Separation, characterization and leaching behaviors of heavy metals in contaminated river sediments

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Abstract

In this research, the sequential extraction test was conducted to understand the characteristic of heavy metals in the sediment. Subsequently, the pH-dependent leaching test, percolation test were subjected to explore the possible leaching of heavy metals and stabilizing mechanism. Finally, based on the resuts of pH dependent test,the acid/chemical washing were applied to predict long-term, leaching characteristics. The results from the sediment characteristic analyses showed that the concentrations of heavy metals (such as Cu, Pb, Zn, Ni, and Cr) in river sediments exceeded the upper limit of Sediment Quality Standard of Taiwan, implying further decontamination works should be addressed. Results from the chemical washing (extraction) showed that the heavy metal removal efficiency was good when washed with 2N HCl for 120 minutes; the order of removal efficiency was Ni 90% > Zn 87% > Pb 85% > Cu 83% > Cr 70%. For chelation extraction, the suitable operating condition was achieved with 0.5M Citric Acid after 120 minutes contact; the order of heavy metal ion capturing efficiency was Zn 61% > Ni 54% > Pb 40% > Cu 36% > Cr 24%. Comparing the heavy metal bonding types before and after chemical washing (extraction) showed that some metal ions exist in residual forms in the sediments (Ni, Zn, Cu); however, after the washing process, the heavy metal ions became more exchangeable forms with higher bioavailability.

Keywords: sediment, heavy metal, leaching test, chemical washing

1. Introduction

The rapid industrial development and rising populations have resulted in the increase of industrial and agricultural investments in Taiwan, which unfortunately has led to the increasing potential risk of waste contaminated soils and pollution of the major and minor rivers in Taiwan. This not only directly or indirectly influences the natural load-bearing capacity of the environment, but also causes disruption of the ecological balance, dissemination of diseases, lowering of land values, and gravely affects the population's health. The irrigation water quality of certain agricultural regions in Taiwan has been polluted by the waste drainage from up-stream industrial areas or illegal factories. Polluted water is then channeled into farm lands from irrigation ditches, contaminating the soils, and leading to many incidents of agricultural soil contamination in Taiwan.

To investigate the severity of the heavy metal pollution of the farm lands in western Taiwan (Figure 1), the Taiwan Environment Protection Agency (Taiwan EPA) conducted heavy metal tests in the agricultural river irrigation water of Taoyuan, Hsinchu, Taichung and Changhua counties, and found that over 41.3% of sediments are severely contaminated; 13.2% irrigation water quality has exceeded standards, and 18.8% agricultural soil has exceeded standards. Subsequently, the Taiwan EPA formulated an estimate of the total areas of "high pollution potential monitoring points (regions with high risks of heavy metal pollution)"; 78 acres in Luzhu, Taoyuan County; 97 acres in Dali, Taichung; 472 acres of Hemei and Huatan Townships, Changhua County; the total area is 647 acres, with 13 acres residing in areas with highest risks. While the Taiwan EPA has spent hundreds of millions to remediate over 200 acres of cadmium-polluted farm lands in the Changhua County, but there are still metal hardware and electroplating factories that are illegally discharging their poisonous drainages into the irrigation systems. It was estimated that over two hundred acres of farmlands in Hemei and Huatan Townships have been contaminated by heavy metals such as cadmium and nickel, due to prolonged exposure to irrigation water polluted by electroplating and hardware drainage. According to the Taiwan EPA's data (EPA, 2011), there are currently 664 soil and ground water pollution remediation and control sites all over Taiwan, and the majority (82%) are heavy metal polluted; 22% are organic polluted sites, and 2% are both. In all heavy metal polluted sites, the majority are affected by copper and zinc pollution, occupying 50 and 23 percents of the total polluted sites, respectively. The statistics showed that heavy metal pollutants from copper and zinc are responsible for the majority of contaminants in polluted soil and ground water sites in Taiwan.

Figure 1 The map of Taiwan (applied from mypaper.pchome.com.tw (before 2010))

2. Experimental

2.1 Sampling of the contaminated river sediment

The heavy metal containing sediment used in this research came from various sections of an irrigation river from a county (city) in Central Taiwan. After collection, the samples were dried and baked at a high temperature, and then sealed for storage. The samples were rich in organic matters and composed of mixtures of large and fine particles.

2.2 Analysis of the base characteristics of contaminated river sediment

1) Grain diameter distribution

To investigate the grain diameter distribution of the river sediment, the dried samples were screened using different standards of sieving mesh. A 100g of sample was weighted and placed in testing sieves of 5, 50, 100, 230 and 400 mesh, and wet-sieved with a sonicator with a liquid:solid ratio of 1:20. The residual sediments from the screening were baked dry and weighted. The procedures were repeated to obtain a less than 10% variation from each data, and the grain diameter distribution of the sediment was obtained.

2) pH value

The pH value of the heavy metal contaminated river sediment was performed with the hydrogen ion concentration index (pH value) testing method of the EPA (NIEA R208.02C). 20g of contaminated river sediment sample was weighted and placed in a 50ml beaker. 40 ml of reagent was added to the sample, then the glass lid was placed on the beaker and the suspensions was continuously stirred for 5 minutes, and let sit for 15 minutes for most of the solids to deposit on the bottom. The pH value of the liquid phase layer was measured with a pH electrode.

3) Sequential extraction experiment

In this research, a 5-step sequential extraction method is employed to test the five states (exchangeable, carbonate-bound, Fe and Mn oxide-bound, organically bound and residual) of the heavy metal Cu, Cr, Ni, Pb and Mn in the contaminated river sediment, analyzing the solid phase combination states between the metallic elements and the river sediment.

3. Results and Discussion

3.1 Basic Characteristics

To understand the basic characteristics of the river sediments, the grain diameter distribution, heavy metal concentration and surface state were analyzed and quantified as the reference basis for all subsequent steps of the study. The result of the component analysis of the heavy metal contaminated river sediment is shown in Table 1.

Table 1 Component Analysis of the Heavy Metal Contaminated River Sediment

Testing items	Units	Sample No. 1		Sediment Quality Standards of Taiwan	
		Total digested	XRF	Upper limit	Lower limit
Cadmium (Cd)	mg/kg	ND	ND	2.49	0.65
Chromium (Cr)	mg/kg	720	287.6	233	76.0
Copper (Cu)	mg/kg	2980	1257	157	50.0
Nickle (Ni)	mg/kg	1060	430.6	80.0	24.0
Lead (Pb)	mg/kg	286	107.7	161	48.0
Zinc (Zn)	mg/kg	3280	1276	384	140
Mercury (Hg)	mg/kg	ND	ND	0.87	0.23
pH value		5.92			

The results showed that the heavy metal concentrations in sample no.1 have all exceeded the upper limit set by the control standards of the river sediment. Looking at the heavy metal concentration by grain diameters of each layer of sediment (Table 2), it was clear that the heavy metal concentration distributions across coarse and fine grains were consistent and all have exceeded the control standards. Future investigation on the coarse and fine grains is warranted.

3.2 Acidic-washing processing

10 g of heavy metal contaminated sediment samples was measured and added with different concentration of inorganic acids H_2SO_4, HCL and HNO_3. The sediment mixture was then extracted with a rotary extractor. Semi-dynamic leaching tests were conducted with reaction times of 30, 60 and 120 minutes to leach the heavy metals. After the extraction was completed, the mixture was filtered through 0.45μm membrane. The filtrate was collected and placed in an ICP-OES instrument to analyze the containing heavy metal elements. The results were shown as Figure 2.

Table 2 Heavy metal concentration in various grain diameters of sample No.1

		Heavy metal concentration (mg/kg)					
		Cd	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
>300 μm		ND	740	3920	802	412	1744
150-300 μm		ND	1076	4396	1156	516	2676
63-150 μm		ND	272	1908	466	304	828
37-63 μm		ND	368	2346	566	348	1172
＜37 μm		ND	770	3222	1048	432	2682
Sediment	**Upper limit**	2.49	233	157	80	161	384
	Lower limit	0.65	76.0	50.0	24.0	48.0	140

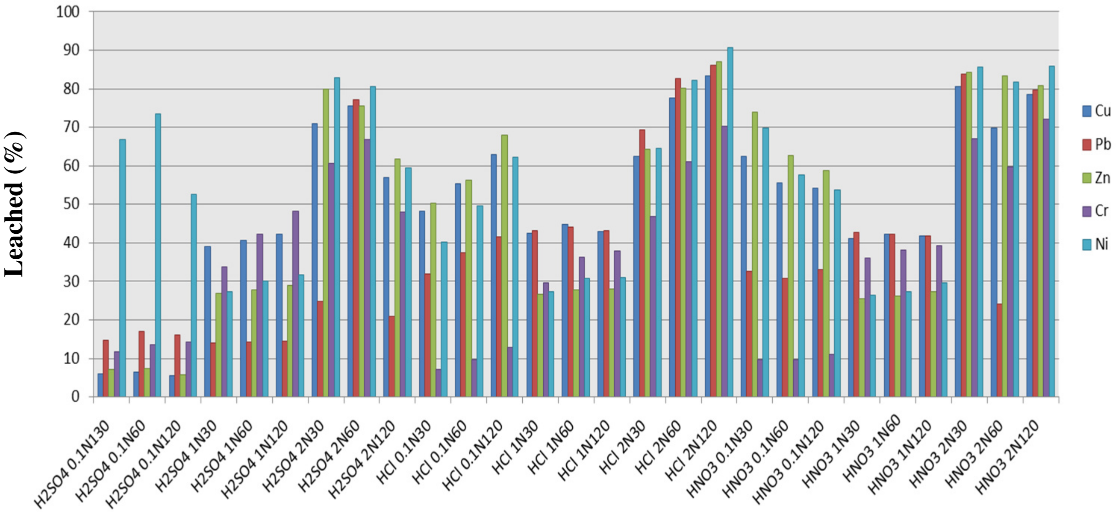

Figure 2 Leaching percentage of heavy metals in sample no.1 under different conditions of acids, concentrations and reaction time

The results have indicated that the effects of acidic washing did not increase with the increases in concentrations and reaction time, and that different heavy metals have different acidic washing results, and vary with different acid types and concentrations. Figure 2 shows that the effects of nitric and hydrochloric acids were better than sulfuric acid; at lower concentrations, Cu, Zn and Ni had better leaching results; the optimal acidic washing conditions of sample no.1 were found to be washing 120 minutes with 2N HCL, which produced Cr(70.18%), Cu (83.32%), Ni (90.74), Pb (85.98%) and Zn (87.07%).

3.3 Extraction processing

In this step, 10 g of the heavy metal contaminated sediment samples was added with different concentrations of citric acid, malic acid and EDTA. The sediment mixture was then extracted with a rotary extractor. Semi-dynamic leaching tests were conducted with reaction times of 30, 60 and 120 minutes to leach the heavy metals. After the extraction was completed, the mixture was filtered through 0.45μm membrane. The filtrate was collected and placed in an ICP-OES instrument to analyze the containing heavy metal elements (as shown in Figure 3).

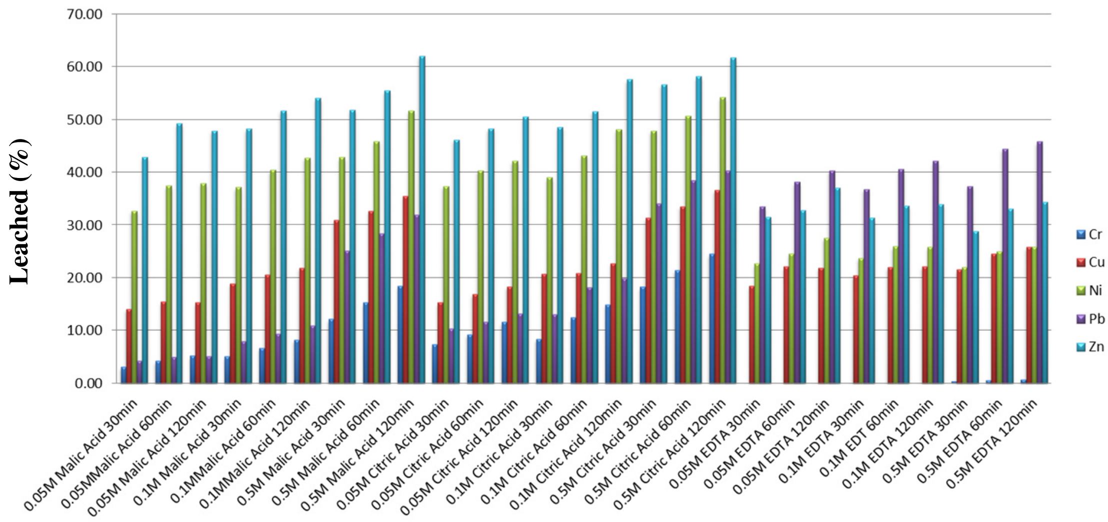

Figure 3 Leaching percentage of heavy metals in sample no.1 under different conditions of extraction agents, concentrations and reaction time.

The test results showed that EDTA had varied extraction efficiency on different heavy metals, which was especially pronounced in organic and residual states (residual and organic heavy metals). The larger the total concentration, the worse the extraction efficiency of EDTA is for that particular soil or heavy metal. The test results of different concentration and reaction times of chelating agents on sample no.1 have shown that the better leaching rate of copper (Cu) was achieved at 120 minutes of 0.5M citric acid (36.69%); for lead (Pb), 0.5M EDTA for 120 minutes (45.83%); for zinc (Zn), 0.5M malic acid for 120 minutes (62.1%).

4. Conclusions

1. The heavy metal concentrations in sample no.1 have all exceeded the upper limit set by the control standards of the river sediment.
2. The effects of acidic washing did not increase with the increases in concentrations and reaction time. Results showed that the effects of nitric and hydrochloric acids were better than sulfuric acid. The optimal acidic washing conditions of sample no.1 were found to be washing 120 minutes with 2N HCL, which produced Cr(70.18%), Cu (83.32%), Ni (90.74), Pb (85.98%) and Zn (87.07%).
3. The results of different concentration and reaction times of chelating agents on sample no.1 have shown that the better leaching rate of copper (Cu) was achieved at 120 minutes of 0.5M citric acid (36.69%); for lead (Pb), 0.5M EDTA for 120 minutes (45.83%); for zinc (Zn), 0.5M malic acid for 120 minutes (62.1%). Thus, acid washing/chelating agent extraction treatments of the river sediment take the potential leached volumes into consideration.

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