Int. J. Environ. Sci. Technol. (2013) 10:315–324
DOI 10.1007/s13762-012-0116-9

ORIGINAL PAPER

Identification of potential soil adsorbent for the removal of hazardous metals from aqueous phase

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Received: 20 November 2011 / Revised: 31 May 2012 / Accepted: 2 August 2012 / Published online: 14 December 2012

Abstract The present study attempted to identify the efficient hazardous metal-removing sorbent from specific types of soil, upper and middle layer shirasu, shell fossil, tuff, akadama and kanuma soils of Japan by physico-chemical and metal (arsenic, cadmium and lead) removal characterizations. The physico-chemical characteristics of soil were evaluated using X-ray diffraction and scanning electron microscopy with energy dispersive spectroscopy techniques, whereas metal removal properties of soil were characterized by analyzing removal capacity and sorption kinetics of potential metal-removing soils. The chemical characteristics revealed that all soils are prevalently constituted of silicon dioxide (21.83–78.58 %), aluminum oxide (4.13–38 %) and ferrous oxide (0.835–7.7 %), whereas calcium oxide showed the highest percentage (65.36 %) followed by silicon dioxide (21.83 %) in tuff soil. The results demonstrated that arsenic removal efficiency was higher in elevated aluminum oxide-containing akadama (0.00452 mg/L/g/h) and kanuma (0.00225 mg/L/g/h) soils, whereas cadmium (0.00634 mg/L/g/h) and lead (0.00693 mg/L/g/h) removal efficiencies were maximum in elevated calcium oxide-containing tuff soil. Physico-chemical sorption and ion exchange processes are the metal removal mechanisms. The critical appraisal of three metal removal data also clearly revealed cadmium > lead > arsenic order of removal efficiency in different soils, except in tuff and akadama soils followed by lead > cadmium > arsenic. It clearly signified that each type of soil had a specific metal adsorption affinity which was regulated by the specific chemical composition. It may be concluded that akadama would be potential arsenic-removing and tuff would be efficient cadmium and lead-removing soil sorbents.

Keywords Isotherm · Removal efficiency · Scanning electron microscopy · Soil characterization · X-ray diffraction

Introduction

Contamination of hazardous metals into aquatic environment is a growing concern worldwide because it has caused severe and persistent hazardous problems in different domains of the environment during the last few decades. Of the 11 hazardous priority substances in the list of pollutants contained in the Water Framework Directive, arsenic (As), cadmium (Cd) and lead (Pb) are the major ones (Directive 2000/60/EC 2000). Discharge of hazardous metal-contaminated effluents into the environment is a tremendous problem affecting water and soil quality, and hence presenting a direct danger to human health and various forms of life (Aksu 2005; Kratochvil and Volesky 1998). Arsenic, Cd and Pb can cause various dysfunctions and chronic alterations in the nervous system and gastrointestinal tract even at low concentrations (Choudhury and Mudipalli 2008; Roberts 1999). Allergies

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are not uncommon and repeated long-term contact with some metals or their compounds may even cause cancer (International Occupational Safety and Health Information Centre 1999).

The surface and groundwater contamination by As has already been reported as a cause of acute toxic metal poisoning with severe health risks by various scientists (Hemond and Solo-Gabriele 2004; Murphy et al. 1989). Despite the presence of various chemical and glass industries, the weathering process of rocks is the primary cause of As contamination in water and soils. According to Robertson (1989), the main natural sources of this element in soils are As-bearing rocks and minerals. Cadmium is a biologically nonessential, non-biodegradable, persistent type of ‘priority pollutant’ (Campbell 2006) that easily accumulates in sediments and aquatic organisms (by bioaccumulation and biomagnifications), thus causing a gross biological impact. The sources of Cd contamination are mining and smelting processes of lead and zinc, nickel–cadmium batteries, polyvinyl chloride plastics, paint pigments, insecticides, fungicides and commercial fertilizer industries. Lead has been used by man for many years and can be regarded as a long-lasting environmental pollutant. Industry produces about 2.5 million tons of Pb per year throughout the world and is used in producing storage batteries, insecticides, plastic water pipes, beverages, ointments and medical concoctions for flavoring and sweetening (Nadeem et al. 2005) that ultimately lead to aquatic contamination.

Thus, industrial and agricultural wastewater effluents contain one or more of these toxic metals with rather higher concentrations than permissible discharge levels of effluents. Therefore, it becomes necessary to remove metals from wastewater to a feasible extent by an appropriate treatment to control the problem of hazardous metal pollution in the environment. Various improved and innovative methods such as reverse osmosis, precipitation, coagulation, ion exchange, solvent extraction, adsorption, membrane filtration, ultra-filtration and photoreduction have been developed to remove metal pollutants from contaminated water and wastewater (Bailey et al. 1999; Barron-Zambrano et al. 2002; Chen and Wang 2000; Hunsom et al. 2005; Kentish and Stevens 2001; Pacheco et al. 2006). Among the above-mentioned processes, adsorption plays a pivotal role in removing metals from the aqueous phase using various biomaterial sorbents, algae (Holan et al. 1993), fungi, sugar cane bagasse (Cerino Córdova et al. 2011; Peterlene et al. 1999), rice husk, wheat barn (Nouri et al. 2007), pine bark, olive cake (Doyurum and Celik 2006), coconut husk, chitin (Benguella and Benaissa 2002), ash, activated carbon (Jusoh et al. 2007; Onundi et al. 2011; Zavvar Mousavi and Seyedi 2011), etc. Clays, zeolite, calcite, manganese nodule residue (Agrawal and Sahu 2006; Tashauoei et al. 2010), perlite (Hasan et al. 2006) and peat (Gabaldon et al. 2006) have also been employed to remove metals from the water phase. Also, low-cost natural clay/soil is used to develop high-throughput inorganic adsorbent as well as membrane filter in removing heavy metals from aqueous phase. Clay/soil and waste materials are used as modified potential tools in removing heavy metals and various toxic compounds for the reclamation of the aquatic environment (Bhakta and Munekage 2008, 2009).

On account of the above, it is also apparent that some of the metal removal techniques are inadequate and expensive in the practical field. Moreover, materials used in these techniques are not sufficiently available and very expensive to treat the massive amount of effluent water; it is unaffordable for small-scale industries especially in underdeveloped as well as developing countries. Therefore, an affordable, low-cost metal removal technology is required. The aquatic ecosystem minimizes and balances the negative impact of hazardous compounds by a mechanism using abiotic and biotic ecosystem components, for example, sediment and aquatic organisms remove heavy metals from water and accumulate within them (Bhakta and Munekage 2008; Das and Jana 1999; Ferard et al. 1983; Jana and Das 1997). Stemming from the above understanding, the development of promising, eco-friendly and low-cost water reclamation technology using potential sorption criteria of specific soil is important and necessary in the present hazardous metal polluting scenario of aquatic environment. From the above points of view, therefore, the present study has been aimed at finding out the As-, Cd- and Pb-specific efficient soil adsorbents by assessing (1) physico-chemical and (2) metal sorption properties of soils to remove hazardous metals from the aqueous phase. The study was carried out in 2009 at the Department of Environmental Engineering, Kochi University, Kochi, Japan.

Materials and methods

Soil, sampling and processing

The present study selected six kinds of specific soil, procured from different parts of Japan, including upper layer shirasu (S_1, pH 6.57), middle layer shirasu (S_2, pH 7.01) and lower layer shell fossil (S_3, pH 9.22) soils of Kagoshima prefecture (31°37′N, 130°32′E), tuff soil (S_4, pH 9.03) of Shimane prefecture (35°10′59″*N*, 132°30′*E*), akadama (S_5, pH 6.09) and kanuma soils (S_6, pH 5.25) of Tochigi prefecture (36°45′*N*, 139°45′*E*). The diversified physico-chemical specificities of soils compared to other soils found in Japan are the primary basis for the selection of soils (Table 1). Moreover, soil types S_1–S_3 are frequently used in ceramic production, whereas S_5 and S_6

Table 1 Physico-chemical characteristics of soils employed in the study

Soil types and location	Local name of Soil	Collected layer and physical nature of soil
Meadow soil association, Kagoshima	Upper layer shirasu soil (S_1)	Top layer of shirasu soil (0.5 m). Coarse whitish, sandy in nature. No detectable amount of organic matter content was found
Meadow soil association, Kagoshima	Middle layer shirasu soil (S_2)	Collected from 2 m depth of shirasu soil. Fine whitish, sandy in nature. No detectable amount of organic matter content was found
Meadow soil association, Kagoshima	Lower layer shell fossil soil (S_3)	Four meter depth of shirasu soil is fine, whitish in color. No detectable amount of organic matter content was found
Meadow soil association, Shimane	Tuff soil (S_4)	Collected from surface layer of volcanic soil in this region. It has cement-like physical appearance and heavier than land soil due to having ash fragments of rock. No detectable amount of organic matter content was found
Recent volcanic soil, Tochigi	Akadama soil (S_5)	Located at 2 m depth of volcanic ash soil, brown in color. It is fluffy, loamy soil and a bit heavier than kanuma. Organic matter content was 0.09 %
Recent volcanic soil, Tochigi	Kanuma soil (S_6)	Three meter deeper layer of volcanic ash soil layer. It is also fluffy, less dense, very lightweight and whitish yellow in color. Organic matter content was 0.86 %

soils are highly porous in nature and widely used as horticulture bed for heavy water retention capacity.

Soils were collected from three places of each region, air dried, homogenized by mortar and pestle and sieved through mesh (0.404 mm) for the experiment.

Characterization of soil

Mineralogical characterization of soil was performed by X-ray diffraction (XRD, X'Pert PRO, Philips) in the Center for Advanced Marine Core Research, Kochi University, Japan. Morphological and chemical characterizations of soil samples were also executed by scanning electron microscopy (SEM) using a JEOL model equipment coupled with energy-dispersive spectroscopy (EDS) facility (JSM-6500F, JEOL) in the same research center.

Identification of potential metal-removing soil

The potential metal-removing soils were identified through the assessment of metal removal criteria of soils.

Metal removal experiment was carried out using 63 conical flasks (0.1 L) following the batch operation mode in laboratory condition (20 °C). All conical flasks were randomly divided into three groups (21 × 3) for three metals: As, Cd and Pb. Each group was further subdivided into seven batches having three replicates (7 × 3)—one batch employed for control received no soil and the other six batches were used for the six types of soil (called as S_1–S_6). Each conical flask was provided with the respective soil at the rate of 1 g/L and filled with As solution (0.5 mg/L, pH 7.62) in the first group, Cd solution (0.5 mg/L, pH 4.35) in the second group and Pb solution (0.5 mg/L, pH 6.81) in the third group at the rate of 0.1 L/flask. The experiment continued for 72 h. Arsenic and Cd solutions were prepared from standard stock solutions of arsenic(III) trioxide (As_2O_3) and cadmium chloride ($CdCl_2$) (Cica-Reagent, Kanto Chemical Co., Inc., Tokyo, Japan), respectively, whereas Pb solution was prepared using lead(II) nitrate ($Pb(NO_3)_2$, Sigma-Aldrich Chemical GmbH, Germany).

Metal removal criteria of six different soils were determined by calculating the metal removal efficiency (MRE) using the modified equation of Bhakta and Munekage (2008) as follows:

$$\mathrm{MRE} = \frac{C_\mathrm{i} - C_\mathrm{f}}{M(t_\mathrm{f} - t_\mathrm{i})} \quad (1)$$

where C_i and C_f are the initial and final concentrations (mg/L), respectively; M is the mass (g) of soil and t_i and t_f are the initial and final times (h).

Sorption isotherm of the identified potential metal-removing soil

After selection of potential metal-removing soils, the isotherm studies of soil-specific metals (As or Cd or Pb) were performed by batch operation mode using the effect of soil doses in removing metals from water. Different doses of As-removing soil (2, 4, 6, 8 and 10 g/L), Cd-removing soil (1, 2, 3, 4 and 5 g/L) and Pb-removing soil (0.5, 1, 2, 5 and 10 g/L) were used in glass bottles (0.2 L) to equilibrate the known concentration (10 mg/L) of the respective metals—As, Cd and Pb solutions (0.1 L) prepared from the above-mentioned standards. All glass bottles were shaken in a reciprocating shaker with a capacity of 200 excursions/min (epm) at 25 °C for a contact period of 12 h.

At equilibrium, the amounts of target metals adsorbed (q_e, mg/g) onto the corresponding soils were found by following mass balance relationship equation (Eq. 2) (Rozada et al. 2008):

$$q_e = \frac{(C_0 - C_e)V}{M} \qquad (2)$$

where C_0 (mg/L) and C_e (mg/L) are the initial and the equilibrium water phase concentrations of metal, respectively, V (L) is the volume of the solution and M (g) is the mass of soil.

The results were fitted following the equations of Langmuir (Eq. 3) and Freundlich (Eq. 4) isotherm models described by Rozada et al. (2008) as below:

$$q_e = \frac{Q^0 K_L C_e}{1 + K_L C_e} \qquad (3)$$

where Q^0 (mg/g) and K_L (L/mg) are the Langmuir parameters related to the maximum capacity of adsorption and to the binding energy of adsorption, respectively.

$$q_e = K_F C_e^{1/n} \qquad (4)$$

where K_F (L/mg) is the Freundlich constant, C_e (mg/g) is the equilibrium liquid phase concentration and $1/n$ is the heterogeneity factor.

Practical approach of metal-contaminated water treatment: sorption, desorption and resorption

Ten liters of each metal (1 mg/L)-challenged water was made with the above-mentioned standard solutions and employed for sorption study using potential metal-removing soils. Each metal (As or Cd or Pb)-challenged water (10 L) was treated with 10 g (1 g/L) of the respective identified soil in the treatment chamber of the experimental apparatus and continuously mechanically agitated (200 epm) for 6 h. The initial and final pH of the treated water were measured. To quantify the desorption capacity, metals (As, Cd and Pb) loaded above soils were collected, gently washed (once) by Milli Q water to remove unbound metals and centrifuged. One gram of each washed soil was agitated with 10 mmol/L EDTA (ethylenediamine teraacetic acid as desorbent) solution at the rate of 1 g/L for 60 min and the concentration of the metal in the solution was examined. Reusability was assessed by the resorption process using the above desorbed soils. One gram of each dried desorbed soil was employed in 1 L of the respective metal solutions (1 mg/L) to determine the percentage resorption capacity.

Analysis of metals

Water samples were collected from experimental vesicles, centrifuged and analyzed using the atomic absorption spectrophotometer (Analyst 200, Perkin Elmer) to determine As, Cd and Pb metal contents of water at the wavelengths 193.7, 228.8 and 422.67 nm, respectively.

Concentrations of Na, K, Ca and Mg in water were examined by ion chromatography (ICS 900, Dionex Corporation, Sunnyvale, CA, USA) using a CS12A column. Ten milliliters of filtered water was used for ion chromatography following the conditions: flow rate 1 mL/min, pressure 1,100–1,200 psi and temperature 20 °C.

Statistical analysis

Data (mean of three replicates) obtained from the experiments were used for statistical analysis using one-way ANOVA (Gomez and Gomez 1984). In case of significant difference, the ANOVA was followed by an LSD (least significance difference) test using statistical package EASE and MSTAT. All statistical tests were performed at 5 % probability level.

Results and discussion

Characterization and identification of soil

XRD patterns of the six soils are shown in Fig. 1. It shows that quartz was predominant with the presence of albite in S_1 and S_3, calcium mordenite in S_5 and anorthite in S_6, whereas S_2 was predominantly anorthite with the association of albite and S_4 was predominantly magnesium calcite with quartz (Table 2).

The morphological structure and chemical composition of soils obtained from SEM–EDS analysis are shown in Fig. 2 and Table 3, respectively. The SEM of soil particles revealed a clear picture of morphological information and microscopic surface texture of soils. Table 3 shows the percentage composition of different chemical constituents obtained by EDS analysis of six soils. It was also observed that the particles of all soils predominantly constituted of silicon dioxide (SiO_2, 21.9–78.6 %), aluminum oxide (Al_2O_3, 4.0–38 %) and ferrous oxide (FeO, 0.84–7.75 %) except soil S_4 where calcium oxide (CaO) showed the highest percentage (65.4 %) followed by SiO_2 (21.9 %). The percent abundance of SiO_2 was highest in S_1 and minimum in S_4, whereas maximum and minimum abundances of Al_2O_3 were found in S_6 and S_4, respectively. The major chemical composition of soils is similar to that of zeolites with some exceptions. A small percentage of cuprous oxide (CuO) was also found in S_5 (2.6 %) and S_6 (3.7 %) type of soils. The remaining constituents were present in very negligible percentages.

The concentration of As, Cd and Pb ranged from 0.174 to 0.5 mg/L, 0.043 to 0.5 μg/L and 0.00048 to 0.5 mg/L in water of six types of soil throughout the period of experimentation, respectively. Significant soil-dependant responses were pronounced in As, Cd and Pb adsorption process (ANOVA, $P < 0.05$). Arsenic removal was maximum (0.326 mg/L) in S_5 soil exhibiting the following order

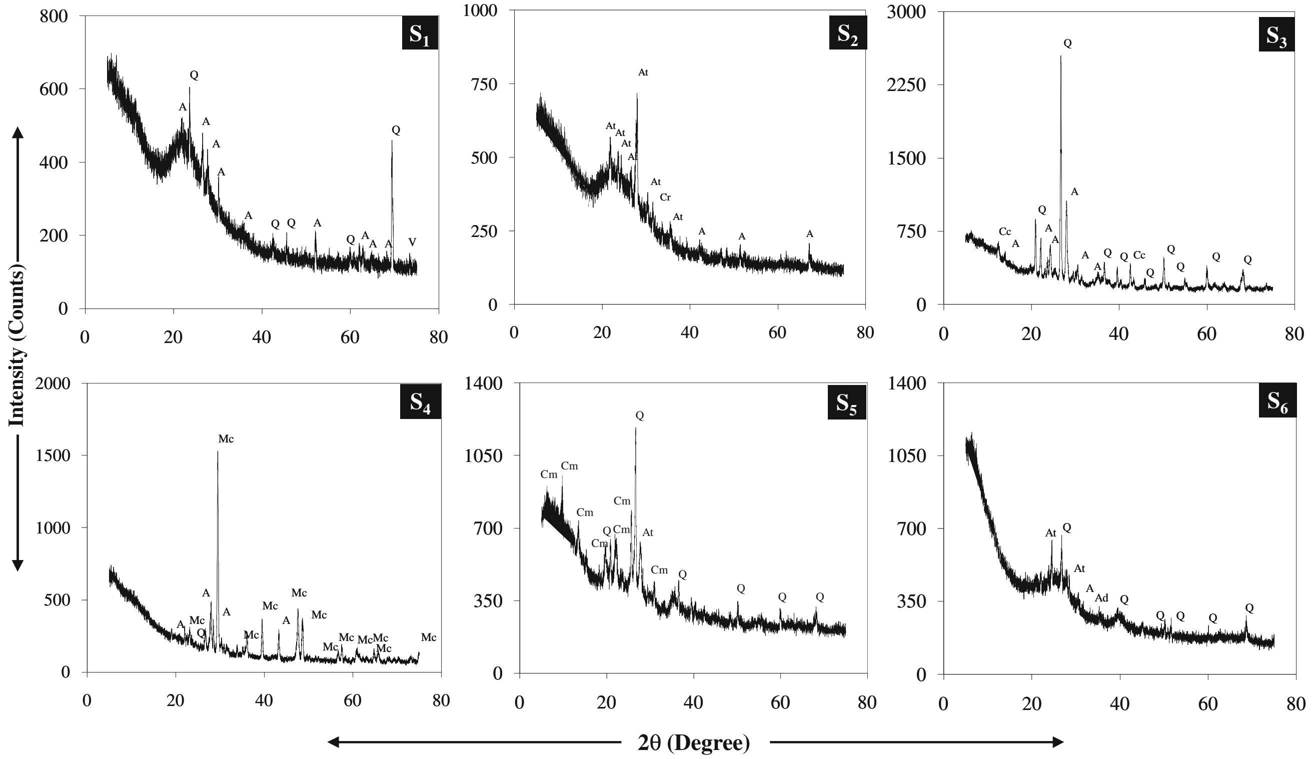

Fig. 1 XRD pattern of mineralogical characteristics of six soils (S_1–S_6) used in the experiment (*Q* quartz, *A* albite, *V* vermiculite, *At* anorthite, *Cr* cristobalite, *Cc* clinoclore, *Mc* magnesium calcite, *Ad* andesine and *Cm* calcium mordenite)

Table 2 XRD scores of different mineral constituents of six soils (S_1–S_6)

Minerals	Types of soil					
	S_1	S_2	S_3	S_4	S_5	S_6
Quartz	33	–	69	32	69	33
Albite	22	33	53	28	–	–
Vermiculite	11	–	–	–	–	–
Anorthite	–	51	–	–	36	43
Cristobalite	–	28	–	–	–	–
Clinoclore	–	–	35	–	–	–
Magnesium calcite	–	–	–	70	–	–
Andesine	–	–	–	–	–	27
Calcium mordenite	–	–	–	–	44	–

of variation: $S_5 > S_6 > S_3 > S_4$ and $S_2 > S_1$. Removal of As by S_5 soil was markedly higher (101–3,160 %) than that of the remaining types of soil. Arsenic concentration of water registered a gradual declining trend with time in all soils (Fig. 3). Maximum removal of Cd (0.457 mg/L) was found in S_4 exhibiting the following order of variation: $S_4 > S_5 > S_3$ and $S_6 > S_2 > S_1$ (Fig. 3). Cadmium removal of S_4 was 6.7, 13.7, 16.4, 28.7 and 44.6 % greater than that of S_5, S_3, S_6, S_2 and S_1, respectively. Temporally, there was a sharp decreasing trend in the concentration of Cd at 3 h and gradually decreased thereafter in all soils (Fig. 3). A surprisingly elevated amount of adsorptions of Pb was observed in S_4 (0.499 mg/L) and S_5 (0.489 mg/L), whereas S_1 (38 μg/L) showed minimum level of adsorption (Fig. 3). The total Pb adsorption of S_4 was 2, 115, 371, 692 and 1,114 % higher than that of S_5, S_3, S_6, S_2 and S_1, respectively. Likewise Cd, a sharp decrement was found at 3 h in the Pb concentration of S_4 and S_5, and showed a slow decreasing trend in the rest of the soil types employed.

The MREs varied from 0.00014 to 0.00452 mg/L/g/h, 0.00439 to 0.00634 mg/L/g/h and 0.00053 to 0.00693 mg/L/g/h in As, Cd and Pb, respectively. Soil types S_5 (0.00452 mg/L/g/h) and S_6 (0.00225 mg/L/g/h) exhibited remarkably higher MREs in As, whereas significantly elevated MRE values of Cd (0.00634 mg/L/g/h) and Pb (0.00693 mg/L/g/h) were observed in S_4 (Fig. 4).

The results clearly demonstrated that total metal removal (As, 0.010–0.326 mg/L; Cd, 0.316–0.457 μg/L; Pb, 0.038–0.499 mg/L) (Fig. 3) and MRE (Fig. 4) varied substantially in different soils. These variations were supposed to be associated with the variations in the chemical compositions of soils found in XRD and SEM–EDS analysis. Soil (Gillis and Miller 2000), clay (Jones and Galan 1988) and sediment (Bhakta and Munekage 2008) have significant capacity to remove heavy metals from the aquatic environment.

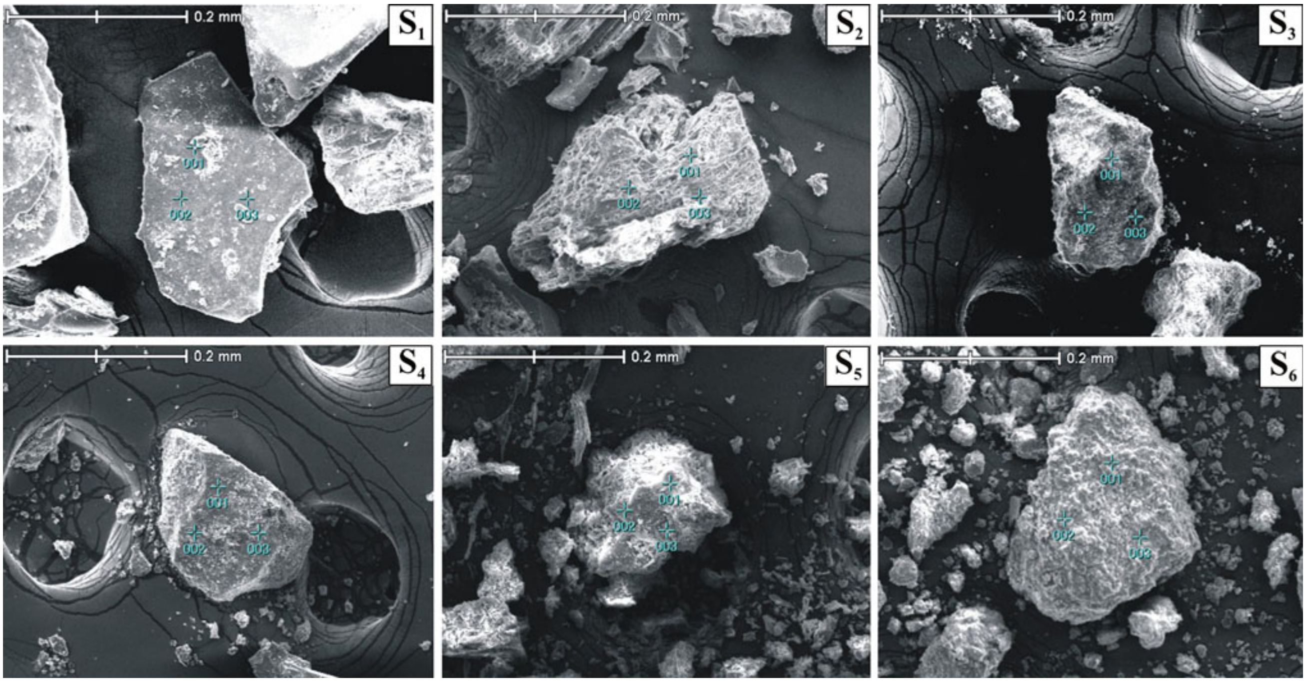

Fig. 2 SEM micrographs of six soils (S_1–S_6) employed in the experiment

Table 3 Percentage composition of chemical constituents in six soils (S_1–S_6) examined

Chemical composition (wt %)	Types of soil					
	S_1	S_2	S_3	S_4	S_5	S_6
SiO_2	78.6	71.5	73	21.9	58.1	50.1
Al_2O_3	12.37	14	12.9	4.0	25.8	38
FeO	0.84	2.38	7.41	7.75	6.67	5.07
K_2O	3.29	3.7	0.965	0.48	1.905	1.5
CaO	0.87	2.23	2.98	65.4	1.915	0.38
CuO	0	0	0	0	2.6	3.7
Na_2O	2.11	1.61	0.565	0.09	1.125	0.05
MgO	0.285	2.55	0.76	1.3	0.69	0.205

Arsenic removal efficiencies were higher in S_5 (242–3128 %) and S_6 (70–1500 %) than those of the remaining soil types, which indicated that both S_5 and S_6 types of volcanic soil may be considered as efficient As-removing agents from water column among the examined six types of soil (Fig. 4). It also reveals that S_5 is superior in removing As compared to S_6. In S_5 and S_6 soils, the major driving forces for exhibiting the maximum As-binding affinity are (1) presence of quartz, anorthite and calcium mordenite (Fig. 1) as crystalline phase and (2) presence of higher amount of Al_2O_3 as well as lower percentage of SiO_2 (Table 3). Basically, these two chemical criteria of S_5 and S_6 soils are supposed to be associated with the removal of maximum amount of As from the water column compared to remaining soils. Aluminum and iron oxides were found to be good and inexpensive adsorbents in removing As from water (Gulledge and O'Connor 1973; Jeong et al. 2007). According to Zeng (2003), As (V) adsorption capacity of SiO_2 is very low and no adsorption efficiency was found for As(III). Soil type S_4 showed higher Cd (7–44 %) and Pb (2–1,114 %) removal efficiencies than the remaining five types of soil (Fig. 4), which suggests that possessing the highest amount of quartz, albite, magnesium calcite (Fig. 1) and CaO (65.4 %) (Table 3) in soils is an important reason for its better binding affinity to Cd and Pb. O'Hara and Surgi (1988) immobilized Cd and Pb using calcium hydroxide and phosphate. On the contrary, reduced metal removal efficiencies were found in the remaining soils (S_1, S_2 and S_3) probably due to the presence of higher percentage of SiO_2 and lower percentage of metal-specific constituents (Al_2O_3 and CaO). Our study also clearly revealed that As removal capacity of Al_2O_3 was significantly higher, whereas CaO showed a good Cd and Pb removal ability among the examined metal oxides (unpublished). In spite of that, we determined that Al_2O_3 and CaO incorporation improved the As, Cd and Pb removal efficiency of soil (unpublished). It was also observed that detectable amount of organic matter content was not found in S_1, S_2, S_3 and S_4, whereas S_5 (0.09 %) and S_6 (0.86 %) registered a very low level of organic matter. These results clearly supported that toxic metal sorption capacity of the investigated soils was probably regulated by the mineral/metal oxide content of the soils, but it was not influenced by organic matter content of soil. According to Jones and Galan (1988), minerals are responsible for structural adsorption, and rheological and thermal properties in clay. Furthermore, it can be

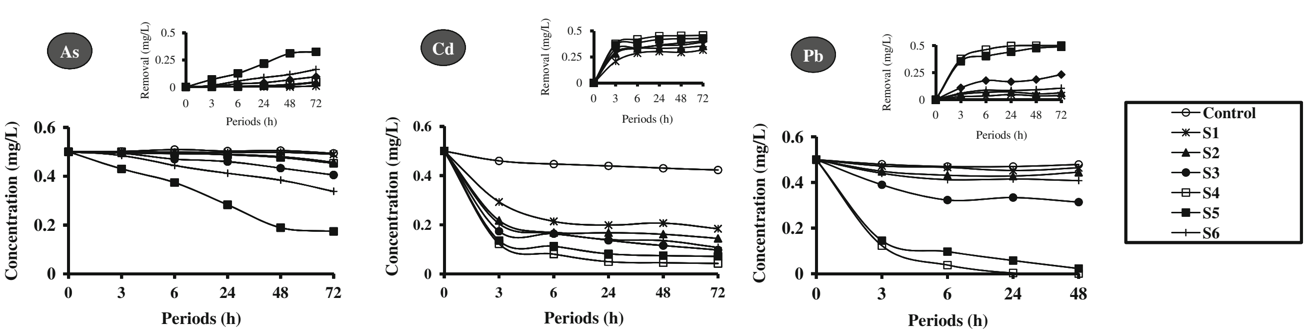

Fig. 3 Decreasing temporal responses of toxic metals concentration in water of different types of soil (S_1–S_6) employed in experiment (*Insets* show amount of toxic metals removed from water column with time)

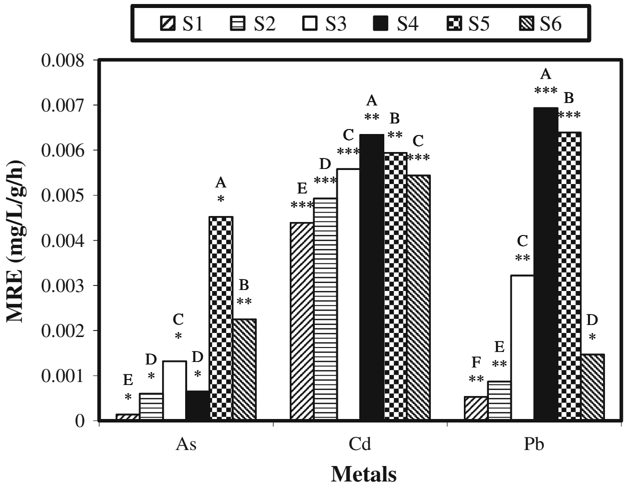

Fig. 4 Metal removal efficiency (MRE) criteria of six types of soil (S_1–S_6). Same script (*A*–*F*) over the bars of six soil types for each toxic metal revealed lack of significant difference. *Asterisks* (*) over the same three bars of each soil types in three metals depicts the preferential adsorption (*** > ** > *) of metals

demonstrated that minerals/metal oxides of soil play a significant role in metal sorption process by forming ion complex (outer and inner-sphere complex of soil) between the toxic metals of the solution and the surface functional groups of minerals in the porous soils. According to Stumm (1992), surface metal ions coordinate to water forming a Lewis acid site, and then a dissociative chemisorption (chemical bonding to the surface) leads to a hydroxylated surface with surface OH groups. Zeng (2003) proposed that Fe–Si binary oxide complexes improve As removal capacity. It can also be drawn herein that chemical sorption mechanism is a regulating force to remove hazardous metals from the water phase as found in zeolite (Erdem et al. 2004), because the chemical compositions of tested potential metal-removing soils are very similar to zeolite.

Critical appraisal of MRE of three metals clearly revealed that each soil type showed higher degree of removal efficiency in Cd (***), moderate degree of removal efficiency in Pb (**) and lowest degree of removal efficiency in As (*)—i.e., Cd > Pb > As excepting S_4 and S_5 types of soil which exhibited maximum removal efficiency in Pb (***) followed by Cd (**) and As (*)—i.e., Pb > Cd > As (Fig. 4). This result strongly suggested that each soil type has specific priority metal pollutant in their metal removal mechanism from aqueous phase—i.e., preferential metal removal. On the basis of preferential metal removal property, Cd, Pb and As can be designated first, second and third priorities hazardous metals to remove from aqueous phase in case of S_1, S_2, S_3 and S_6 soils, respectively, whereas for S_4 and S_5 soils Pb, Cd and As can be recognized first, second and third priorities hazardous metals to remove from aqueous phase, respectively. Erdem et al. (2004) proposed a sorption selectivity sequence of metals in zeolite. Rozada et al. (2008) suggested that pyrolyzed sludge and chemically activated sludge showed higher adsorption affinity to Hg than to Pb, followed by Cu and Cr.

Sorption isotherm of identified potential metal-removing soil

Since the above metal removal criteria identified the S_5 soil was best for As removal and S_4 soil was efficient for Cd and Pb removal, sorption isotherm studies of As, Cd and Pb were performed with the corresponding soils (Fig. 5). As the doses of soils increased, equilibrium metal uptake decreased until it reached a plateau at higher soil doses in case of the three metals, As, Cd and Pb. In S_5 soil, the correlation coefficients of Langmuir and Freundlich were 0.9397 and 0.9860, respectively for As, whereas the correlation coefficients of S_4 soil were 0.9960 (in Langmuir) and 0.8192 (in Freundlich) for Cd as well as –0.1013 (in Langmuir) and 0.9241 (in Freundlich) for Pb.

In the sorption isotherm study, effect of soil dose revealed that equilibrium metal uptake decreased with the increasing soil dose. It apprehended toward the reason of having higher number of binding sites of metal oxides (especially, Al_2O_3 in akadama and kanuma and CaO in tuff) in the higher doses of the soil adsorbent than those of the lower soil doses for different metal (As, Cd and Pb) ions in solution. The correlation coefficients revealed the experimental data of S_5 (for As) and S_4 (for Pb) well fitted with Freundlich rather than the Langmuir models, whereas Langmuir isotherm for Cd better fitted with the experimental data than the Freundlich model. In this context, it should be mentioned that though the present study is a platform for the identification of metal-removing potential soil components of the environment with an isotherm study, full screen isotherm study regarding the effect of pH, temperature, contact time and initial concentration of different metals is required for better understanding as well as designing the optimum model of these soils based efficient adsorption reactor system before applying to the practical and commercial fields.

Ion concentration of water

Sodium (0.01–15.20 mg/L) and K (0–5.058 mg/L) ions in water increased from initial to final concentrations in As-, Cd- and Pb-treated soils, whereas Mg (0–1.863 mg/L) and Ca (0–10.291 mg/L) showed increasing trend in Cd- and Pb-treated soils except As-treated soils with few variations. In control, the concentration of Na (0–0.042 mg/L), K (0–0.002 mg/L), Mg (0–0.001 mg/L) and Ca (0–0.03 mg/L) showed no remarkable increment compared to the treated groups. Maximum increment of Na (15.14 mg/L) was observed in S_6 of As, whereas K (5.058 mg/L), Mg (1.863 mg/L) and Ca (10.269 mg/L) showed highest concentration increase in S_3, S_5 and S_4 of Pb, respectively.

With some exceptions, the concentrations of the above ions were significantly increased in the water column of different soils, indicating the ion exchange mechanism between the ions of soil (Na, K, Mg and Ca) and toxic metal ions (As, Cd and Pb) of water solution on the surface of the soil particles. Furthermore, it may be suggested that due to the presence of higher amount Al_2O_3, the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cations (Na, K or Ca) which are exchangeable with certain cations in solutions such as As, Cd, Pb, Zn etc. (Barer 1987; Breck 1964). Therefore, it clearly demonstrated that the ion exchange mechanism also plays a role in removing toxic metals from water solution.

Practical approach of metal-contaminated water treatment: sorption, desorption and resorption

A substantial amount of As (0.377 mg/L) was removed by S_5 soil, whereas 0.475 mg/L Cd and 0.510 mg/L Pb were removed by S_4 soils separately (Table 4). The registered initial and final pH values of the treated water are also shown in the Table 4. The pH of treated water is close to normal water pH which is favorable for the environmental aspect. Arsenic desorption capacity was ~95 % in S_5 soil, whereas S_4 soil showed ~93 and ~82 % desorption capacities in Cd and Pd, respectively. Likewise, resorption capacity of S_5 soil was ~88 % for As, and S_4 showed ~85 and ~76 % resorption capacities for Cd and Pb, respectively. Desorption and resorption capacities of examined soils clearly revealed that the adsorption mechanism also plays a role along with ion exchange mechanism to remove hazardous metals from water phase. Though it is difficult to determine the priority mechanism responsible for metal removal process because different mechanisms (physico-chemical sorption and ion exchange) occur simultaneously, the adsorption process can apparently be mentioned as an important mechanism. This study also indicates that it can be recycled by desorption process using EDTA. Finally, the EDTA and metal complexes can easily be separated as solid EDTA and metal salts with the help of sulfuric or hydrochloric acid to avoid the further environmental contamination.

Though practical application and environmental hazardous impacts of spent adsorbent are the major aspects for an adsorbent media, the above practical studies suggested that a small and simple chamber with continuous agitating system is a feasible and affordably convenient approach for applying the identified potential soil adsorbents in the practical field, especially in small-scale industries to treat metal-contaminated water before discharge into the environment. Apart from that application of such potential metal

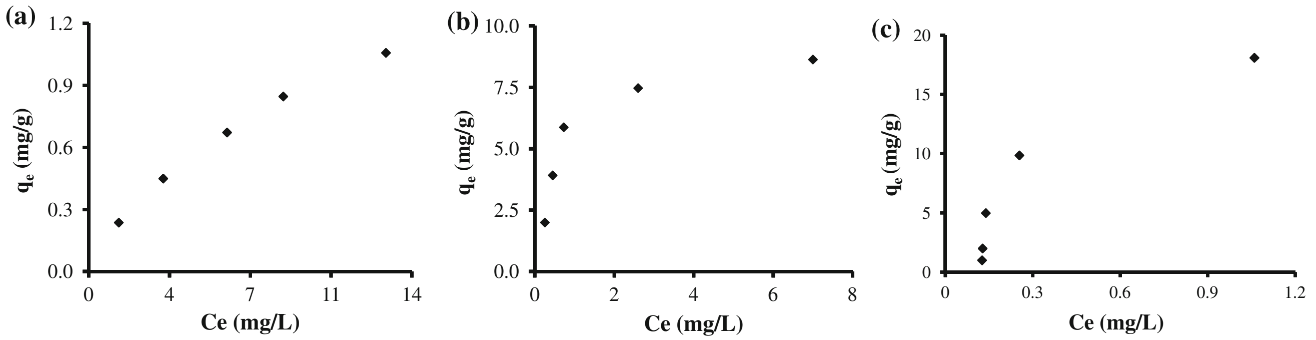

Fig. 5 Experimental sorption equilibrium curve of S_5 soil for As (**a**) and S_4 soil for Cd (**b**) and Pb (**c**)

Table 4 Adsorption of metals by respective soils at 6th hour equilibrium state

Metal specific soil	Challenged metal	Removal of metal (mg/L)	pH	
			Initial	Final
S_5 (Akadama soil)	As	0.377	6.75	6.50
S_4 (Tuff soil)	Cd	0.475	6.50	6.68
S_4 (Tuff soil)	Pb	0.510	6.61	6.89

uptaking soil components as a bed in the artificial wastewater treatment, wetland system would possibly be an effective technique, though it was not considered in the present study. Removal of toxic metals from water column and fixation within this soil bed are the major functional mechanisms of such artificial wetland system of wastewater treatment. Incorporation of clay-based ceramic as a vesicle with plant in the constructed wetland treatment system is a new approach for wastewater reclamation (Bhakta and Munekage 2009; Chen et al. 2006). On the other hand, metal saturated spent soil adsorbents and beds can be recycled by the desorption process and used for land filling maintaining the permissible limit of hazardous metals.

Conclusion

The present study revealed that the investigated soils have excellent hazardous metal removal capacity (As 2.0–65.2 %, Cd 63.2–91.4 % and Pb 13.1–99 %) from water. Besides, an overall discussion affords drawing the following conclusions. Each type of examined soil has a specific metal sorption property which is largely governed by its specific chemical constituents by synergistic effects of physico-chemical sorption and ion exchange mechanisms. More specifically, soil (S_5, akadama) possessing higher percentage of Al_2O_3 is efficient for removing As, whereas higher CaO containing soil (S_4, tuff) has a promising ability to remove Cd and Pb from water. Thus, akadama soil could be used for removing the As and tuff soil would be a potential agent to treat Cd-and Pd-contaminated water.

No preparation cost and costly infrastructure are required to use the identified soil adsorbents. Therefore, identification by determining their chemical properties and eco-friendly application of such types of easily available potential soil components as an adsorbent tool would be a simple and low-cost eco-technology based new approach to treat the massive metal-contaminated effluents.

Acknowledgments The authors are grateful to the Government of Japan for sponsoring the JSPS research grant (No. 20380181) to carry out the present study. The authors express their sincere thanks to K. Fuyukawa for helping in the collection of soil samples used in the experiment and to Dr. Yuhji Yamamoto for extending his kind cooperation in the XRD and SEM–EDS analysis.

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