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A practical soil washing method for use in a Cd-contaminated paddy field, with simple on-site wastewater treatment

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ABSTRACT

Heavy metal contamination in rice paddies is a serious problem in monsoon Asia, and these fields require appropriate restoration measures. Although soil washing is a promising remediation technology, high cost for the treatment on soil washing leachate (wastewater) is one of the critical problems. This study sought to develop a simple method for the restoration of paddy fields by soil washing, with simplified wastewater treatment. Ferric chloride solution ($FeCl_3$) was used as a washing chemical to extract Cd from a soil, which produced the wastewater containing Cd and other metals. Three alkali materials (NaOH, MgO, and $CaCO_3$) were tested to treat the wastewater and determined MgO is optimal. In an on-site experiment, the target pH for wastewater treatment was controlled between 8 and 9 by using MgO. All metals in the wastewater could be effectively removed, reaching levels substantially lower than those permitted by Japanese standards. The treated wastewater could be discharged to agricultural canal. Therefore, our novel simplified method effectively removed heavy metals from the wastewater produced by on-site soil washing and contribute drive down the cost.

1. Introduction

In some regions in Japan, arable soils, and particularly paddy soils, have been heavily polluted with Cd and various other heavy metals because of the rapid industrialization that occurred during the 1960s. The Japanese government urgently enacted the Agricultural Land Soil Pollution Prevention Law in 1970 to cope with this pollution. Under the law, the As, Cd, and Cu were designated as target hazardous substances to be controlled. In particular, Cd has been recognized as one of the most detrimental elements in Japan because it can cause a serious disease, so called *itai-itai disease*. The 1970 law also designated paddy fields as being polluted by Cd if the unpolished rice grains produced in the fields contained more than 1 mg Cd kg^{-1}. In July 2006, the Codex Alimentarius Commission of the Joint FAO/WHO Food Standards Program proposed that the maximum permissible concentration of Cd in polished rice grains should be set at 0.4 mg Cd kg^{-1} (Codex, 2006). A new Japanese standard was enforced in 2011 to implement this level in rice (MOE, 2011).

Since these laws came into effect, many polluted paddy soils have been remediated, mainly by adding a top dressing of unpolluted soil or by replacing the polluted soil with unpolluted soil (Yamada, 2007). However, these practices have become increasingly difficult to implement because of the high costs (\30,000,000–\60,000,000 ha^{-1}) associated with soil replacement and the difficulties in obtaining uncontaminated soil and storing contaminated soil removed from a site. Therefore, the development of less-costly and more effective technologies to restore Cd-polluted paddy soils has become critical in order to maintain Japan's rice production capacity. Moreover, since approximately 34% to 50% of annual Cd intake by Japanese citizens comes from rice (Kawada and Suzuki, 1998), decreasing the Cd content in paddy soils (and thus in rice grains) is necessary in order to alleviate the risk of ingesting hazardous levels of Cd by ensuring the safety of rice, which is a staple Japanese crop.

Various on-site and off-site remediation methods have been used to restore soils contaminated with heavy metals. Soil washing is particularly effective (Mulligan et al., 2001; Vangronsveld and Cunningham, 1998). However, it is conventionally performed off-site, in treatment plants that use extraction reagents to displace heavy metals from the soil into an aqueous solution (Elliott and Herzig, 1999). Soil washing is one of the few treatment alternatives that can permanently remove metal contaminants from soils (Dermont et al., 2008). Various washing

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chemicals such as metal chelating agents, neutral salts, and strong acids have been applied for metal contaminated soils (Davis, 2000; Li et al., 2015). Especially, ethylenediamine tetraacetic acid (EDTA) has been widely used to efficiently remove Cd from contaminated soils (Abumaizar and Smith, 1999; Zeng et al., 2005). However, EDTA has some problems as it remains in the environment due to its low biodegradability (Tandy et al., 2004). EDTA has shown a high environmental burden and thus, some researchers have selected biodegradable chelating agents (Mulligan et al., 1999; Hong et al., 2002; Tandy et al., 2004; Chang et al., 2005). The biodegradable chelating agents are promising from the viewpoint of their environmental impact. Their costs, however, are relatively high for restoration of Cd-contaminated paddy soils. We previously reported that $FeCl_3$ is a promising soil washing chemical, and verified that it effectively decreased Cd levels in soil and rice grains in a laboratory experiment (Makino et al., 2008).

On the other hand, off-site washing is logistically complicated and expensive. Although on-site soil washing could be a suitable alternative, since paddy fields usually have an impervious hardpan layer that keeps the wash solution in the surface layer, few studies of on-site soil washing have been conducted in paddy fields (Makino et al., 2007). Moreover, because most paddy fields are located in rural areas, wastewater generated during soil washing should be treated on-site rather than exported to a distant site for treatment. Although a treatment system equipped with chelating resin has been developed for washing of wastewater on-site (Makino et al., 2007), the cost was relatively high. Therefore, it is necessary to develop a novel cost-effective, high-efficiency wastewater treatment system.

Common wastewater treatment strategies have been reviewed (Fu and Wang, 2011). The pH regulation, adsorption (Cundy et al., 2008; Lee et al., 2012; Mahdavi et al., 2013), flocculation and sedimentation (Pang et al., 2009), membrane separation and filtration (Gherasim and Mikulášek, 2014; Jung et al., 2008), and ion-exchange methods are used. However, these methods were likely too expensive to be practical, or did not remove sufficient quantities of heavy metals. Some researchers have used adsorbent materials to treat wastewater. For example, sand-immobilized iron-oxide nanoparticles have been used to remove Cu^{2+}, Cd^{2+}, and Pb^{2+} from aqueous solutions under both static and dynamic experimental conditions (Lee et al., 2012). Municipal sewage sludge was modified with iron oxide to remove metal ions such as Cu^{2+}, Cd^{2+}, Ni^{2+}, and Pb^{2+} (Phuengprasop et al., 2011). Nanoparticle sorbents (TiO_2, MgO, and Al_2O_3) have been used to remove Cd^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+} from aqueous solutions, and scanning electron microscopy energy-dispersive X-ray spectroscopy revealed that adsorption and precipitation are the main mechanisms of sorption by heavy metals (Mahdavi et al., 2013). MgO nanoparticles have been suggested as promising sorbents because of their high metal uptake capacity (Mahdavi et al., 2013), and can additionally work as an alkali material, and are less toxic than other adsorbents. The increase in pH in paddy soils caused by MgO addition results in the generation of more negatively charged sorption sites on the soil colloids and on organic matter surfaces (Bolan et al., 2014), leading to increased sorption of metal cations. In addition, increased pH may cause the formation of metal–hydroxide species in association with soil colloids, making this a potentially cost-effective way to treat the wastewater produced by soil washing.

The objectives of the present study were to develop a cost-effective, high-efficiency method to remove heavy metals from soil washing wastewater and to verify the practical effectiveness of the treatment system by means of an on-site trial in a paddy field.

2. Materials and methods

2.1. Description of the experimental field and soil properties

Fig. 1 illustrates the layout of the two paddy fields used for the on-site soil washing experiment, which was conducted in Japan's Fukuoka Prefecture. The source of the Cd contamination was fallout from a metal refinery. An irrigation canal supplied water for the paddy fields. Below the A_p horizon, there was an impermeable hardpan. Because of the hardpan, which is a characteristic of the most paddy fields in Japan, drainage is slow and the water requirement of the paddy field is low, at about 0.5 cm day^{-1}. Soils of the plow layer were sampled at five points each in an experimental paddy used for the washing treatment and in a second paddy used for treatment of the wastewater, and were mixed to produce a single composite sample for each paddy. All samples were air-dried and passed through a 2-mm-mesh sieve before analysis.

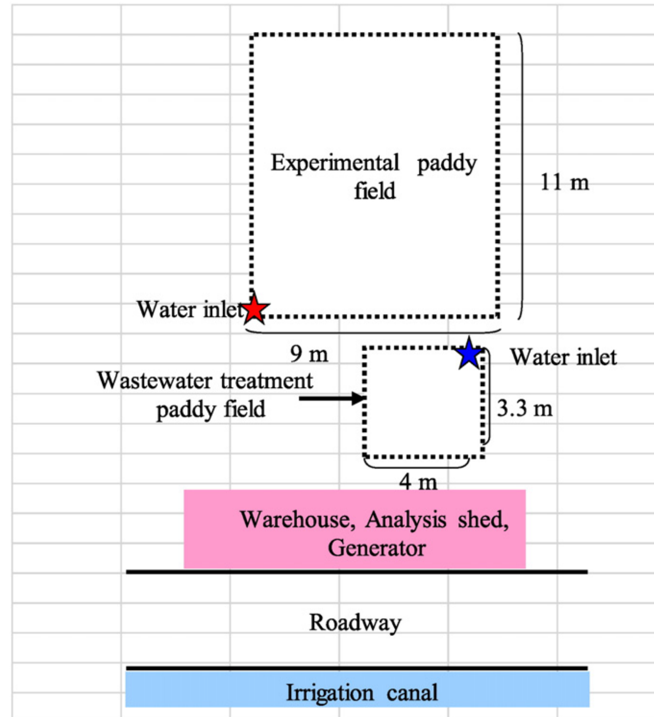

Fig. 1. Schematic representation of an on-site soil washing experiment at the test paddy field.

Table 1 summarizes the most relevant chemical properties of the soil samples collected from the A_p horizon at the experimental site. The soil was classified as a Fluvaquent. X-ray diffraction analysis identified kaolinite, mica, and chlorite in the soil with the soil-clay preparation (Whittig and Allardice, 1986) (JDX-3530, JEOL, Ltd., Tokyo, Japan). The total Cd concentration of the soil was 2.78 mg kg^{-1}, which is substantially higher than the mean values in uncontaminated soils, which average 0.33 mg kg^{-1} in Japan

Table 1
Selected soil properties.

Horizon		Ap
Depth	cm	0–15
pH(H_2O)		5.32
EC	mS cm^{-1}	0.353
[a]TC	g kg^{-1}	43.8
[b]TCd	mg kg^{-1}	2.78
Clay	%	32.3
Silt	%	38.1
Sand	%	29.6
[c]Clay minerals		Kl, Mi, Ch-Vm
Soil type		Fluvaquent

Soil pH (soil: H_2O ratio = 1:2.5) was measured using a pH meter with a glass electrode.
Total carbon ([a]TC) was determined by the dry combustion method.
Total Cd ([b]TCd) content were measured by ICP-OES.
[c] Kl:kaolin minerals, Mi:mica, Ch-Vm:chlolite-Vermicurite intergrade.