screening threshold. The main contaminants are heavy metals (cadmium, nickel, arsenic, cuprum, mercury, lead, chromium, zinc) and organic pollutants. The accumulation of these heavy metals in soils imposes a major ecological and environmental hazard. Indeed, contamination of soil by heavy metals is a major obstacle to sustainable development of agriculture in China, and such contamination must be remedied.

Rehabilitation of soils contaminated by heavy metals is a significant endeavor in modern soil science and a popular research topic among scientists. Several rehabilitation techniques, such as physical, chemical, and biological methods, as well as phytoremediation have been proposed and investigated (Brown et al. 2004; Dermont et al. 2008; Saifullah et al. 2009; Wu et al. 2014). Of these methods, in situ stabilization or solidification (also known variously as passivation, fixation, or immobilization) of heavy metals by chemical amendments has proven to be a promising alternative to the generally expensive and disruptive engineering remediation techniques, such as soil removal or replacement approaches (Geebelen et al. 2003; Selena et al. 2008; Domen et al. 2008). Although the total concentration of hazardous metals in the contaminated soil is largely unaffected by the addition of chemical amendments, the fraction of total metals that move to the solid phase, through either precipitation of discrete minerals or increased metal absorption, increases after chemical amendment (Brown et al. 2005). Thus, heavy metals are less bioavailable in soils treated with this chemical amendment method (Porter et al. 2004; Ownby et al. 2005), which cannot meet the needs of sustainable agriculture (Hmaon et al. 2002; Seungbae et al. 2011).

Traditional agricultural materials, such as lime, phosphates (Ownby et al. 2005; Raicevic et al. 2005), iron oxides, clay minerals (Mcbride and Martinez 2000; René et al. 2007; Geebelen et al. 2002), nanomaterials, and other chemicals, have been found to be effective at reducing the mobility and availability of heavy metals (Jackson and Miller 2000; Kumpiene et al. 2008; Khara et al. 2010; Zhang et al. 2010; Liu and Zhao 2013; Wei et al. 2014; Elkhatib and Moharem 2015). An appropriate amount of lime or carbonates can increase soil pH, thereafter decreasing heavy metal mobility by forming carbonates and oxyhydroxide precipitation (Jackson and Miller 2000). Soluble phosphate causes the formation of Pb phosphate (lead pyromorphite), which is stable and highly insoluble even at a low pH. However, soil pH is lowered by easily soluble phosphoric amendments (Kumpiene et al. 2008). The increased soil acidity may cause leaching of other heavy metals, hence elevating soil toxicity (Ownby et al. 2005). For example, the stability of Cu in soil is strongly pH-dependent. Its mobility increases with decreasing pH (Kumpiene et al. 2008). Although soil contaminated with Pb can be effectively treated with a high dosage of phosphorus compounds (Brown et al. 2004; Porter et al. 2004), the residues of excessive soluble phosphoric amendments remaining in the soil not only alter soil pH and structure, but also potentially cause surface water eutrophication in the catchment (Brown et al. 2004; Kumpiene et al. 2008). It has been found that the total soluble and labile concentrations of Cu were reduced with 5 % noncrystalline alumina and 10 % ferrihydrite, but not with humus and crystalline iron oxide (Mcbride and Martinez 2000). No noticeable effect on metal mobility was observed when relatively low levels of bentonite or clinoptilolite were added to composts (René et al. 2007). Bentonite may have a questionable effect due to its inefficient Pb immobilization whereas zeolite has a potentially adverse effect on soil structure (Geebelen et al. 2002). Owing to its higher reactivity and more cost-effectiveness than other in situ methods, nanohydroxyapatite (n-HAP) has been widely used for immobilizing lead and cadmium in aqueous solutions, contaminated sediments, and soils (Zhang et al. 2010; Liu and Zhao 2013; Wei et al. 2014). However, its potential environmental risks are largely unknown at present. Therefore, it is difficult to assess their environmental benefits and risks fully (Khara et al. 2010).

Recent studies have shown that the choice of amendments depends on the type of soil contaminants (Kumpiene et al. 2008). A single amendment agent is not always successful at solidifying all elements. When soils are contaminated by several elements of different concentrations, the task of selecting the best amendment and remedy measure becomes even more challenging, as it must be effective for all the targeted heavy metals. Therefore, how to design new amendments with a possibility to solidify and remedy multiple elements simultaneously is a research question still to be resolved. At present, sodium dimethyldithiocarbamate (SDD) is a very popular amendment agent in remedying contaminated soils. However, it is not so stable as it has only a single dithiocarboxy chelating group. Thus, there is a need to develop new heavy metal chelating agents with more chelating groups which can potentially improve their stability (Wang et al. 2012a, b).

In this paper, we introduced a novel one-step approach for synthesizing a new chemical amendment agent with three chelating groups, called sixthio guanidine acid (SGA), for solidifying multiple heavy metals, in which guanidine hydrochloride and carbon disulfide were used as raw materials. Assessed in this study were the effects of different molar ratios of carbon disulfide to guanidine hydrochloride, reaction temperature, and dosage of potassium phosphate and potassium hydroxide on SGA yield. We also evaluated SGA comparatively with SDD and n-HAP in stabilizing heavy metals in contaminated soils, including its biodegradability and leachability. A modified Community Bureau of Reference (BCR) method was adopted to study these amendments in great detail.

2 Materials and methods

2.1 Materials and chemicals

Analytical-grade guanidine hydrochloride, carbon disulfide, acetone, ethanol, potassium hydroxide, potassium phosphate, chlorhydric acid, perchloric acid, nitric acid, acetic acid, hydroxylamine hydrochloride, hydrogen peroxide, and ammonium acetate were purchased from Sinopharm Chemical Reagent Co., Ltd. (China) and Nanjing Chemical Reagent Co., Ltd. (China). SDD was obtained from Aladdin Reagent Co., Ltd. (China). n-HAP with an average particle size of 20 nm and 99 % purity was obtained from Nanjing Emperor Nano Material Co., Ltd. (China). All materials were used without further purification.

Polluted soil samples were collected near a metalliferous mining site of Qixiashan in the southeast of Nanjing, China, which has been an important mining region for many years (Hu and Ding 2009; Ding and Hu 2014). Three soil samples, denoted here as S1, S2, and S3, were taken at various distances from the source of contamination at a depth of 0–20 cm using a bamboo spatula. The collected samples were homogenized, air-dried for 15–20 days, and then sieved to <2 mm prior to analysis.

2.2 Synthesis of SGA

SGA was synthesized via the following procedure (Wang et al. 2013): KOH (purity 85 %, 8.9 g), K_3PO_4 (0.6 g), and guanidine hydrochloride (2.87 g, 0.03 mol) were placed in a 50-ml three-necked flask and heated to 40±2 °C in a fixed-temperature water bath. Carbon disulfide (7.5 ml, 0.12 mol) was dissolved in acetone (5 ml). The carbon disulfide solution was then slowly poured into the flask containing guanidine hydrochloride, and the mixture was stirred for 2 h. The resulting product was cooled to below 10 °C, crystallized, and filtered. The filter cake was washed twice with acetone and ethanol to obtain 11.04 g of reddish-brown SGA crystals (molecular formula: $C_4H_5N_3S_6$). This synthesis procedure can be scaled up or down, depending on the amounts of product desired.

2.3 Analytical apparatus and methods

2.3.1 Assessment of SGA biodegradability

Biodegradability of SGA was assessed in accordance with the National Standard of China GB/T 21831-2008 (Chemicals—ready biodegradability: closed bottle test) and OECD-301D (OCED guideline for testing of chemicals, 1992). Biochemical oxygen demand $(BOD)_5$ and chemical oxygen demand (COD) values of 0.01 mol/l SGA and SDD were measured, and their ultimate biodegradability was calculated 28 days after the test.

2.3.2 Total concentration of heavy metals

Total concentration of heavy metals was determined according to the International Organization for Standardization ISO11466:1995 (Soil quality—extraction of trace elements soluble in aqua regia). Three grams of soil sample was placed in a reaction vessel and moistened with 1 ml deionized water. Then, 7 ml nitric acid was added to the sample, followed by 21 ml hydrochloric acid. The resulting mixture was digested and shaken on a reciprocal shaker (Ronghua Instrument Co., Ltd., ZD-85A) for 16 h at the room temperature. The digested mixture was heated in a far-infrared (IR) digestion oven (Siping Electronic Technology Research Institute, LWY-84B) for 2 h to maintain the solution at a distinct micro-boiling state in a digestion tube. The digest was cooled, centrifuged (Shanghai Anting Scientific Instrument Factory, TDL-5-A), and filtered into a 100-ml flask using a 0.45-mm syringe filter. Finally, the filtrate was diluted to 100 ml with distilled water. The total concentration of heavy metals in the resulting filtrate was determined by inductively coupling plasma optical emission spectrometry (ICP-OES; Prodigy, ICP-OES, Leeman Labs) (Brown et al. 2005). All the sample analyses were performed in triplicate for S1, S2, and S3, respectively.

2.3.3 Heavy metal immobilization

A total of 10-g soil sample was mixed with 10 ml deionized water. Appropriate dosages of SGA, SDD, or n-HAP were added to the mixture solution to immobilize heavy metals in the contaminated soil. The mixture was stirred thoroughly, allowed to settle for 1 day, dried at 70 °C, and then sieved to <2 mm prior to BCR analysis. Concentrations of targeted heavy metals in all the three soil samples were measured by using ICP-OES.

A modified three-step sequential BCR extraction procedure according Pueyo et al. (2008) was used to examine speciation of heavy metals in the S1 soil sample.

2.3.4 Leachate extraction tests

Leachate extraction tests were carried out before and after solidification with different amendments in accordance with the National Standard of China HJ/T 557-2009 (Solid waste—extraction procedure for leaching toxicity: horizontal vibration method). Before and after solidification by using different amendments, 4-g soil samples were placed in a reaction vessel, to which 40 ml deionized water was added. Then, the resulting mixture was shaken on a reciprocal shaker (110± 10 time/min) for 8 h at 25 °C. The mixture was centrifuged and filtered using a 0.45-mm syringe filter, and the concentration of targeted heavy metals in the resulting filtrate was measured using ICP-OES.

3 Results and discussion

3.1 Optimal conditions for SGA synthesis

The yield of SGA is mainly affected by three factors of molar ratios of carbon disulfide to guanidine hydrochloride, reaction temperature, and dosage of potassium phosphate and potassium hydroxide. The effect of each factor is elaborated in detail below.

3.1.1 Effects of molar ratio of carbon disulfide to guanidine hydrochloride

In theory, a 3:1-M ratio of carbon disulfide to guanidine hydrochloride enables complete reaction of carbon disulfide with guanidine hydrochloride. In our experiments, we found that excessive carbon disulfide could boost SGA yield. The exact effect of different molar ratios of carbon disulfide to guanidine hydrochloride on SGA yield is shown in Table 1. SGA yield increases with the molar ratio of carbon disulfide to guanidine hydrochloride until 4:1, beyond which SGA yield starts to decrease. For instance, a theoretical molar ratio of 3:1 corresponds to an SGA yield of 65.8 % while a ratio of 4:1 corresponds to a yield of 74.1 %. Thus, a molar ratio of 4:1 is considered the optimal, even though it exceeds the theoretical threshold by 33.3 %.

Table 1 Effects of using different molar ratios of carbon disulfide to guanidine hydrochloride on SGA yield (acetone 5 ml; KOH 7.9 g, guanidine hydrochloride 2.87 g, molar ratio of KOH to guanidine hydrochloride was 4:1; K_3PO_4 1 g; reaction time 2 h; reaction temperature 30 °C)

Mole ratio	Carbon disulfide (ml)	Guanidine hydrochloride (g)	Weight of SGA (g)	Yield of SGA (%)
1:1	1.9	2.87	1.49	12.4
2:1	3.8	2.87	5.12	42.5
3:1	5.7	2.87	7.92	65.8
4:1	7.6	2.87	8.92	74.1
5:1	9.5	2.87	7.54	62.6
6:1	11.4	2.87	5.26	43.7

3.1.2 Effects of reaction temperature

The effects of reaction temperature on SGA yield are shown in Fig. 1. SGA yield increases as the reaction temperature is raised from 25 to 40 °C, beyond which the yield gradually drops. This decrease is due probably to guanidine hydrochloride decomposition at a high temperature. As such, the optimal reaction temperature is considered to be 40 °C.

3.1.3 Dosage of potassium phosphate

In our experiments, we found that potassium phosphate can serve as a catalyst to improve SGA yield in the reaction of carbon disulfide with guanidine hydrochloride. The effects of potassium phosphate dosage on SGA yield are illustrated in Fig. 2. SGA yield increases as the dosage of potassium phosphate rises from 0 to 0.6 g. However, it levels off after the dosage reaches 1.0 g. Thereby, 0.6 g represents the optimal dosage of potassium phosphate.

3.1.4 Dosage of potassium hydroxide

Guanidine is an organic alkali that can react to carbon dioxide in the air to form carbonate. It is unstable under alkaline conditions and can be easily hydrolyzed into ammonia and urea. Under acidic conditions, it is relatively stable. Thus, it is generally stored in salt, such as guanidine hydrochloride and guanidine nitrate. To retrieve pure guanidine, the salt should be treated with an activated carboxylic acid, or with alkali, such as sodium hydroxide and potassium hydroxide. In synthesizing SGA via the reaction of carbon disulfide with guanidine hydrochloride, the first step in acquiring pure guanidine is to remove the undesired chemicals using sodium hydroxide.

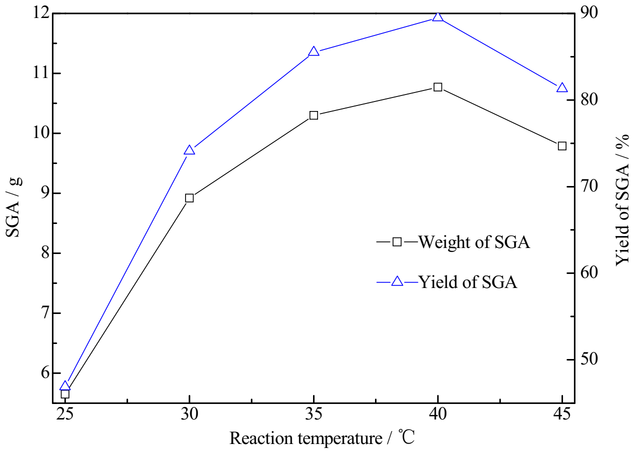


Fig. 1 Effects of reaction temperature on SGA yield (molar ratio of carbon disulfide and guanidine hydrochloride 4:1; acetone 5 ml; KOH 7.9 g, guanidine hydrochloride 2.87 g, K_3PO_4 1.0 g; carbon disulfide 7.6 ml; reaction time 2 h)

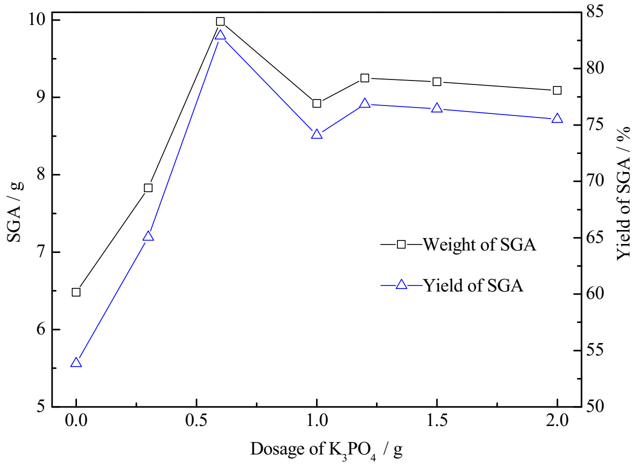


Fig. 2 The effects of K_3PO_4 dosage on SGA yields (molar ratio of carbon disulfide and guanidine hydrochloride 4:1; acetone 5 ml; KOH 7.9 g, guanidine hydrochloride 2.87 g, carbon disulfide 7.6 ml; reaction time 2 h; reaction temperature 40 °C)

The effects of molar ratio of potassium hydroxide to guanidine hydrochloride on SGA yield are shown in Fig. 3. It can be seen that SGA yield increases as the molar ratio rises from 4.0 to 4.5, beyond which it becomes stabilized. This suggests that the optimal molar ratio is 4.5. Thus, the optimal conditions for SGA synthesis are a molar ratio of carbon disulfide and guanidine hydrochloride at 4:1, a reaction temperature of 40 °C, and a reaction time of 2 h, under which SGA yield can achieve as high as 91.5 %.

3.1.5 Characterization of SGA

SGA IR spectra were obtained using an IR spectrometer (IR Prestige-2, Shimadzu) operating in the 4000–400-cm^{-1} range. The KBr pellet technique was utilized to prepare powder samples for IR analysis. An NMR spectrometer (Avance 400, Bruker) was used to obtain the NMR spectra of SGA. The results of IR (KBr disk, cm^{-1}) were as follows: 3140 s (ν N–H), 3300 w (S–H), 1570 (ν N–C), 1650 s (ν C═N) 1390 w (ν N–C═S), 1120 (ν C═S), and 997 (ν C–S). The ^{1}H NMR results were as follows: (D_2O, 500 MHz) *δ* 2.09 (s, –NH). The results of ^{13}C NMR were as follows: (D_2O, 125 MHz), *δ* 216.94–214.99 (═N–CSS–), *δ* 192.86 (–N–**C**SS–), and *δ* 157.88 (–**C**═N–). The determined structure of SGA is confirmed by the IR, ^{1}H NMR, and ^{13}C NMR spectra in Fig. 4.

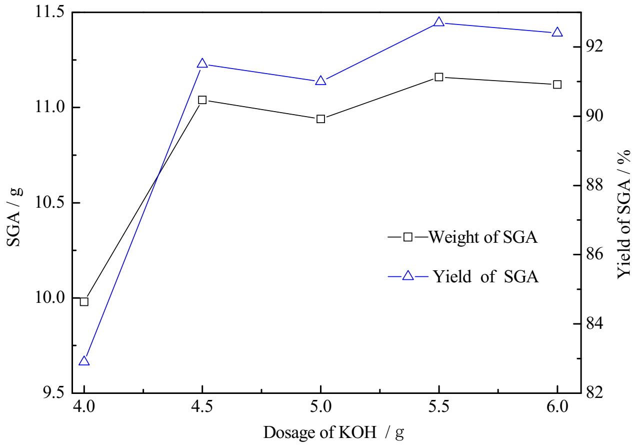


Fig. 3 The effects of KOH on SGA yields (molar ratio of carbon disulfide and guanidine hydrochloride 4:1; acetone 5 ml; guanidine hydrochloride 2.87 g, K_3PO_4 0.6 g; carbon disulfide 7.6 ml; reaction time 2 h; reaction temperature 40 °C)

3.2 Biodegradability of SGA

One of the dilemmas about immobilization treatment is the long-term performance of amendments used. If SGA is biodegradable, its performance cannot be long lasting. If it is not biodegradable, the treatment itself will cause soil contamination. Thus, the biodegradability of SGA was evaluated in terms of the BOD_5/COD ratio (a ratio of $BOD_5/COD > 0.40$ means readily biodegradable (Sarria et al. 2002) or biodegradable if $0.30 \leq BOD_5/COD \leq 0.40$, partially biodegradable if $0.20 \leq BOD_5/COD < 0.30$ (Martins et al. 2010), and nonbiodegradable if $BOD_5/COD < 0.20$ (He et al. 2007)). The solubility of SGA is 6.3 g in 100 g distilled water at 25 °C, and SDD is miscible with water, which indicates that SGA and SDD are highly water-soluble. n-HAP is not water-soluble; thus, its biodegradability cannot be measured according to the regulations of GB/T 21831-2008 and OECD-301D. BOD_5 and COD of 0.01 mol/l have a respective value of 40 and 4580 mg/l for SGA, and their values for SDD are 320 and 2475 mg/l. Thus, their $BOD_5/COD < 0.20$, which means that SGA and SDD are nonbiodegradable. In another experiment carried out in accordance with the OECD-301D standard, it is found that SGA and SDD have an ultimate biodegradability of 13.7 and 21.7 %, respectively, 28 days after the test. Both percentages fall below the passing value of 60 % in accordance with the BOD_5/COD criteria. Therefore, SGA is not deemed to be readily biodegradable, even though it is more stable than SDD.

3.3 Total concentration and bioavailability of heavy metals

3.3.1 Total concentration of heavy metals

The total concentration of heavy metals in all three soil samples is presented in Table 2. They have a high concentration of heavy metals. Moreover, all heavy metals except Pb and As in S3 exceed the quality standards for class 2 soil according to the National Standard of China GB15618-1995 (Environmental quality standard for soils); this grade of soil quality basically exerts no harm or pollution to plants and the environment. The concentrations of As, Cd, Pb, and Zn in S1 are significantly higher than the quality standards set for class 3 soils, a quality suitable for forestry only.

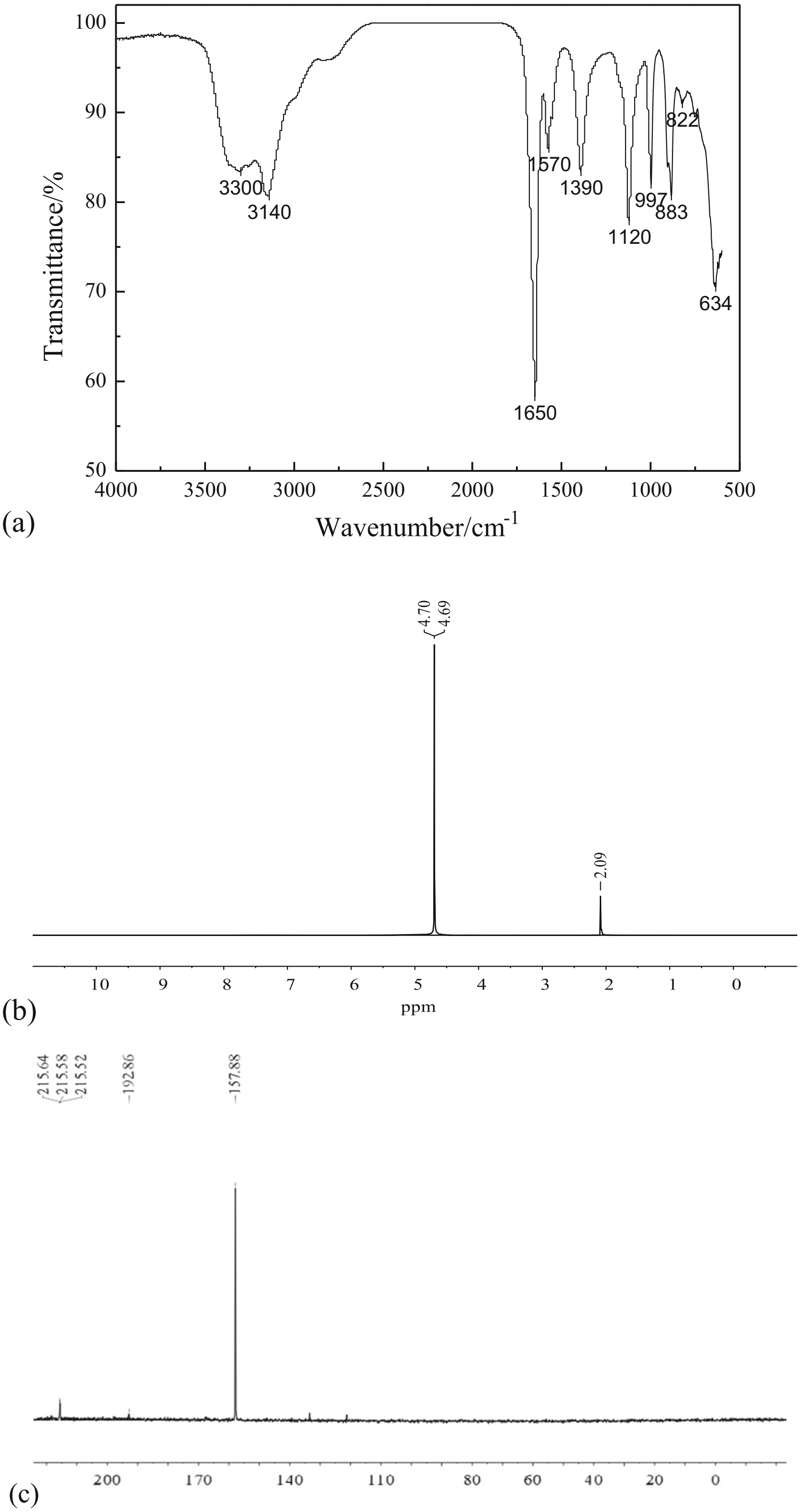


Fig. 4 The IR (**a**), ^{1}H NMR (**b**), and ^{13}C NMR spectra (**c**) of SGA

Specifically, As levels are 8.0-fold higher, Cd levels 29.31-fold higher, Pb levels 3.15-fold higher, and Zn levels 4.85-fold higher than the standards for class 3 soils. These results indicate that the S1 sample is highly contaminated. Therefore, it was analyzed further to study bioavailability of heavy metals.

Table 2 Total concentration of heavy metals in relation to the GB 15618-1995 standards (mg kg^{-1})

Item	S1	S2	S3	Class 2 soils	Class 3 soils
As	320±11.68	110.13±7.13	22.15±1.45	30	40
Cd	29.31±1.01	9.28±0.84	3.30±0.32	0.3	1.0
Ni	158.65±7.11	127.44±5.11	115.66±9.05	50	200
Pb	1677.06±24.60	642.38±10.57	165.04±8.83	300	500
Zn	2426.91±24.33	480.06±13.34	355.6±9.10	250	500

3.3.2 Bioavailability of heavy metals

The modified BCR sequential extraction process for speciation analysis of heavy metals is an effective method for recognizing the environmental behavior and bioavailability of heavy metals. Four fractions of heavy metals in contaminated soils are defined according to the revised BCR process, namely, acid-soluble, reducible, oxidizable, and residual. The mobility and bioavailability of these fractions follow the sequence of acid-soluble > reducible > oxidizable > residual. Generally, acid-soluble fraction of heavy metals can be released and converted into free metal ions that can be directly used biologically due to their weak binding capacity with soil. Therefore, heavy metals in the acid-soluble fraction are not stable and impose grave risks of contamination. Results of speciation analysis of heavy metals in S1 by BCR are presented in Table 3, and the proportion of each heavy metal is shown in Fig. 5.

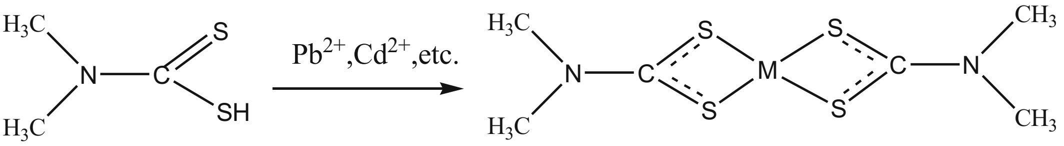
As shown in Fig. 5, the acid-soluble proportion of Zn, Ni, Cd, As, and Pb in S1 is 42.14, 32.48, 19.56, 13.97, and 2.54 %, respectively. Of these, Zn and Ni have higher mobility and bioavailability than others and are therefore more likely to be released into the environment.

The reducible fraction of heavy metals follows the order of Pb (79.60 %) > Zn (38.71 %) > Ni (29.45 %) > Cd (24.21 %) > As (17.51 %), while the oxidizable fraction follows the order of Cd (12.93 %) > Zn (6.33 %) > Ni (4.69 %) > As (4.45 %) > Pb (3.54 %). The reducible and oxidizable fractions of heavy metals are more stable than the acid-soluble fractions. If external conditions change, these fractions may be released into the environment and used biologically, which means that these fractions are potentially bioavailable.

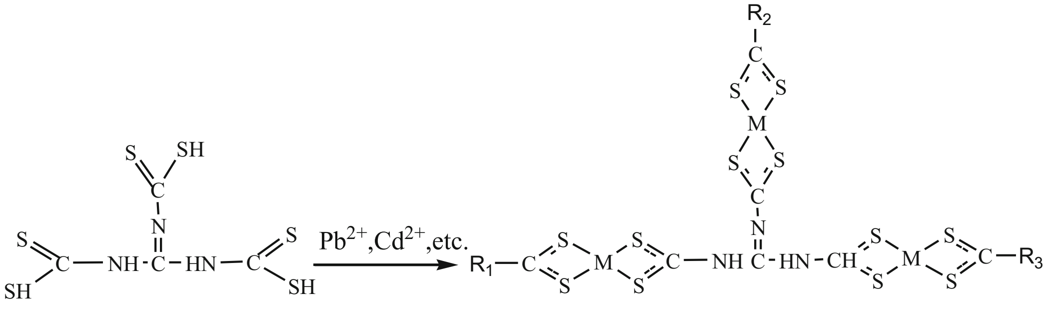
Residual fractions are retained in minerals such as quartz. Their very low mobility means that they are not easily released under natural conditions. The residual fraction of heavy metals follows the order of As (64.07 %) > Cd (43.30 %) > Ni (33.38 %) > Pb (14.34 %) > Zn (12.82 %). The largest residual fraction of S1 is As (64.07 %), making it the least bioavailable metal.

3.4 Heavy metal immobilization with SGA

In order to compare their effectiveness, 0.05 mol/kg SGA, SDD, and n-HAP were used to immobilize heavy metals in the S1 sample by adding 10 ml deionized water to 10 g of the soil sample. The chelating equation of SDD with the heavy metals and three bonding sites of SGA for heavy metal immobilization is shown in Eqs. (1) and (2), respectively.



(1)



(2)

Table 3 Speciation analysis of heavy metals by modified BCR sequential extraction (mg kg^{-1}) and its recovery (%) of the metals in S1 sample

Elements	Acid soluble	Reducible	Oxidizable	Residual	Total concentration	Recovery[a] (%)
As	42.64	53.45	13.57	195.54	320	95.38
Cd	5.93	7.34	3.92	13.13	29.31	103.45
Ni	54.21	49.16	7.83	55.72	158.65	105.21
Pb	43.84	1377.79	61.2	248.17	1677.06	1.03.21
Zn	1048.26	962.83	157.55	318.96	2426.91	102.50

[a] The recovery of the metal was calculated by the following formula:Recovery $= \frac{\text{Acid soluble+Reducible+Oxidisable+Residual concentration}}{\text{Total concentration}} \times 100\%$

SDD has a single dithiocarboxy chelating group, and the targeted metal ions can be precipitated with a single-point structure, while SGA owns three chelating groups; its coordination complex is a two-dimensional structure, just like a network when SGA is utilized to precipitate the targeted metal ions. Therefore, the complex of SGA with metals might have more stability due to its multiply hydrosulfide groups that bind with heavy metals very efficiently.

The mobility of As and other heavy metals in soil is controlled mainly by precipitation or adsorption process (Kumpiene et al. 2008). Compared with cationic metals, the particular mechanism of As precipitation is often complex and process-specific and, in some cases, is not even completely understood (US EPA. EPA-542-R-02-004, 2002). Several researchers have demonstrated that the formation of $Ca(AsO_4)_2$ and $CaHAsO_3$ precipitates reduced the mobility of As in contaminated soil (Dutré et al. 1999; Vandecasteele et al. 2002). It is also suggested that As mobility is reduced by the formation of amorphous iron III arsenate ($FeAsO_4{\cdot}H_2O$) (Carlson et al. 2002). When SGA was added to the S1 sample (or when SGA reacts with cationic metals, such as Pb, Cd, Cu, etc.), the H^+ ion in SGA could desorb metals such as Ca^{2+} and Fe^{3+} from soil surface or dissolve them from soil phase (Davis 2000). The high Ca^{2+} content enables the formation of Ca–As precipitates (Lee et al. 2011), such as $Ca(AsO_4)_2$ and $CaHAsO_3$, which solidifies As.

The concentrations of heavy metal species after solidification by 0.05 mol/kg SGA, SDD, and n-HAP were measured by BCR, and the proportions of heavy metal species are shown in Fig. 5.

As shown in Fig. 5, the acid-soluble proportions of As, Cd, Ni, Pb, and Zn after solidification were lower than those before solidification. For example, the acid-soluble proportion of Cd follows the order of SGA (6.17 %) < SDD (15.25 %) < n-HAP (18.45 %) < blank (19.56 %). Thus, compared with SDD and n-HAP, SGA was superior in comprehensively solidifying As, Cd, Ni, and Pb. Addition of chemical amendments did not modify the total concentrations of heavy metals in S1, although their speciation proportions changed. In the amended S1 sample, Cd, Ni, and Pb in the acid-soluble fraction treated with SGA were lower than those in fractions treated with SDD or n-HAP, as shown in Fig. 5. This result indicates that SGA exhibits an excellent capability in comprehensively solidifying Cd, Ni, and Pb.

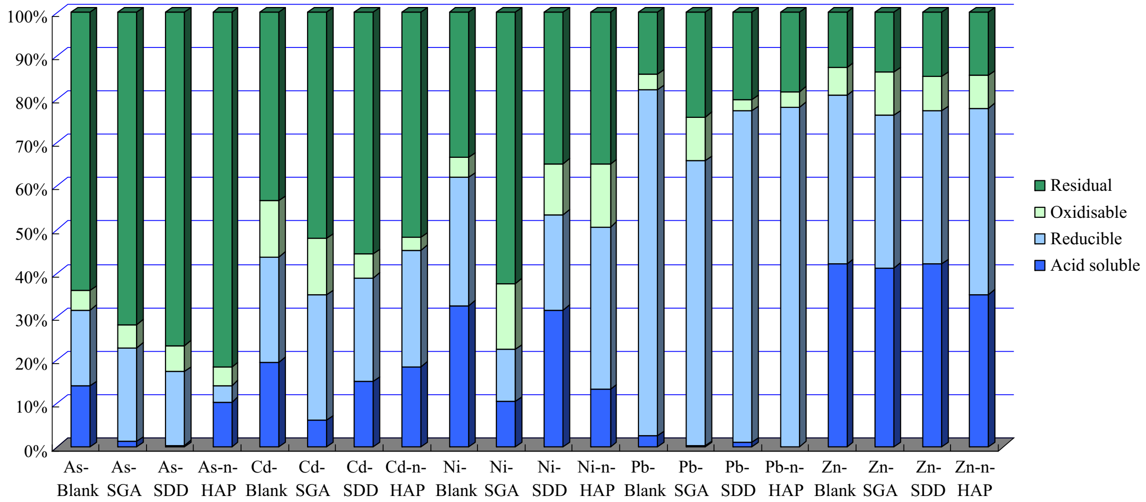


Fig. 5 Proportions of heavy metal species in the S1 soil sample determined using BCR after solidification by chemical amendments using 0.05 mol/kg SGA, SDD, and n-HAP (blank, no chemical amendment; As-SGA, As-SDD, and As-n-HAP indicate speciation proportions of As when remediated using SGA, SDD, and n-HAP, respectively; the same nomenclature is followed for other heavy metals)

3.5 Heavy metal solidification efficiency of SGA

Solidification efficiency (r) can be calculated using the concentration of heavy metal species before (C_0) and after (C_1) soil solidification by chemical amendment agents (Eq. (1)). The calculated values of r for different metals are listed in Table 4.

$$r = \frac{C_0 - C_1}{C_0} \tag{3}$$

The results show that the r of SGA for acid-soluble Cd is 69.81 % and follows the order of SGA (69.81 %) > SDD (21.42 %) > n-HAP (10.29 %). All the chemical amendment agents used in the study exhibit a low r for Zn. Cesur and Aksu (2006) found that the chelate stability and binding affinity of metal-sodium diethyldithiocarbamates (denoted as DDTC, which had one group S═C–SH and similar molecule structure as SDD) decreased in the following order: Pb^{2+}, Ni^{2+}, Cd^{2+}, Fe^{2+}, Zn^{2+}; Jiří and Jaromír (1968) gave the stability constants (logK) order of metal-DDTC chelate following Cu^{2+}(14.1) > Pb^{2+} (5.74) > Cd^{2+}(5.13) > Zn^{2+}(2.54), while Liao et al. (2008) calculated the stability constants of targeted metal-DDTC complexes of Cu $(DDTC)_2$, Pb $(DDTC)_2$, Cd $(DDTC)_2$, and Ni $(DDTC)_2$ which were 4.05×10^{11}, 2.67×10^{11}, 2.14×10^{11}, and 4.01×10^{10}, respectively. Their logK of metal-SGA was calculated according Liao et al. (2008), which follow the sequence of Pb^{2+} (11.03) > Ni^{2+} (10.57) > Cd^{2+} (10.14) > Zn^{2+} (8.61), and the result was in accordance with previous works showing that the binding capacity of SGA for Cd is larger than that for Zn. Compared with SDD and n-HAP, SGA showed a better comprehensive solidification performance for As, Cd, Ni, and Pb, which could be due to its ability to bind with heavy metals very efficiently (Wang et al. 2012a, b). When 0.10 mol/kg SGA was used, the solidification efficiency (r) was more than 90 % for all the heavy metals, which indicated that nearly all the targeted metals in the S1 sample were immobilized.

Some r values are negative for certain heavy metals. This is because upon solidification by chemical amendment agents, the mobile forms of these heavy metals are converted into stable metals with low solubility. While the total concentration of heavy metals in the soil remains unchanged after chemical amendment, these heavy metals migrate and transform from active species into passive forms. For example, the passivated fraction increased from the acid-soluble to the other heavy metal species, which resulted in C_1 being greater than C_0. Taken together, our results indicate that SGA exhibits a promising potential for in situ remediation of soils contaminated by As, Cd, Ni, Pb, and Zn.

Table 4 Solidification efficiency (r) of heavy metals in S1 by chemical amendments (%)

Item		As	Cd	Ni	Pb	Zn
Acid soluble	SGA	90.24	69.81	70.12	91.45	2.87
	SDD	96.93	21.42	3.21	62.23	4.10
	n-HAP	25.33	10.29	60.04	95.60	21.12
Reducible	SGA	−35.70	−14.03	61.78	15.70	10.01
	SDD	−2.15	3.81	25.94	9.63	12.42
	n-HAP	77.74	−5.31	−23.37	7.62	−4.86
Oxidizable	SGA	−32.72	4.59	−200	−192.61	−55.26
	SDD	−42.96	57.40	−151.34	30.34	−19.97
	n-HAP	4.127	78.06	−199.75	6.21	−14.14
Residual	SGA	−23.45	−15.08	−73.85	−72.47	−7.20
	SDD	−26.21	−30.77	−3.89	−32.29	−11.21
	n-HAP	−28.72	−13.71	−1.72	−19.83	−6.89

3.6 Leachability of SGA

Leaching performance before and after solidification with different amendment agents was assessed in accordance with HJ/T 557-2009, and the results were compared with the thresholds in the National Standard of China GB 5085.3-2007 (Identification standards for hazardous wastes—identification for extraction toxicity), as shown in Table 5.

Leachability can predict both the potential mobility of metals to groundwater and their bioavailability to plants under natural conditions (Hartley et al. 2004). Leachate extraction tests reveal that addition of amendment agents into the contaminated soils reduces the release intensity of heavy metals and transforms them from mobile into stable metals with low solubility, which is consistent with the above heavy metal solidification results. Comparison of results from contaminated soils treated with SGA, SDD, and n-HAP, (Table 5) shows that SDD and n-HAP still impose a higher risk than SGA in that the mobility of residual metals may be leached to groundwater or bioavailable to plants.

When 0.15 mol/kg, the three times molar amount of SDD was used as SGA, the solidification efficiency (r) for acid-soluble As, Cd, Ni, Pb, and Zn was 97.17, 80.24, 83.76, 93.92, and 37.81 %, respectively, which indicated the stabilization capability, and r of SDD was more than that of SGA for

Table 5 Leaching performance of amendments in comparison with the thresholds in GB 5085.3-2007 of China (mg/l)

Element	Nontreatment	SGA	SDD	n-HAP	Threshold
As	0.13	ND	ND	ND	5
Cd	0.067	0.0084	0.0092	0.031	1
Ni	0.048	ND	0.023	0.016	5
Pb	0.21	ND	0.14	ND	5
Zn	5.26	0.14	3.24	0.96	100

ND not detected or lower than the detectable limits of ICP-OES all the targeted heavy metals if they had same chelating groups, while its leaching performance was still less than that of SGA: ND for As and Cd, 0.016 mg/l Ni, 0.06 mg/l Pb, and 0.79 mg/l Zn. Thus, SGA has the potential for comprehensive in situ remediation of soils contaminated with several heavy metal elements of various concentration levels.

4 Conclusions

In this study, we designed a novel heavy metal chelating agent with three dithiocarboxy chelating groups (SGA) that was synthesized using guanidine hydrochloride and carbon disulfide in one step. This agent was used to remedy soils contaminated with multiple heavy metals of various concentration levels far exceeding the relevant government-set thresholds. The maximum yield of SGA can be achieved as high as 91.5 % under the optimal reaction conditions of a molar ratio of 4:1 (carbon disulfide to guanidine hydrochloride), a reaction temperature of 40 °C, and a reaction time of 2 h. SGA has an ultimate biodegradability of 13.7 %, which is not deemed to be readily biodegradable. The solidification efficiency for acid-soluble Cd follows the order of SGA (69.81 %) > SDD (21.42 %) > n-HAP (10.29 %). The bioavailability and mobility of As, Cd, Ni, Pb, and Zn in highly contaminated soils can be reduced via chemical amendments using SGA, SDD, and n-HAP. Moreover, SGA is especially effective at solidifying Cd with the acid-soluble proportion being 6.17 %, much lower than 15.25 % achieved by SDD, 18.45 % by n-HAP (18.45 %), and 19.56 % without any treatment. Of the chemical amendment agents tested, SGA is the most effective in comprehensively solidifying As, Cd, Ni, and Pb in the soil samples. Thus, it has the potential for in situ rehabilitation of soils contaminated with multiple heavy metals of a very high concentration.

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References

Brown S, Chaney R, Hallfrisch J, Ryan JA, Berti WR (2004) In situ soil treatments to reduce the phyto-and bioavailability of lead, zinc, and cadmium. J Environ Qual 33:522–531

Brown S, Christensen B, Lombi E, McLaughlin M, McGrath S, Colpaert J, Vangronsveld J (2005) An inter-laboratory study to test the ability of amendments to reduce the availability of Cd, Pb, and Zn *in situ*. Environ Pollut 138:34–45

Carlson L, Bigham JM, Schwertmann U, Kyek A, Wagner F (2002) Scavenging of As form acid mine drainage by schwertmannite and ferrihydrite: a comparison with synthetic analogues. Environ Sci Technol 36:1712–1719

Cesur H, Aksu C (2006) Determination of cadmium and zinc in fertilizer samples by FAAS after solid-phase extraction with freshly precipitated manganese-diethyldithiocarbamate. Anal Sci 22:727–730

Davis AP (2000) Chemical and engineering aspects of heavy metal-contaminated soils. Rev Int Contam Ambient 16:169–174

Dermont G, Bergeron M, Mercier G, Richer-Laflèche M (2008) Soil washing for metal removal: a review of physical/chemical technologies and field applications. J Hazard Mater 152:1–31

Ding Z, Hu X (2014) Ecological and human health risks from metal(loid)s in peri-urban soil in Nanjing, China. Environ Geochem Health 36:399–408

Domen L, Luo C, Li X (2008) The use of chelating agents in the remediation of metal-contaminated soils: a review. Environ Pollut 153:3–13

Dutré V, Vandecasteele C, Opdenakker S (1999) Oxidation of arsenic bearing fly ash as pretreatment before solidification. J Hazard Mater 68:205–215

Elkhatib EA, Moharem ML (2015) Immobilization of copper, lead, and nickel in two arid soils amended with biosolids: effect of drinking water treatment residuals. J Soils Sediments. doi:10.1007/s11368-015-1127-1

Geebelen W, Adriano DC, van der Lelie D, Mench M, Carleer R, Clijsters H, Vangronsveld J (2003) Selected bioavailability assays to test the efficacy of amendment-induced immobilization of lead in soils. Plant Soil 249:217–228

Geebelen W, Vangronsveld J, Adriano DC, Carleer R, Clijsters H (2002) Amendment-induced immobilization of lead in a lead-spiked soil: evidence from phytotoxicity studies. Water Air Soil Pollut 140:261–277

Hartley W, Edwards R, Lepp NW (2004) Arsenic and heavy metal mobility in iron oxide-amended contaminated soils as evaluated by short-and long-term leaching tests. Environ Pollut 131:495–504

He Q, Yao K, Sun D, Shi B (2007) Biodegradability of tannin-containing wastewater from leather industry. Biodegradation 18:465–472

Hmaon RE, Mclaughlin MJ, Cozens G (2002) Mechanisms of attenuation of mental availability in situ remediation treatments. Environ Sci Technol 36:3991–3996

Hu X, Ding Z (2009) Lead/cadmium contamination and lead isotopic ratios in vegetables grown in peri-urban and mining/smelting contaminated sites in Nanjing, China. B Environ Contam Tox 82:80–84

Jackson BP, Miller WP (2000) Soil solution chemistry of a fly ash-, poultry litter-, and sewage sludge-amended soil. J Environ Qual 29:430–436

Jiří S, Jaromír R (1968) Metal chelate exchange in the organic phase—II: extraction and exchange constants of dithizonates and diethyldithiocarbamates. Talanta 15:505–514

Khara DG, Annika F, Nanna BH, Eva E, Poul LB, Anders B (2010) Environmental benefits and risks of zero-valent iron nanoparticles (nZVI) for in situ remediation: risk mitigation or trade-off. J Contam Hydrol 118:165–183

Kumpiene J, Lagerkvist A, Maurice C (2008) Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments—a review. Waste Manag 28: 215–225

Lee SH, Kim EY, Park H, Yun J, Kim JG (2011) In situ stabilization of arsenic and metal-contaminated agricultural soil using industrial by-products. Geoderma 161:1–7

Liu R, Zhao D (2013) Synthesis and characterization of a new class of stabilized apatite nanoparticles and applying the particles to in situ Pb immobilization in a fire-range soil. Chemosphere 91:594–601

Liao Q, Li Y, Xiang B, Chen L, He W, Zhang Q (2008) Stability of Cu^{2+}, Pb^{2+}, Cd^{2+} and Ni^{2+} complexes of sodium diethyldithiocarbamate. Fine Chem 25:281–283 (in Chinese)

Martins RC, Amaral-Silva N, Quinta-Ferreira RM (2010) Ceria based solid catalysts for Fenton's depuration of phenolic wastewaters, biodegradability enhancement and toxicity removal. Appl Catal B-Environ 99:135–144

Mcbride MB, Martinez CZ (2000) Copper phytoremediation in a contaminated soil: remediation tests with adsorptive materials. Environ Sci Technol 34:4386–4391

Ownby DR, Galvan KA, Lydy MJ (2005) Lead and zinc bioavailability to Eisenia fetida after phosphorus amendment to repository soils. Environ Pollut 136:315–321

Porter SK, Scheckel K, Impellitteri CA, Ryan JA (2004) Toxic metals in the environment: thermodynamic considerations for possible immobilisation strategies for Pb, Cd, As, and Hg. Crit Rev Environ Sci Tec 34:495–604

Pueyo M, Mateu J, Rigol A, Vidal M, López-Sánchez JF, Rauret G (2008) Use of the modified BCR three-step sequential extraction procedure for the study of trace element dynamics in contaminated soils. Environ Pollut 152:330–341

Raicevic S, Kaludjerovic-Radoicic T, Zouboulis AI (2005) In situ stabilization of toxic metals in polluted soils using phosphates: theoretical prediction and experimental verification. J Hazard Mater 117: 41–53

René VH, Tony RH, Abir A, Andy JM, Mike LJ, Sabeha KO (2007) Remediation of metal contaminated soil with mineral-amended composts. Environ Pollut 150:347–354

Saifullah EM, Qadir M, Caritat PD, Tack FMG, Laing GD, Zia MH (2009) EDTA-assisted Pb phytoextraction. Chemosphere 74:1279–1291

Sarria V, Parra S, Adler N, Péringer P, Benitez N, Pulgarin C (2002) Recent developments in the coupling of photoassisted and aerobic biological processes for the treatment of biorecalcitrant compounds. Catal Today 76:301–315

Selena M, Alessandro C, Massimo P, Giacomo C (2008) Immobilization of heavy metals in contaminated soils through ball milling with and without additives. Chem Eng J 142:271–284

Seungbae L, Jinsung A, Young-Jin K, Kyoungphile N (2011) Binding strength-associated toxicity reduction by birnessite and hydroxyapatite in Pb and Cd contaminated sediments. J Hazard Mater 186: 2117–2122

U.S. EPA (2002) Solid waste and emergency response, arsenic treatment technologies for soil, waste, and water. EPA-542-R-02-004

Vandecasteele C, Dutré V, Geysen D, Wauter G (2002) Solidification/stabilization of arsenic bearing fly ash from metallurgical industry. Immobilization mechanism of arsenic. Waste Manag 22:143–146

Wang FH, Hao HT, Lei W, Xia MZ, Wang FY (2013) Synthesis of sixthio guanidine acid, a novel heavy metals chelating agent and its performance. CN 201310516300.0 (in Chinese)

Wang FH, Ji YX, Wang JJ (2012a) Synthesis of heavy metal chelating agent with four chelating groups of N1, N2, N4, N5-tetrakis (2-mercaptoethyl)benzene-1,2,4,5-tetracarboxamide (TMBTCA) and its application for Cu-containing wastewater. J Hazard Mater 241–242:427–432

Wang FH, Shi WY, Wang ZL (2012b) Quantum chemistry study on six heavy metal ions complexes with dimethyldithiocarbamate. Comput Appl Chem 29:647–650 (in Chinese)

Wei W, Cui J, Wei ZG (2014) Effects of low molecular weight organic acids on the immobilization of aqueous Pb (II) using phosphate rock and different crystallized hydroxyapatite. Chemosphere 105:14–23

Wu G, Kang H, Zhang X, Shao H, Chu L, Ruan C (2010) A critical review on the bio-removal of hazardous heavy metals from contaminated soils: issues, progress, eco-environmental concerns and opportunities. J Hazard Mater 174:1–8

Wu ZG, Wang F, Gu CG, Zhang YP, Yang ZZ, Wu XW, Jiang X (2014) *Aquamicrobium terrae* sp. nov., isolated from the polluted soil near a chemical factory. Antonie Van Leeuwenhoek 105:1131–1137

Zhang Z, Li M, Chen W, Zhu S, Liu N, Zhu L (2010) Immobilization of lead and cadmium from aqueous solution and contaminated sediment using nano-hydroxyapatite. Environ Pollut 158:514–519