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Influences of thermal decontamination on mercury removal, soil properties, and repartitioning of coexisting heavy metals

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ABSTRACT

Thermal treatment is a useful tool to remove Hg from contaminated soils. However, thermal treatment may greatly alter the soil properties and cause the coexisting contaminants, especially trace metals, to transform and repartition. The metal repartitioning may increase the difficulty in the subsequent process of a treatment train approach. In this study, three Hg-contaminated soils were thermally treated to evaluate the effects of treating temperature and duration on Hg removal. Thermogravimetric analysis was performed to project the suitable heating parameters for subsequent bench-scale fixed-bed operation. Results showed that thermal decontamination at temperature >400 °C successfully lowered the Hg content to <20 mg kg^{-1}. The organic carbon content decreased by 0.06–0.11% and the change in soil particle size was less significant, even when the soils were thermally treated to 550 °C. Soil clay minerals such as kaolinite were shown to be decomposed. Aggregates were observed on the surface of soil particles after the treatment. The heavy metals tended to transform into acid-extractable, organic-matter bound, and residual forms from the Fe/Mn oxide bound form. These results suggest that thermal treatment may markedly influence the effectiveness of subsequent decontamination methods, such as acid washing or solvent extraction.

1. Introduction

Hg is an extremely toxic element that has caused serious environmental pollution in many industrialized countries. US Environmental Protection Agency (USEPA) reported that 290 sites on the National Priorities List were contaminated by Hg and 173 of these 290 were soil-contaminated sites (USEPA, 2007). In addition, Hg is the contaminant on third rank in the 2007 CERCLA Priority List of Hazardous Substances reported by the Agency for Toxic Substances and Disease Registry (ATSDR, 2011). In Taiwan, a number of contaminated sites contain a marked amount of Hg (Taiwan EPA, 2010). Public concerns and requests on remediation of these sites arise due to a significant threat of Hg to the safety and health of humans and the ecosystem.

Technologies for remediating soils contaminated by heavy metals have been well developed and employed (Dermont et al., 2008a). USEPA (2007) and Otto and Bajpai (2007) have summarized 8 remediation techniques at pilot or full scale for Hg-contaminated soil, waste, and water. Factors affecting the performance and cost of remediation were also provided. Among these applicable techniques, solidification/stabilization, soil washing, thermal treatment, and vitrification were considered feasible for soil and waste treatment. New techniques for Hg removal from soil or water have also been developed. For example, Zhuang et al. (2003) has researched remediating Hg-contaminated soil with lignin derivatives containing an abundance of oxygen-containing functional groups.

Soil washing and chemical extraction are frequently used to remove heavy metals from contaminated soils (Dermont et al., 2008b; Leštan et al., 2008). Compared to other heavy metals, Hg was difficult to remove using general chemical extraction (Wasay et al., 1995). Thermal treatment has been shown to effectively remove contaminants with a high vapor pressure, such as organochlorines and Hg (de Percin, 1995; Chang and Yen, 2006). The Hg decontamination level depends on the treating temperature, elapsed time, the texture of soils, and Hg speciation, which varies with different soil pHs and oxidation–reduction potentials (Davis et al., 1997; Biester et al., 2002; Sladek et al., 2002; do Valle et al., 2006).

Thermal treatment may greatly affect soil properties. Roh et al. (2000) intended to remove Hg from soil at 400 and 600 °C; experimental results showed that the 600 °C treatment caused drastic changes in soil characteristics, including an increase in soil pH, dehydration of silicate clay minerals, and a reduction in the content of organic carbon and nitrogen. They also found that thermal treatment at 600 °C induced the formation of sand-sized aggregates. Other studies also showed that the reduction of organic carbon, nitrogen, and other nutrient elements took place when the

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slash-and-burn fires or forest fires were applied on soil (Sertsu and Sánchez, 1978; Ketterings et al., 2000). Importantly, the changes in properties of topsoil were more severe due to direct exposure to fire. Besides, thermal treatment darkened the soils, mainly due to the oxidation of Fe, dehydroxilation of Fe-laden minerals, and possible conversion of organic matter (Sertsu and Sánchez, 1978; Ulery and Graham, 1993).

The forms of heavy metals can be considerably influenced by thermal treatment, based on results from the sequential extraction procedure (SEP) (Tack and Verloo, 1993; Chan et al., 2000; Bruder-Hubscher et al., 2002; Kirk et al., 2002; Chou et al., 2009). In Taiwan, some Hg-contaminated sites also contain high amounts of heavy metals, such as Cr, Cu, and Pb. To successfully remove all the metals, a multiple-step decontamination approach, namely, a treatment train should be considered. By applying the thermal desorption as the first step to remove Hg, the impacts caused by heat on the soil properties and potential mobility of metals should be understood. As thermal treatment has been widely used in site remediation, most early research focused on how to enhance the removal efficiency of targeted pollutants. Little has been reported on the variation of soil properties and the distribution and mobility of other heavy metals caused by thermal decontamination. This information is imperative for re-utilizing the treated soils. The intent of this study was thus to provide a better understanding of how the Hg removal efficiency, the changes in chemical and mineralogical properties of soils, and the forms of metals were affected by thermal decontamination.

2. Experimental

2.1. Soil sample preparation

Soil samples (designated A, B, and C) were collected from three actual contaminated sites in southern Taiwan for testing. Soil A was obtained from a site dumped with Hg-contaminated deposits and solid waste. Soils B and C were sampled from two chlor-alkali plants which was highly contaminated by Hg-containing sludge. Soil samples were air-dried, followed by removal of particles with sizes larger than 2 mm using a standard 10-mesh sieve, and stored before sample characterization and thermal decontamination tests.

2.2. Soil sample characterization

Soil samples prior to and after thermal treatment were characterized as follows. Soil colors were determined with a Munsell soil color chart which has been extensively used to describe soil color. The pH was measured in deionized water using a solid to liquid ratio of 1:1 according to the scheme of Taiwan EPA (NIEA S410.62C). Cation exchangeable capacity (CEC) was measured using the ammonium acetate method (pH = 7.0) according to Thomas (1982). Organic carbon determination was performed according to the Walkley–Black wet oxidation method (Nelson and Sommer, 1982). Particles size distribution was determined according to Gee and Bauder (1986). Dithionite–citrate–bicarbonate extractable iron (Fe_d) and manganese (Mn_d) was analyzed according to Mehra and Jackson (1960). Clay minerals were analyzed with X-ray diffraction (Rigaku Rint 2000). The morphology of soils was observed using a scanning electron microscope (Hitachi S-3000N).

2.3. Total mercury and metal analysis

The total concentration of Hg in contaminated soils prior to and after thermal treatment was determined following the acid digestion scheme of Taiwan EPA (NIEA M317.02C). A brief description was provided here for clarity. Soil of 1 g was accurately weighted and placed in a 250-mL Erlenmeyer flask. Deionized water of 5 mL and aqua regia of 5 mL were added into the flask, which was put on a hot plate for 3 min. The Erlenmeyer flask was covered with a watch-glass during the heating process to prevent the volatilization loss of Hg. The digestion at 95 °C for 30 min was then performed after 50 mL deionized water and 15 mL potassium permanganate were added, and the solution allowed to cool to room temperature. The digestion solution was filtered and diluted with deionized water to 100 mL. The total Hg content was then measured using a cold vapor atomic absorption spectrometer (CETAC M-6100).

The total concentration of heavy metals, including Cr, Cu, Ni, Pb, and Zn, was determined following the aqua regia digestion method (NIEA S321.63B). Soil of 3 g sieved with a standard 100-mesh (0.15 mm) screen was placed into a 100-mL beaker. The beaker was covered with a watch glass and stayed for 16 h after 21 mL of HCl and 7 mL of HNO_3 were slowly added. The beaker was then put on a hot plate and boiled for 2 h. The digestion solution was filtered and diluted with deionized water to 100 mL after 10 mL of 10% HNO_3 was added. The total concentrations of heavy metals were measured using a flame atomic absorption spectrometer (FAAS, Hitachi Z-2300).

2.4. Thermogravimetric analysis (TGA) and bench-scale fixed-bed thermal treatment

Thermogravimetric data of soil samples were obtained using a thermobalance (Thermo Cahn TG-2121). Approximately 20 mg of soil aliquot was placed in an open platinum crucible, hung in the furnace, and precisely weighted with the thermobalance. TGA was then performed from room temperature to 900 °C at a N_2 flow of 90 N cm^3 min^{-1} and a heating rate of 5 °C min^{-1}.

According to the results obtained from TGA, the bench-scale thermal decontamination of soil samples was carried out. Approximately 10 g of soil was placed in a vertical stainless-steel fixed-bed tubular reactor and thermally treated at various temperature and duration. The reactor tube has a 25-mm id. The experiments were operated at a N_2 flow rate of 60 N cm^3 min^{-1} and a heating rate of 5 °C min^{-1}.

2.5. SEP

Even though the method does not precisely distinguish the species of heavy metals, the results from SEP have been extensively used to implicate the mobility and bioavailability of heavy metals in soils (Bacon and Davidson, 2008). The fractionation of metals in soils, including Cr, Cu, Ni, Pb, and Zn, was operationally defined according to Tessier et al. (1979) using various extractants. The metal was fractionated into (i) exchangeable, (ii) carbonate, (iii) Fe/Mn oxide bound, (iv) organic-matter bound, and (v) residual fraction. Aqua regia, instead of $HClO_4$/HF suggested by Tessier et al. (1979), was used as the extractant to determine the residual fraction. Three replicated samples were measured in all cases. The metal concentration in each solution was determined by the aforementioned FAAS. Because the concentrations of metals in soils B and C were below the regulation values of Taiwan EPA, only soil A were analyzed with the SEP.

The fractionation of Hg was determined according to Neculita et al. (2005), with modification that potassium permanganate digestion was used to determine the residual fraction.

3. Results and discussion

3.1. Basic properties of soil samples

The soils sampled from three contaminated sites showed variation in their properties (Table 1). Soil A was sampled from a site