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Assessment of soil washing for both heavy metals and petroleum contaminated soils using various washing solutions

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Abstract

Bench-scale soil washing experiments were conducted to remove both heavy metals (Pb, Cu, Zn) and petroleum from contaminated soils. Diverse washing solutions including hydrochloric acid (HCl), nitric acid (HNO₃), sulfuric acid (H₂SO₄), tartaric acid (C₄H₆O₆) and ethylenediaminetetraacetic acid (C₁₀H₁₆N₂O₈, EDTA) were used. The concentration of the washing solutions used in this study ranged from 0.1 M to 3 M with a liquid to solid ratio of 10. The soil washing results showed that hydrochloric acid (HCl) was the best washing solution at 3M for heavy metals removal. Other washing solutions also showed a significant removal of heavy metals, except for sulfuric acid (H₂SO₄). Sulfuric acid (H₂SO₄) had the worst performance of all the washing solutions with respect to removing Pb. 1M HCl and HNO₃ were sufficient for effective Pb and Cu removal and all of the tested washing solutions at a concentration of 0.1 M were able to pass the Korean warning standard for Zn removal. In the case of TPH removal, tartaric acid (C₄H₆O₆) was the best washing solution for the removal of TPH from contaminated soil. Overall, tartaric acid (C₄H₆O₆) could be a viable washing solution for the removal of both heavy metals (Pb, Cu, Zn) and TPH from contaminated soils.

Keywords soil washing, heavy metals, petroleum, hydrochloric acid, tartaric acid, TPH

Introduction

The railroad is well known as an eco-friendly transportation system. But, for the past few decades, there has been many incidents of contamination at railway facility sites. Industrial and municipal solid wastes that were produced as a by-product to maintain and fix trains were dumped at underground railroad depot areas. The Yongsan railroad depot located in Seoul, the Republic of Korea, was established in 1905 and was used until 1980s. Heavy metal and petroleum are the main contaminants at the site. The total amount of contamination is approximately 692,973 m². Specifically, the amount of heavy metal contamination is estimated to be 134,861 m² while the amount of petroleum contamination is estimated to be 148,223 m². The amount of both heavy metal and petroleum contaminated soil is estimated to be 21,163 m². Remedial action was taken to clean the soil at the site.

There are various remediation techniques that are available at this time. However, current soil environment laws in the Republic of Korea are based on source reduction instead of risk reduction. Specifically, aqua regia extraction is used to evaluate the effectiveness of the remediation process for heavy metal contaminated soils. Therefore, among various remediation techniques such as phytoremediation, electro kinetics, stabilization/solidification, soil washing, thermal desorption, land farming, soil vapour extraction, etc., soil washing is the most viable technology to remove both heavy metals and petroleum in contaminated soil. In terms of the effectiveness of the soil washing process, the selection of the type of washing solution is the most important factor and it depends on the target contaminants, the bonding/chelating strength of the extraction solution, and the soil characteristics [2].

An intensive study focused on a single type of contaminant (i.e., either heavy metal or organic contaminants). For instance, Moutsatsou et al. (2006) studied washing of a soil heavily contaminated by mining and metallurgical activities. They reported that hydrochloric acid showed a high extraction efficiency for heavy metals and metalloids (Pb, As, Cu, Zn, Mn and Fe). Ko et al (2006) reported that similar extraction results were obtained for Zn and Ni (cationic) removal with HCl, H₂SO₄ and H₃PO₄. Also they reported that the As (anionic) extraction rate was higher for H₂SO₄ and H₃PO₄ as compared to HCl, due to competitive oxyanions (PO₄³⁻ or SO₄²⁻). Moon et al (2012) reported that the soil washing effectiveness on Zn contaminated soil using various washing solutions and HCl was the best washing solution option to remove Zn from the contaminated soil.

Paterson et al. (1999) used five different surfactants (P103, P105, F108, Triton X 100, Tween 20) in soil washing experiments and these treatments were effective for the extraction of polycyclic aromatic hydrocarbons.

Moreover, Madadian et al. (2014) tested two different surfactants (Triton X 100, Brij 35) for the removal of polycyclic aromatic hydrocarbons in contaminated soil with effective soil washing results (the biggest removal of total PAH was 81.66%).

Only limited studies are available regarding the two different coexisting types of contaminants. Zhang et al. (2007) used ethylenediaminetetraacetic acid (EDTA) and sodium dodecyl sulfate (SDS) enhanced washing for Pb and marine diesel fuel contaminated soil. They reported that multi-stage washing with a solution of low concentration EDTA and SDS may be recommended when the concurrent serious heavy metal and MDF contamination is present. Moreover, as for the optimal washing sequence, EDTA soil washing followed by SDS addition achieved the highest Pb removal efficiency, while SDS soil washing followed by EDTA addition achieved the highest MDF removal efficiency (Zhang et al., 2007). Khodadoust et al. (2005) evaluated different extraction agents for the removal of phenanthrene and heavy metal (Pb and Zn) from a contaminated soil. They reported that the sequential use of 0.2M EDTA followed by 5% Tween 80 or 5% Tween 80 followed by 1M citric acid was found to be effective for the removal of both heavy metals and phenanthrene.

In this study, various washing solutions such as hydrochloric acid (HCl), nitric acid (HNO₃), sulfuric acid (H₂SO₄), tartaric acid (C₄H₆O₆) and ethylenediaminetetraacetic acid (EDTA) were used to remove both petroleum and heavy metals (Pb, Cu and Zn) in a contaminated soil. These washing solutions were demonstrated for heavy metal removal in a contaminated soil but they were not applied to petroleum contaminated soil because it is considered less effective as compared to surfactants. Therefore, it is worth investigating the effectiveness of TPH removal in both heavy metal and petroleum contaminated soil using the aforementioned washing solutions. The effectiveness of the washing process was evaluated by measuring the residual heavy metals (Pb, Cu and Zn) and TPH concentrations after the washing process. The residual Pb, Cu, Zn and TPH concentrations were compared to the Korean warning standard of 200 mg/kg, 150 mg/kg, 300 mg/kg and 500 mg/kg for residential area (area 1), respectively. The purpose of this study was to evaluate the treatment performance of various soil washing for the remediation of both heavy metal and petroleum contaminated soil. Also, optimum soil washing conditions were investigated.

Experimental methodology

Contaminated soil

The heavy metal and petroleum contaminated site is located at the Yongsan railroad depot in Seoul City, Republic of Korea. The contaminated soil samples were collected from the site at a depth of 0~30 cm from the soil surface. The soil was then air-dried and passed through a #10 mesh (2mm) to remove the large particles such as cobbles and gravel.

Soil washing process

Reagent grade hydrochloric acid (HCl), nitric acid (HNO₃), sulfuric acid (H₂SO₄, SA), tartaric acid (C₄H₆O₆, TA) and ethylenediaminetetraacetic acid (C₁₀H₁₆N₂O₈, EDTA) were used as extraction agents. These washing solutions are widely used for the removal of heavy metals. Moreover, these washing solutions were also used for petroleum removal since no studies have been reported which indicate that they are not effective. The concentration of the washing solutions was varied from 0.1 M to 3 M. The washing process was performed with 5 g of soil mixed with 50 mL of washing solution in a 125 mL plastic bottle. The suspensions were then shaken at 200 RPM for 1 hour at 20°C in a shaking incubator (LabTech, Daihan, Republic of Korea). Following the shaking process, the suspended solids were separated by filtration with a 0.45-μm micropore filter and air-dried. After the washing process, the Pb, Cu, Zn and TPH concentrations in the soil were measured based on the Korean Standard Test methods and compared to the Korean warning standards for a residential area [5].

Physicochemical analyses

The contaminated soil was characterized using a particle size analyzer (PSA) in accordance with the United States Department of Agriculture (USDA). The soil pH was measured in accordance with ASTM method D 4980-89. The bulk chemistry of the contaminated soil was measured using X-ray fluorescence (XRF, ZSX100e, Rigaku, Japan). The total Pb, Cu and Zn concentrations in the contaminated soil were obtained by total digestion using a 3:1 HCl/HNO₃ solution. The soluble Pb, Cu and Zn concentrations were analyzed using an inductively coupled plasma-optical emission spectrometer (ICP-OES, Optima 7000DV) (PerkinElmer, CT, USA).

The TPH concentration in the contaminated soil was determined in accordance with the Korean Standard Test Method: 10 g of soil was mixed with anhydrous sodium sulfate in a beaker and 100 mL of dichloromethane was added to the mixed material. The soil was then ultrasonically extracted twice for 3 min each time. The extract was then filtered using 5B filter paper and the extractant was concentrated using a rotary evaporator

until 2mL of solution was obtained. The TPH concentration in the final solution was analyzed using gas chromatography fitted with a flame ionization detector (HP-6890, Agilent Tech., USA).

Sample analyses were conducted in duplicate or in triplicate, and the average values were reported. The average values were reported only if the individual measurements were within an error range of 10 %. For QA/QC purposes, two quality control standards and matrix spikes were used to validate the accuracy and performance of the equipment.

X-ray diffraction (XRD) analysis

In order to obtain the mineralogical information for the contaminated soil, XRD analysis was performed. The sample was air-dried and hand-pulverized to pass through a #200 sieve. A step-scanned XRD pattern was collected using a PANalytical XRD instrument (X'Pert PRO MPD). The XRD analysis was conducted at 40 kV and 30 mA using a diffracted beam graphite-monochromator with Cu radiation. The XRD pattern was collected in the 2θ range of 5° - 65° with a step size of 0.02° and a count time of 3 s per step. The Jade software version 7.1 (MDI 2005) and the powder diffraction file (PDF)-2 reference database from the international center for diffraction database (ICDD) (ICDD 2002) were used in order to qualify the XRD pattern.

Results and discussion

Characterization of contaminated soil

The physicochemical properties of the contaminated soil are presented in Table 1. Specifically, the soil pH was determined to be 6.62 and the contaminated soil was classified as loamy sand (Table 1). The soil was composed of 86.4% sand, 5.6% silt and 7.9% clay. The organic matter content was determined to be 0.48% and the CEC value was measured at $11.7 \text{ cmol}^+/\text{kg}$. The total Pb, Cu, Zn and TPH concentrations in the soil were approximately 842 mg/kg, 438 mg/kg, 375 mg/kg and 200 mg/kg, respectively. The mineralogical information obtained from XRD analysis is presented in Table 1. Quartz (SiO_2 , PDF# 46-1045), calcite (CaCO_3 , PDF# 05-0586), albite [(Na, Ca)Al(Si, Al) $_3\text{O}_8$, PDF# 41-1480], microcline (KAlSi_3O_8 , PDF# 19-0932) and muscovite-1M [$\text{KA}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$, PDF# 07-0025] were the main phases identified in the contaminated soil. The bulk chemistry of contaminated soil was provided in Table 2.

Soil washing

The soil washing results are presented in Figures 1 through 4. The soil washing results using DI water were reported in order to compare the washing results from various washing solutions. Soil washing using DI water can expose the metal fraction that is weakly bound to the soil particles or sorbed on the outer surfaces of soil particles (Mann, 1999). The maximum removal of heavy metals from contaminated soil using DI water was 3.2% for Pb and the TPH extraction rate was less than 2.5%. The removal effectiveness of heavy metals and TPH depends on how strongly the contaminants are bound to the soil particles. In the case of heavy metals, the heavy metals should be associated with the following fractions: ion exchangeable, adsorbed, precipitated, organically bound or trapped in an insoluble form in the soil matrix (Mann, 1999). Moutsatsou et al. (2006) reported that the soil solubility in DI water was below 50 mg/kg and below 1% for all tested metals because the bulk of the metals were very tightly bound to the soil particles.

In the case of Pb removal, soil washing using HCl and HNO₃ showed a significant reduction of Pb removal from contaminated soil (Fig. 1). HCl extraction was better than HNO₃ at high concentrations (> 2M) as compared to extraction of Pb with DI water. Moutsatsou et al. (2006) also reported that Pb extraction with 6M HCl (83%) outperformed Pb extraction with 6M HNO₃ (44%). Pb extraction with HCl and HNO₃ was much better than the extraction results for TA and EDTA. Pb extraction with EDTA up to 0.5M was better than TA but it was limited due to the solubility of EDTA. The soil washing results using H₂SO₄ were not effective as compared to the other washing solutions tested in removing Pb from contaminated soil. H₂SO₄ was the worst case washing solution in this study and the Pb concentrations were virtually unchanged after 1M H₂SO₄ was applied. This may be due to the presence of PbSO₄ in contaminated soil which can be precipitated as an insoluble salt ($K_{sp} \text{ PbSO}_4 = 1.82 \times 10^{-8}$) (Moutsatsou et al. 2006). Similar poor extraction results using H₂SO have been reported for Pb when compared to HCl extraction. In addition, Pb removal increases with increasing washing solution concentrations. Overall, the best Pb removal result was attained with the 3M HCl solution. The Pb concentrations were less than the Korean warning standard of 200 mg/kg for a residential area with 1M HCl and HNO₃ and 3M TA. In the case of EDTA, 0.5M was the maximum concentration applied due to solubility limitations where Pb removal of approximately 63% was obtained and failed to meet the Korean warning standard. The use of H₂SO₄ also failed to meet the Korean warning standard even though 3M was used.

In the case of Cu removal, the most effective washing solution was HCl and the least effective washing

solution was TA (Fig. 2). Cu removal of approximately 91% was obtained with the 3M HCl solution. However, Moutsatsou et al. (2006) reported that only 51% of the Cu was mobilized with 3M HCl due to the precipitation of CuCl_2 . This may not be the case in this study because a high Cu removal rate was attained with the HCl solution. The Cu concentrations were less than the Korean warning standard of 150 mg/kg for residential areas with 1M HCl and HNO_3 and 2M H_2SO_4 . TA failed to meet the Korean warning standard of 150 mg/kg even though a 3M washing solution was used. A Cu removal rate of approximately 55% was obtained with the 3M TA solution. With respect to EDTA, the Cu removal rate was 49% with 0.5M.

In the case of Zn removal, the highest removal of Zn was obtained with 3M HCl and the worst Zn removal rate was attained with TA (Fig. 3). A previous study also showed that the best Zn removal was obtained from HCl extraction (Moon et al. 2012). Zn removal with 2M and 3M H_2SO_4 was better than Zn removal with 2M and 3M HNO_3 . Similar results have been reported by Moutsatsou et al. (2006) that Zn mobilization was highest (97%) with 6M HCl and 6M H_2SO_4 (78%) showed a better mobilization rate as compared to 6M HNO_3 (45%). A washing solution concentration of only 0.1 M was needed in order to pass the Korean warning standard of 300 mg/kg for a residential area because the initial Zn concentration was not that high (375 mg/kg).

In the case of TPH removal, the Korean warning standard for TPH for a residential area is 500 mg/kg. Therefore, the soil studied here is not considered TPH contaminated soil. However, it was worth investigating the washing results using the same solutions studied for heavy metal removal. Strong acids such as HCl, HNO_3 and H_2SO_4 showed limited TPH removal as compared to organic acids such as EDTA and TA. TPH removal achieved the best results using a 3M TA solution which provided a TPH removal of 82.4%. In the case of EDTA, a removal of approximately 39% was obtained with the 0.5M EDTA solution. Choi (2005) reported that TPH removal by an organic acid was not caused by a reduction of surface tension because TPH is a hydrophobic organic compound. The surface tension of strong acids and organic acids was measured using a ITOH interfacial tensiometer (ITOH, Japan) and ranged from 71 to 74 mN/m at 16.9°C which was not significantly different from the surface tension of DI water at 73.1 mN/m. Therefore, the attraction between the acids and TPH molecules may be the main mechanism for TPH removal (Choi 2005).

Conclusions

Both heavy metals (Pb, Cu and Zn) and petroleum contaminated soil was washed with hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4), tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) and ethylenediaminetetraacetic acid

(C₁₀H₁₆N₂O₈, EDTA). The washing solution concentrations ranged from 0.1 to 3M with a liquid to solid ratio of 10. The washing solutions were applied to the contaminated soil in order to examine the removal of Pb, Cu, Zn and TPH. The soil washing results showed that hydrochloric acid was the best washing solution for heavy metal removal while tartaric acid was the best washing solution for TPH removal. Pb removal using H₂SO₄ had the worst Pb removal performance and failed to meet the Korean warning standard. 1M HCl and HNO₃ were sufficient for effective Pb and Cu removal and compliance with the Korean warning standard while washing solutions with concentrations of 0.1 M were necessary for Zn removal. Overall, for the consideration of both heavy metals (Pb, Cu and Zn) and TPH removal, tartaric acid could be a viable washing solution since strong acids failed to provide effective TPH removal. In order to apply specific washing solutions to the contaminated soil, the soil type, type of contaminant, soil mineralogy and concentration, etc. should carefully be considered to obtain effective washing results.

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Table 1 Physicochemical and mineralogical properties and total concentrations of heavy metals and TPH in the soil

Soil properties	Contaminated soil	Korean warning standards ^a
Soil pH	6.62	
Organic matter content (%) ^b	0.48	
Composition (%) ^c		
CEC (cmol ⁺ /kg)	11.7	

Sand	86.4	
Silt	5.6	
Clay	7.9	
Texture ^d	Loamy sand	
Heavy metals and TPH (mg/kg)		200
Pb	842	150
Cu	438	300
Zn	375	500
TPH	200	
	Quartz	
	Calcite	
Mineral compositions ^e	Albite	
	Microcline	
	Muscovite	

^aKorean warning standards for soils in residential areas

^bOrganic matter content (%) was calculated from measured loss-on-ignition (LOI) (Ball 1964, FitzPatrick 1983)

^cSoil classification was conducted using a particle size analyzer (PSA); Sand, 20-2,000 μm ; silt, 2-20 μm ; clay, <2 μm

^dSoil texture as suggested by the United States Department of Agriculture (USDA)

^eMineral compositions were obtained using the Jade software

Table 2 Major chemical composition of contaminated soil

Major chemical properties (wt%)	
SiO ₂	74.2
Al ₂ O ₃	12.7
Na ₂ O	1.44
MgO	0.83
K ₂ O	4.07
CaO	1.39
Fe ₂ O ₃	3.97
SO ₃	0.21
P ₂ O ₅	0.12
Cl	0.02

Fig. 1. Pb concentrations remaining in the soil after DI water, hydrochloric acid (HCl), nitric acid (HNO₃),

sulfuric acid (H_2SO_4), tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$, TTA) and ethylenediaminetetraacetic acid ($\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$, EDTA) washing

Fig. 2. Cu concentrations remaining in the soil after DI water, hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4), tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$, TTA) and ethylenediaminetetraacetic acid ($\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$, EDTA) washing

Fig. 3. Zn concentrations remaining in the soil after DI water, hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4), tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$, TTA) and ethylenediaminetetraacetic acid ($\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$, EDTA) washing

Fig. 4. TPH concentrations remaining in the soil after DI water, hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4), tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$, TTA) and ethylenediaminetetraacetic acid ($\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$, EDTA) washing

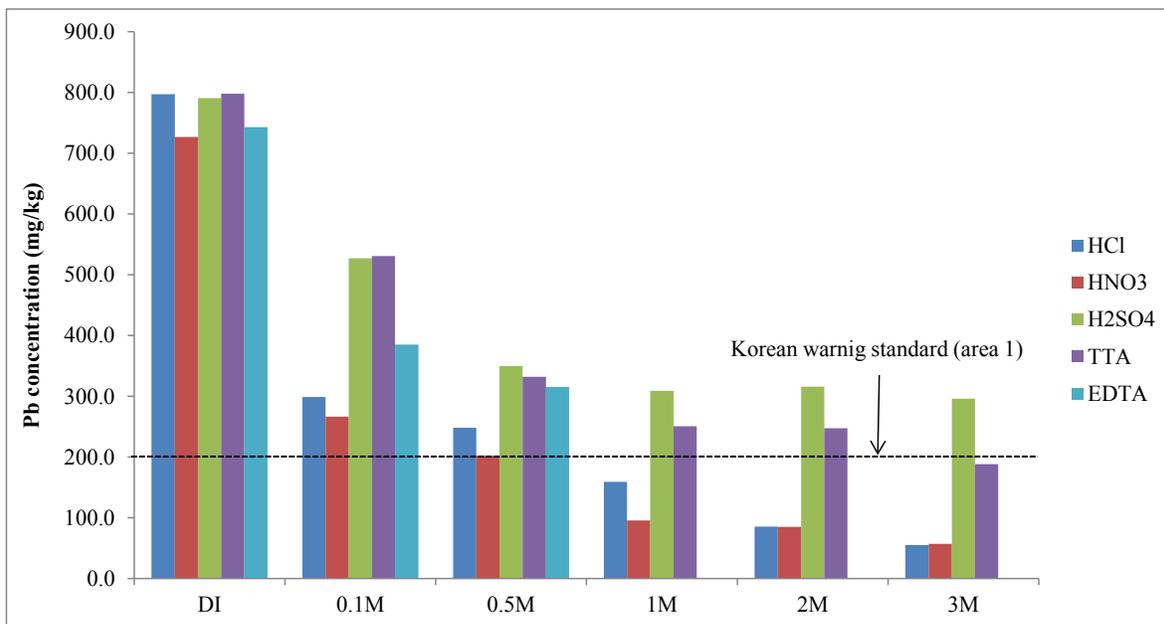


Fig. 2

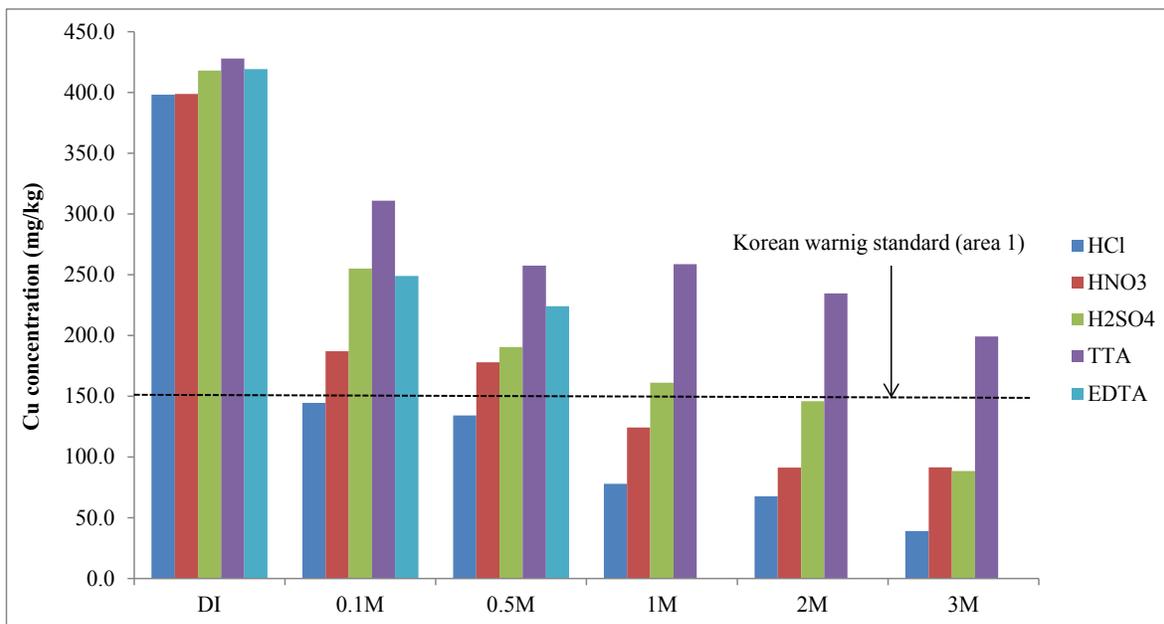


Fig. 3.

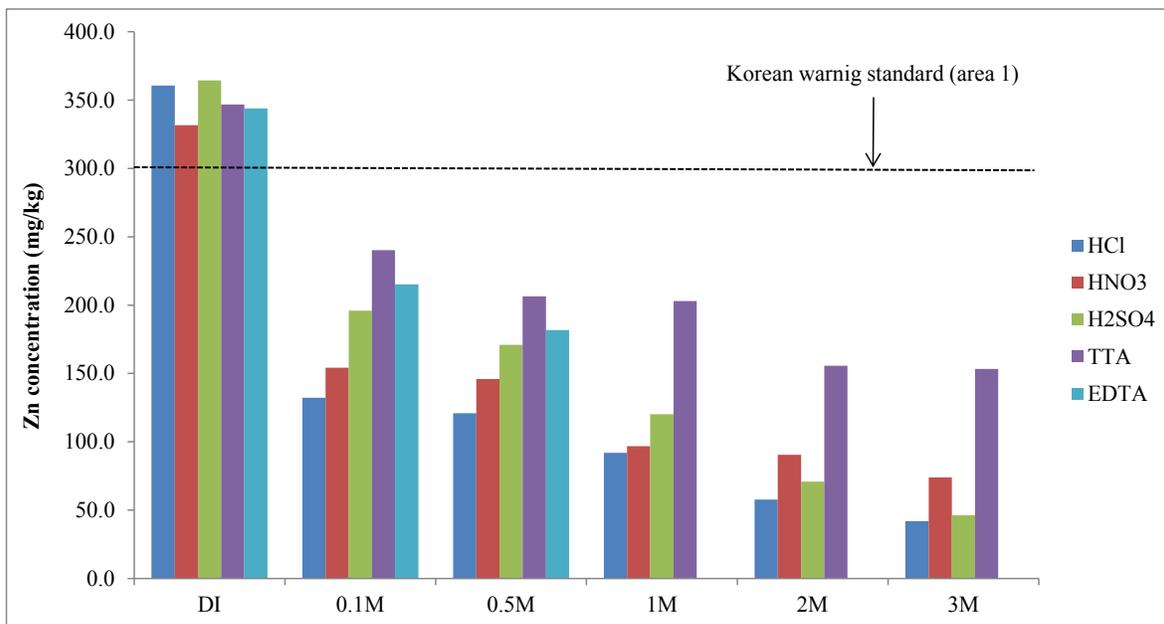


Fig. 4.

