Research article

Subcritical water treatment of explosive and heavy metals co-contaminated soil: Removal of the explosive, and immobilization and risk assessment of heavy metals

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ABSTRACT

Co-contamination of explosives and heavy metals (HMs) in soil, particularly army shooting range soil, has received increasing environmental concern due to toxicity and risks to ecological systems. In this study, a subcritical water (SCW) extraction process was used to remediate the explosives-plus-HMs-co-contaminated soil. A quantitative evaluation of explosives in the treated soil, compared with untreated soil, was applied to assess explosive removal. The immobilization of HMs was assessed by toxicity characteristic leaching procedure tests, and by investigating the migration of HMs fractions. The environmental risk of HMs in the soil residue was assessed according to the risk assessment code (RAC) and ecological risk indices (E_r and RI). The results indicated that SCW treatment could eliminate the explosives, >99%, during the remediation, while the HM was effectively immobilized. The effect of water temperature on reducing the explosives and the risk of HMs in soil was observed. A marked increase in the non-bioavailable concentration of each HM was observed, and the leaching rate of HMs was decreased by 70–97% after SCW treatment at 250 °C, showing the effective immobilization of HMs. According to the RAC or RI, each tested HM showed no or low risk to the environment after treatment.

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1. Introduction

Heavy metals (HMs) contamination of soil is a worldwide problem, especially at many military active sites, and more specifically at shooting ranges. There are more than 3000 active small arms firing ranges in the USA and approximately 1400 are distributed in the Republic of Korea (Moon et al., 2013). In Korea, shooting range sites throughout the country are associated with the lead (Pb) deposition of 267 tons annually (Ahmad et al., 2014). Army firing range soils are contaminated with mainly Pb, due to the bullets and their fragments, along with antimony (Sb), arsenic (As), copper (Cu), nickel (Ni), zinc (Zn), and silver (Ag). In Pb bullets, metallic Pb comprises 95–97% of the weight, with Sb contributing 0.4–2%, and Sn, Se, Mn, Cd, Cr, Cu, and Ni having average concentrations >30 mg/kg (Cao et al., 2003; Yin et al., 2010). After weathering, Pb bullets are composed mostly of $PbCO_3$ and $PbCO_3(OH)_2$ (Yin et al., 2010), which may increase the Pb availability in the environment and pose a risk to ecological systems (Migliorini et al., 2004; Yin et al., 2010). Furthermore, the use of explosives in military operations has resulted in soil pollution with explosive-HMs co-contamination, posing ecological and health hazard. 2,4,6-Trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) are common contaminants around active military firing ranges (Wang et al., 2012).

The development of explosive-HMs co-contaminated soil remediation technology is of great interest. The objective of such remediation technologies is to extract/degrade organic explosives together with immobilization of the HMs in the soil. HMs immobilization has been used widely in soil remediation (Ahmad et al., 2012a; Houben et al., 2012; Jiang et al., 2012; Moon et al., 2013; Ok et al., 2011; Puga et al., 2015; Uchimiya et al., 2010). Subcritical water (SCW) extraction treatment could be an effective remediation technique for this purpose.

The primary mechanisms of explosives removal by SCW are similar to those of other extraction methods using organic solvents because the water can become such a solvent under subcritical conditions, offering a unique opportunity for solubilization and

separation (Islam et al., 2014b). Also, under subcritical conditions ($100 \leq T \leq 374$ °C and <22.1 MPa), concentrations of H^+ and OH^- are greatly increased by the self-ionization of water molecules (Kuhlmann et al., 1994; Oh et al., 2011). Accordingly, it is hypothesized that SCW can also effectively oxidize organic explosive compounds, resulting in the degradation and removal of explosives in soil residue. In addition, an increased OH^- ions in SCW could be a factor in metal immobilization by increasing negatively charged sites on soil particles, ion exchange, precipitation of metal oxides, and co-precipitation with carbonates and soil minerals (Ahmad et al., 2012a; Ok et al., 2011). Elevated OH^- could also induce the solubilization of Al and Si from clay, and they are then available to form cementitious hydrates such as calcium aluminum hydrate (CAH) and calcium silicate hydrate (CSH) (Gougar et al., 1996). Furthermore, the decomposition of the carbonate form of alkaline earth metals, leading to the formation of metals oxides, which are much less prone to leaching, resulting in the immobilization of HMs in the soil. In the case of Pb, metallic Pb after oxidation leads to the formation of insoluble PbO (Yin et al., 2010).

$$2\ Pb(s) + O_2 \rightarrow 2PbO(s)$$
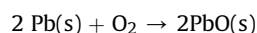
Recently, sub- and super-critical water technology had been shown to positively stabilize HMs in soil/sludge residue (Chen et al., 2014; Huang et al., 2011; Leng et al., 2014; Li et al., 2012; Shi et al., 2013a, 2013b; Yuan et al., 2015; Zhai et al., 2014). The mobile and easily available HM fractions (acid soluble, exchangeable, and reducible fractions) were mainly transformed into relatively stable forms (oxidizable and residual fractions) after hydrothermal treatment, resulting in the immobilization of HM, decreasing their direct toxicity, and therefore significantly reducing the environmental risk. Devi and Saroha (2014) reported that the increasing temperature in hydrothermal treatment of pulp/paper sludge enhanced the stabilization of HMs in bio-char and the potential risk of HM pollution from the biochar was reduced significantly. Similar observations have been reported in the literature (Shi et al., 2013a; Zhai et al., 2014). Moreover, over the last several years, attempts have been made to use SCW to extract or decompose polycyclic aromatic hydrocarbons, pesticides, polychlorinated biphenyls, and other organic contaminants in soils (Chang et al., 2011; Hashimoto et al., 2004; Islam et al., 2014a, 2013, 2014b; Kirmizakis et al., 2014; Lagadec et al., 2000; Yang et al., 1995).

In the previous study (Islam et al., 2015), the lab-scale destruction of TNT and RDX on contaminated soil using SCW, was studied. Although SCW extraction treatment has been proved to destruct explosives individually, as far as TNT-RDX-HMs co-contamination is concerned, this study examines simultaneous degradation of explosives (TNT and RDX) and the immobilization of HMs at different experimental conditions. So far, this SCW extraction treatment has not been applied to TNT-RDX-HMs co-contaminated soil.

The main objectives of this study are to assess the removal of explosives in co-contaminated soil and to assess the immobilization of HMs by examining the leachability, analyzing the fractional transformation, and evaluating the eco-toxicity and bioavailability of HMs.

2. Materials and methods

2.1. Co-contaminated soil

Soil was collected from a military site in Korea where the explosives concentration was low. Thus, the soil was spiked using a spiking solution (solvent) containing explosives (TNT and RDX), followed by a mixing process using a rotating mixture to get

contaminated soil. The detailed steps were presented in a previous report (Islam et al., 2015). The soil sample was air dried and sieved using a 20-mesh sieve. The soil sample was then kept at room temperature, and prior to the experimental study, soil was aged for about three months. Selected physicochemical properties of the soil and the levels of HMs and spiked explosives concentrations were measured (Table 1).

2.2. Subcritical water extraction procedure

The decontamination experiment on the soil was carried out in a laboratory-scale SCW extractor, with deionized water as the only solvent. Fig. 1 depicts the apparatus, which was also described in the previous work (Islam et al., 2013, 2014b, 2015). The extraction apparatus consists of a high pressure pump, a pre-heater, an extraction cell surrounded by a thermocouple-controlled heating furnace, a digital pressure gage, a cooling system, and a back pressure regulator. The water temperature of the system was monitored by a thermocouple introduced in the stainless steel tubing, with a T-fitting at the outlet of the pre-heating unit, and at the outlet of the extraction cell. The cooling system consisted mainly of a hollow cylinder, with tubing, in which cold water was circulated.

The extraction cell was loaded with 12 g of co-contaminated soil, capped with stainless steel micro-filter (0.5 μm), and was then placed into the heating chamber. After assembling the apparatus, distilled water was delivered by the pump to the preheating section at 1.0 mL/min. Then, it was passed through the extraction vessel preloaded with the soil. After the extraction cell, the mixed water/analyte passed through the cooling system, and was then collected in a glass vial. The extraction experiment was carried out for 1 h at 150, 200, and 250 °C, and accordingly, the pressure of the reactor was maintained at the vapor pressure of steam at those temperatures, were 0.48, 1.52, and 3.95 MPa, respectively. Continuous flowing SCW has been considered to avoid the repartitioning of contaminants to the soil upon cooling, which usually occurs in a non-flowing SCW extraction system. After the water extractions were complete, pumping and heating were stopped, pressure was released to the atmosphere, and the reactor was left to cool. The extracted soil was then collected to determine the residual concentration of explosives and HMs. Each experiment was performed in duplicate and the average value was used in this study.

2.3. Analysis

The pH was measured at a 1:5 soil/water solution ratio and the soil particle size distribution was measured using the micropipette method (Miller and Miller, 1987). Soil organic matter (SOM) content was calculated from measured loss-on-ignition (Ok et al., 2007). In terms of explosives concentration determinations in soil and process effluent water, samples from each extraction experiment were analyzed using USEPA method 8330, and following the methodology described by Hawthorne et al. (2000). Briefly, the soil sample was diluted with 30 mL of acetonitrile, and extracted by sonication for 18 h. Extracts were stored at 4 °C, until analysis by HPLC, with UV detection at 245 nm, with solvent programming and a water/acetonitrile (50:50) mixture. All analyses were conducted with a Waters HPLC (model 2787), equipped with a C-18 HPLC column. Peak identification and quantification were based on known standard compounds.

The sequential extraction procedure proposed by Tessier et al. (1979) was used to analyze the speciation of Cd, Cu, Pb, and Zn in soil samples, presented in sequence as exchangeable metals (F1), metal bound to carbonate (F2), metals associated with Fe/Mn oxides (F3), fraction bound to organics (F4), and metals in the residue