ENGINEERING AND ECONOMICAL EVALUATION OF CADMIUM CONTAMINATED PADDY SOIL RESTORATION USING ZEROVALENT IRON PARTICLES AS GREEN SOIL AMELIORANT AND SOIL WASHING AGENT

VINITA KHUM-IN

A Thesis Submitted to the Graduate School of Naresuan University
in Partial Fulfillment of the Requirements
for the Doctor of Philosophy in (Environmental Engineering)
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By VINITA KHUM-IN

has been approved by the Graduate School as partial fulfillment of the requirements for the Doctor of Philosophy in Environmental Engineering of Naresuan University

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Title ENGINEERING AND ECONOMICAL EVALUATION OF CADMIUM CONTAMINATED PADDY SOIL RESTORATION USING ZEROVALENT IRON PARTICLES AS GREEN SOIL AMELIORANT AND SOIL WASHING AGENT

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Academic Paper Thesis Ph.D. in Environmental Engineering, Naresuan University, 2019

Keywords Cadmium soil amendment soil washing electrokinetic solar power zero valent iron biochar paddy soil cost-benefit analysis Monte Carlo simulation community driven

ABSTRACT

This study was conducted to evaluate remediation techniques for Cd contaminated soil in paddy fields in Mae Sot District, Tak Province, and Northwestern Thailand. These areas in important agricultural areas have fields that are contaminated with Cd. Studies have shown that rice samples from these areas contain unsafe levels of Cd and effect on health villagers. It is necessary therefore to find methods to decontaminate these fields. The remediation techniques included using ZVI for Cd immobilization as a soil amendment, separation of contaminated ZVI from the soil by the machine as soil washing on paddy field as pilot-scaled and solar-powered electrokinetic separation in the batch experiment. In addition, the economic decision analysis was assessed to make an appropriate decision on a remedial selection. The pilot-scale experiments on Cd-contaminated paddy restoration performed via magnet-assisted soil washing using zerovalent iron (ZVI) particles and compared soil amendment using biochar, ZVI, and a combination of biochar and ZVI (BZVI) by researchers and community researchers. Magnet-assisted soil washing followed by ZVI amendment (0.5%) successfully reduced the Cd concentration in rice grain to 0.33 mg kg^{-1} to lower than the safety guideline (0.4 mg kg ^{1}) and caused slight stress on rice growth. Therefore, a magnet-assisted soil washing followed by the ZVI amendment (0.5%) is a promising alternative from all compared techniques. An alternative technique to the batch experiment, using ZVI (MZVI, NZVI, and Fe-rod) with the solar-powered electrokinetic separation was evaluated for this Cd contaminated area in the batch experiment. The results revealed the application EK&NZVI with SC can increase the voltage (from 6.61V to 7.38V), decrease the Cd in soil (53.14%-66.31%) and increase the Cd adsorption in NZVI (16.5%-20.66%) more than other iron (MZVI and Fe-iron). The EK&NZVI with SC is also able to reduce the exchangeable CD form and increase Fe-Mn oxide and residual forms especially Fe-Mn oxide. Therefore, using EK&NZVI with SC is the best for Cd reduction and Cd movement to the cathode region when compared to MZVI and Fe-iron.

However, techniques (biochar amendment, soil washing and electrokinetic) were assessed with the integrated economic decision analysis. The decision analysis will make an appropriate decision on a remedial selection with maximum social benefit. Alternative techniques were compared with phytoremediation and other risk assessments and management activities in the past and using Monte Carlo Simulation to predict the health costs of a villager living an area where there are contamination problems. This result indicates that the highest cost is in non-remediation and the only risk assessment and management by the Thai government around 3.6 million-baht rai^{-1} year^{-1}, which was derived from health costs. While the alternative restoration costs present lower costs due to the reduction of the health costs of villagers and imply that in that area, they should apply the alternative restoration methods for reducing contamination and adverse health effects. This study recommends applying soil washing for Cd contamination in agricultural soil in the Mae Sot District, Tak Province in Thailand at an approximate cost of 1,404-baht rai-1 over 2 years.

ACKNOWLEDGEMENTS

The success of this research can be attributed to extensive support and assistance from my major advisor, Associate Professor Tanapon Phenrat. I deeply appreciate him for his valuable guidance, informative discussions, and encouragement during this thesis.

I am extremely grateful to my Co-advisor, Associate Professor Sampan Nettayanun for warm and useful advice about my thesis.

I am extremely grateful to my internal examiners, Associate Professor Pajaree Thongsanit and Dr. Wisa Supunpaibul, and my external examiner, Dr. Peerapat Kosolsaksakul for their suggestions and useful comments.

I am deeply thankful to all my relatives, my research teams and community research, especially Yarnnapat Praimeesub for all their support, suggestions and help.

I would like to specially thank the Department of Civil Engineering, The Engineering faculty, Naresuan University for all the necessary equipment, laboratory facilities and help.

I am thankful to the National Research Council of Thailand and the Office of Higher Education Commission (OHEC) and the Research Program of Toxic Substance Management in the Mining Industry, Center of Excellence on Hazardous Substance Management (HSM), Chulalongkorn University, Thailand for the financial support for this project.

Finally, I would like to express my deepest appreciation to my family for their support, love, and encouragement. They gave to me throughout the time of my study.

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ABBREVIATIONS

Cd	Cadmium	Fe	Iron
Zn	Zinc	EU	European Union
EPA	Environmental Protection Agency	WHO	World Health Organization
USDA	United States Department of Agriculture	FAO	Food and Agriculture Organization
PCD	Pollution Control Department	IWMI	International Water Management Institute
LDD	Land Development Department	PDI	Padaeng Industry
DPIM	Department of Primary Industries and Mines	DOA	Department of Agriculture
CUP	Contracting Unit for Primary Care	DOAE	Department of Agriculture Extension
MOAC	Ministry of Agriculture and Cooperatives	MOE	Ministry of Education
CE	Control experiment	SEM	Scanning electron microscope
ZVI	Zero Valent Iron	XRD	X-ray diffraction
BZVI	ZVI and biochar	VSM	Vibrational sample magnetometer
NZVI, nZVI	Nano zero valent iron	BET	Brunauer Emmett Teller
MZVI	Micro zero valent iron	FTIR	Fourier-transform infrared spectroscopy
Fe-Rod	Iron rod	AAS	Atomic absorption spectroscopy
CEC	Cation exchange capacity	OC	Organic carbon
OM	Organic matter	DI	Deionized
EK	Electrokinetic	SC	Solar Cell
V	Volt	EC	Electrical conductivity
ORP	Oxidation-reduction potential	GI	Germination index
µg day^{-1}	Microgram per day	rpm	Revolutions per minute
mol L^{-1}	Mole per liter	RfDs	Reference doses

V cm^{-1}	Volt per Centimeter	CKD	Chronic Kidney Diseases
mg	Milligram	EF	Enrichment factor
kg	Kilogram	TF	Translocation factor
g	Gram	CBA	Cost-Benefit Analysis
g kg^{-1}	Gram per kilogram	MCS	Monte Carlo Simulation
mg kg^{-1}	Milligram per kilogram	NPV	Net present value
m^{3}	Cubic meter	NBPV	Net benefit present value
m	Meter	PV	Present value
hrs, h	Hour	CI	Confidence Interval
cm	Centimeter	CPI	Core consumer price index
°C	Degree Celsius	IR	Intake rate
mm	Millimeter	BW	Body weight
mL	Milliliter	PTWI	Provisional tolerable weekly intake
kg rai^{-1}	Kilogram per rai	M	Mass
baht kg^{-1}	Baht per kilogram	ton rai^{-1}	Ton per rai
baht ton^{-1}	Baht per ton	µg g^{-1}	Microgram per gram

CHAPTER I

INTRODUCTION

Introduction

Cadmium (Cd) contamination of soils especially, paddy soils, which come from anthropogenic processes such as, fertilizers, mine or biosolids, are an accumulation problem for the production of food for people and animals. This problem occurs around cities worldwide, particularly in Asia. In Asia the Cd content of rice grain grown in metal-contaminated paddy soils near abandoned metal mines in South Korea was found to exceed the safety guidelines (0.2 mg Cd kg^{-1}) set by the Korean Food and Drug Administration (KFDA) (Ok et al., 2011). Several cities in Southern China have Cd-contaminated rice from extensive metal contamination of paddies with the rapid expansion of nonferrous metal mining and smelting activities (Hu, Cheng, & Tao, 2016). The Cd contamination in agricultural soils in Mae Sot District, Tak Province and Northwestern Thailand because the mining of zinc deposits in the area are located uphill of the Mae Tao creeks which led to the movement of Cd and Zn along the creeks to contaminate paddy fields downstream (Akkajit, 2015). These problems lead to human health risks because Cd can be up taken to each part of the rice plant particularly, rice grain (**Figure 1**). Therefore, it can accumulate in the body with each meal (Bolan et al.,2013). Cd is a non-essential and toxic element for living organisms. In humans, it mainly affects the kidneys and the skeleton. In addition, it is a carcinogen by inhalation when people are exposed to low levels of cadmium over a prolonged period. The United States Environmental Protection Agency (U.S. EPA) has established reference doses (or RfDs) for cadmium of 0.0005 mg kg^{-1}day^{-1} for exposures through water, and 0.003 mg/kg/day for exposure through food (UNEP, 2010). While Cd maximum levels in polished rice, what is main product from paddy area, is 0.4 mg kg-1 (Codex Alimentarius Commission, 2018).

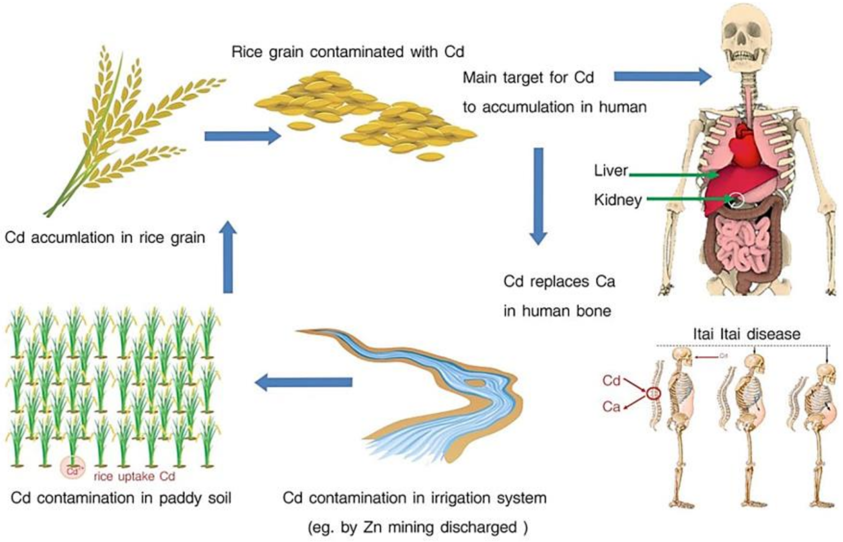


Figure 1 Pathway of cadmium exposure from contaminated paddy soils

Many remediation technologies were used for soils contaminated with heavy metals, such as solidification/stabilization, soil washing, soil flushing, electrokinetic or phytoremediation (Jankaite, & Vasarevicius, 2005). Selection of the most suitable remediation method depends on the kind of pollutants, the concentration of pollutants and site characteristics. The soil amendment technique is used in Cd contaminated soils in several cities. This method is the mixing of heavy metal contaminated soils with soil stabilizers. Heavy metals in the amended area are chemically precipitated, complexation and sorption mechanisms between the pollutant and soil stabilizers. This technique can help reduce the bioavailability of contaminants to plants and metal leaching into groundwater (Allen et al., 2007). Zero valent iron (ZVI) is an effective and cheap amendment for reducing the mobility and bioavailability of heavy metals in contaminated soils (Kumpiene et al., 2006). When ZVI is added to the soil, it oxidizes to form iron oxides that have a high surface area and sorption capacity. The variable surface charge and large number of reactive terminal hydroxyl groups is a prominent feature to adsorb ions from heavy metals (Komarek, Vanek, & Ettler, 2013; Tiberg et al., 2016). Although using ZVI amendment can immobilize the bioavailable heavy metals in rice grain, this technique is suitable for less heavy metal contaminated soils as the pollutants, though neutralised, are still in the soil. On the other hand, if we use this method in heavily polluted areas or remove polluted soil, we should support this by other alternative methods such as, soil washing. Soil washing is an ex situ remediation operating chemical and physical extraction and isolation technique to remove pollutants (organic, inorganic, and radioactive pollutants) from soils (Anderson, 1993). In addition, Electrokinetic (EK) is a remediation for heavy metal separation from soil. EK removes contaminants by the application of a low level electric field via two electrodes directly inserted in the soil specimen, thus forming an electric field in the targeted soil area (Cameselle, & Gouveia, 2018). Application EK with ZVI may enhance the removal of Cd from soil.

This study was conducted to evaluate the remediation techniques for Cd contaminated soil in paddy fields in Mae Sot District, Tak Province, and Northwestern Thailand. The concept of this study is using ZVI for Cd immobilization, the separation of contaminated ZVI from soil by machine as soil washing and solar-powered electrokinetic separation for Cd contaminated soil remediation (**Figure 2**).

In addition, the alternative restoration technique in this study is considered as part of an economic analysis where it is evaluated in terms of cost and benefits. This process was estimated in terms of cost-benefit compared with the assessment and management by the Thai government in order to make an appropriate decision on the remedial selection with maximum social benefit. The cost-benefit analysis (CBA) is applied to the environmental policies in order to compare social costs and benefits (Feuillette et al., 2016; Hansson, 2007). Assessment of values through monetary indicators is relatively easy when they are connected with market prices (e.g. material cost, the product of rice), but it is more complex to capture the non-market cost (e.g. health cost) (Feuillette et al., 2016). Monte Carlo Simulation (MCS) is one of the most common methods applied to accommodate the uncertainties associated with many risk-related problems or complex problems, and it has been recognized as a means of quantifying variability and uncertainty in risk assessments by the National Academy of Sciences and USEPA. This technique provides a quantitative way to estimate the probability distributions for exposure and health risks within the validity of the assessment model (Poulter, 1998; Qu, Sun, Wang, Huang, & Bi, 2012; USEPA, 1997; Zupunski et al., 2010).

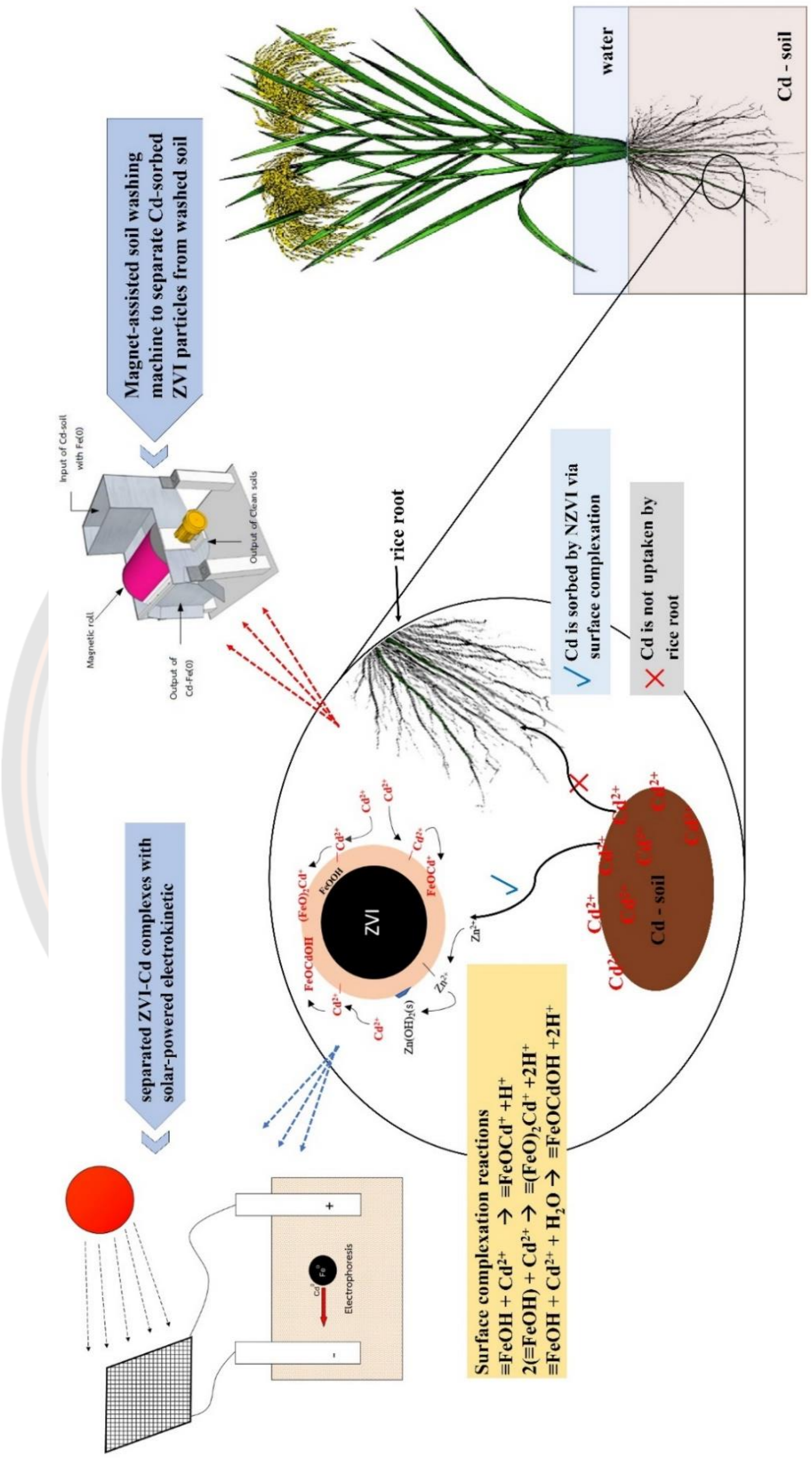


Figure 2 Schematic model of this research for Cd contaminated in paddy soil

Therefore, this study not only evaluates a feasibility of three remediation techniques but an integrated economic decision analysis for the Cd contaminated agricultural area in Mae Sot District and Tak Province in order to make appropriate decisions on remedial selection with maximum social benefit.

Research Aim

1. This research develops and examines remediation techniques including soil amendment and soil washing with ZVI particles into pilot scale with community researchers for cadmium contaminated soil in paddy fields at Mae Sot District, Tak Province, Thailand
2. This research investigates the solar-powered electrokinetic separation for stabilization and remediation of cadmium contaminated soil in the laboratory
3. This study involved an integrated economic decision analysis including the analysis of the expenses of health risk by Monte Carlo simulation and the remediation cost as well as other risk management activities in the past and in the future in the Cd contaminated agricultural area in Mae Sot District, Tak Province, Thailand

Research Significance

In this case, the Cd contaminates the soil and accumulates in crops. The Mae Sot District is of significance as Cd concentrations in paddy soil and rice samples was found to exceed the European Union (EU) standard by72 times and 80% of the Food and Agriculture Organization and Japanese standards respectively (Padungtod et al.,2006). When this area was contaminated with Cd paddy soil and crops especially, rice, were found to have unacceptably high levels of Cd. When tested, residents were found to have Cd levels in their urine that are higher than the World Health Organization (WHO) standard of 2 ug g^{-1} creatinine for environmental exposure. Importantly, many studies in this cadmium-contaminated area have shown positive relationships between high urinary cadmium levels and renal dysfunction, bone toxicity, hypertension and urinary stone disease (Honda et al., 2010; Limpatanachote et al., 2010; Songprasert et al., 2015; Swaddiwudhipong et al., 2012). The local people are understandably concerned about the contamination of their land as it has a direct impact on their health. In addition, Mae Sot District are one area of paddy soils which produce up to 14,000 tons of rice per year. Mae Sot jasmine rice came second in the national rice competition in 2002 (Phenrat, & Otwong, 2015). Moreover, Thailand is an international leader in the production and export of rice. Therefore, this problem has serious implications for the Thai economy and the traditional rice culture of residents along with the health of consumers.

Research Scope

1. Study area is the Cd contaminated soil in paddy area at Mae Sot District, Tak Province, Thailand
2. For field scale, including soil amendment and magnetic-assisted soil washing, demonstrate with community researchers and using ZVI particles was compared to the efficiency of Cd immobilization, such as biochar
3. For lab scale, including solar-powered electrokinetic separation conducted in a laboratory by using contaminated soil from the Phatat Pha Daeng sub-districts and using ZVI particles was compared with Nano zerovalent iron and iron rod
4. The economic impact assessment including health impact, the expenses and cost-benefit of risk management was evaluated through the timelines of Cd contamination in this area, which input data from departmental reports such as, the Pollution Control Department, are compared with the expense and cost-benefit of remedial methods from this study.

Research Hypothesis

Based on the well-established ability of ZVI to adsorb metals and its magnetic characteristic lead to the assumption that it can effectively immobilize Cd in soil and can easily separate the Cd-ZVI from paddy soil. In addition, Cd removal efficiency from soil increases when using ZVI with solar-powered electrokinetic separation. In addition, an appropriate remediation technique was considered from the economic analysis accuracy via the cost-benefit analysis and Monte Carlo simulation.

CHAPTER II

Literature Review

Situation of Cd contaminated paddy soil in Mae Sot District, Tak Province, Thailand

Cadmium (Cd) contamination of agricultural soils and crops in Phatat Pha Daeng and Mae Tao Mai sub-districts, Mae Sot, Tak Province, Thailand (location in **Figure 3**) is a situation that is well known for the levels of contamination. It has continuously gained media and public attention since 1998 (Padungtod et al., 2006; Simmons et al., 2005). The agricultural system with high levels of cadmium concentration were irrigated by the upper stretches of Mae Tao Creek, which passes a zinc (Zn) mining zone, and along with other activity causes such as phosphate fertilizer, Zn mining is considered to be the major cause of contamination in the area (Phenrat, & Otwong, 2015).

The Pha Daeng ('red cliff') area near the border with Myanmar, contains the largest Zn deposit in Thailand, and of the highest quality anywhere in Asia. Zn mining dates back to 1969, and the Thai Zinc Company extracted a total of around 230,000 tons between then and 1982. Then the Pha Daeng company started Zn mining and had produced a total of more than 7 million tons of ore up to 2012. Another Zn mining operator was the Tak Mining company, which started around 1985 and ended operations in 2003. Neither environmental nor health impact assessment was mandatory before 1992. In addition, to be a rich deposit of Zn ore, Mae Sot district is also home to Karen hill people (mostly of the Papakayo tribe) who live by rice cultivation. One area, Mae Tao, used to produce up to 14,000 tons of rice per year. Mae Sot jasmine rice came second in the national rice competition in 2002, but the following year the International Water Management Institute (IWMI) reported cadmium contamination of fields and crops in three sub-districts (Phenrat, & Otwong, 2015).

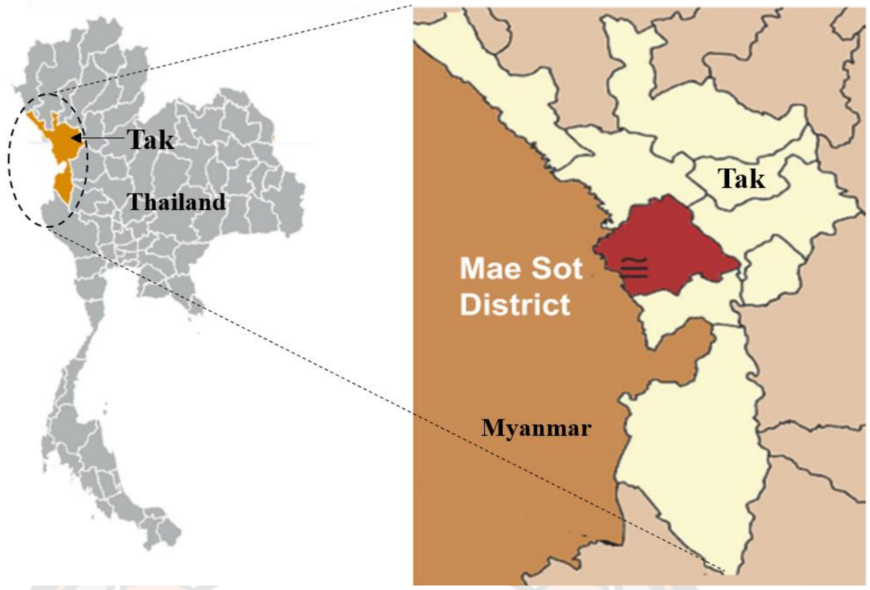


Figure 3 Location of the study area, Mae Sot District, Tak Province, Northern Thailand

Source: Prasad et al., 2015

The discovery of Cd contamination in this area was first found in 1998. Dr. Robert W. Simmons, a senior researcher at the International Water Management Institute (IWMI) and his team in cooperation with Dr. Pichit Pongsakul, a soil and plant expert at the Department of Agriculture, Ministry of Agriculture, Thailand conducted a jointly quantified soil and rice cadmium assessment in Mae Sot district. Their findings reported that Cd concentration of 154 soil samples were 1.13–94 times the European Economic Community (EEC) Maximum Permissible (MP) soil cadmium concentration of 3.0 mg kg^{-1} and 1,800 times the Thai standard of 0.15 mg kg^{-1}. While rice samples from 90 fields were found to be 0.1 to 4.4 mg kg^{-1} rice which exceeded the mean background Thai rice Cd concentrations as reported by Pongsakul and Attajarusit (1999) was 0.043 ± 0.019 mg kg^{-1}rice. In 2001-2003, IWMI and the Department of Agriculture (DOA) expanded the second phase of the study by extending the study area to the downstream part of the Mae Tao Creek. Cd concentrations in the soil and rice samples were reported to be 72 times the European Union (EU) standard and 80% of

Food and Agriculture Organization (FAO) and Japanese standards respectively (**Figure 4** and **Figure 5**) (Padungtod et al., 2006; Simmons et al, 2005).

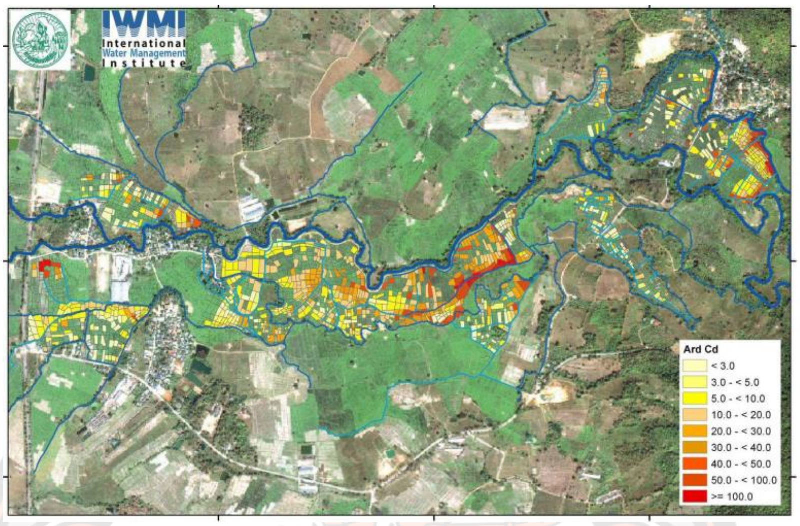


Figure 4 Total soil Cd (mg kg-1) in 1,090 fields from IWMI-DOA survey

Source: Simmons et al., 2005

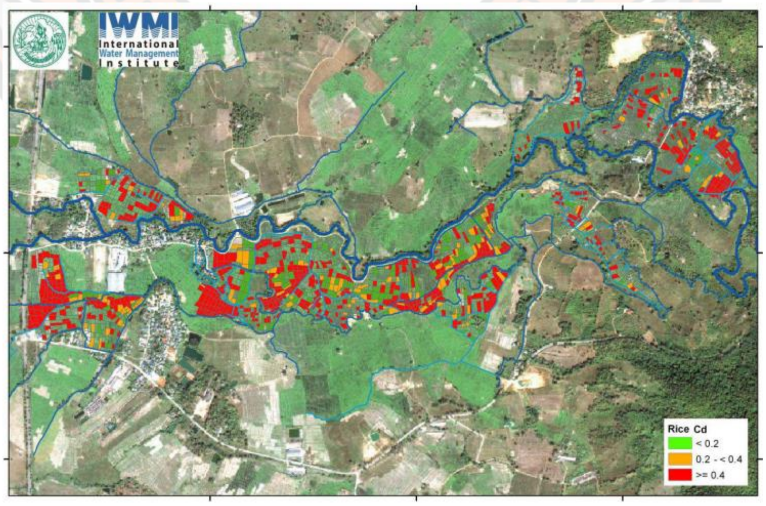


Figure 5 Rice grain Cd (mg kg-1) in 1,067 fields from IWMI-DOA survey

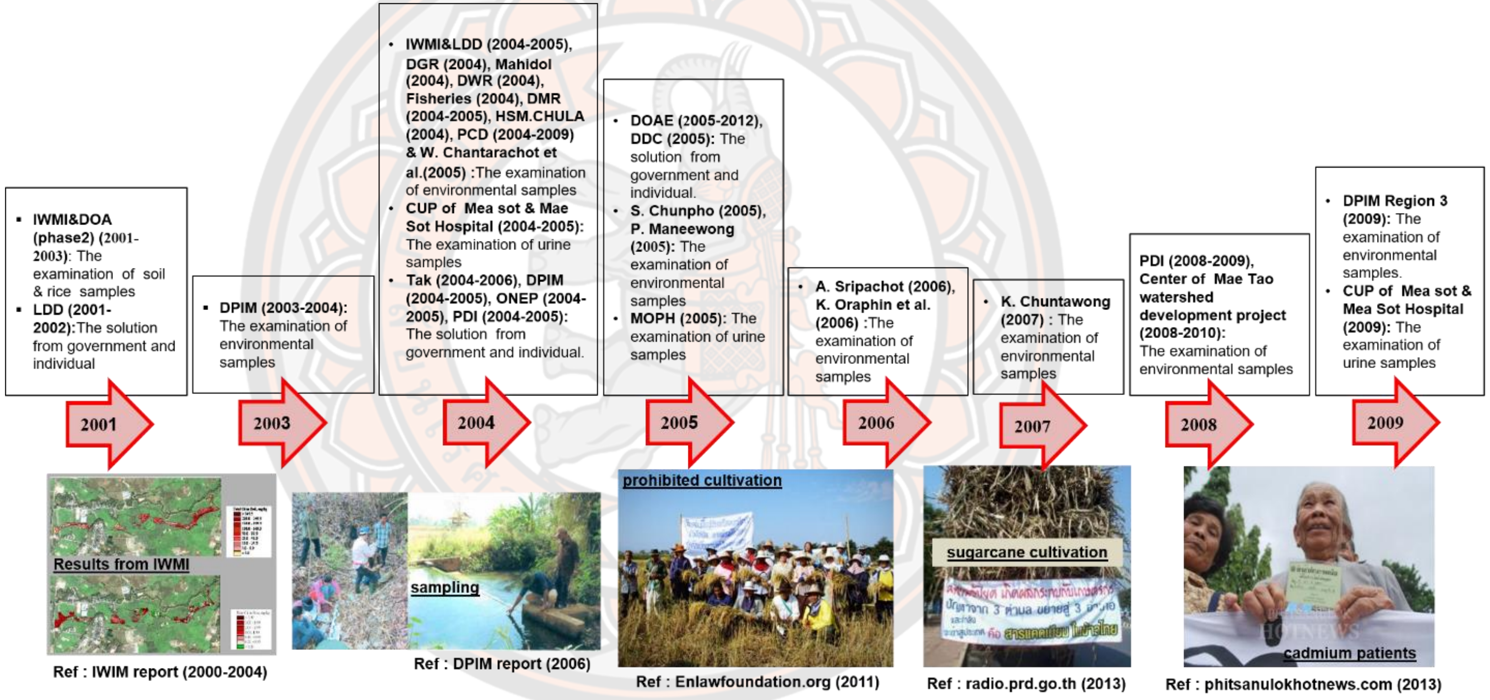
Source: Simmons et al., 2005

In the Mae Sot District, Tak Province, Thailand, a population screening survey for cadmium exposure using U-Cd measurement from 2004 and 2009 was first and second conducted among 7,697 and 6,748 residents, respectively, aged 15 years and older living in these contaminated villages. Of persons in both surveys who consumed rice grown locally, 55.5% in the first survey and 61.3% in the second survey had urinary cadmium levels > 2 ug g^{-1} creatinine that higher the World Health Organization standard of 2 2 ug g^{-1} creatinine for environmental exposure. In both surveys, prevalence of high urinary cadmium associated with consumption of locally grown rice was greater than that for tobacco smoking (Padungtod et al., 2006; Swaddiwudhipong et al., 2010). Importantly, many researches in this cadmium contaminated area have shown positive relationships between urinary cadmium and renal dysfunction, bone toxic effects, hypertension and urinary stone disease (Honda et al., 2010; Limpatanachote et al., 2010; Songprasert et al., 2015; Swaddiwudhipong et al., 2012)

This uncovering gained Thai government attention which lead to investigation, and solution processes and a health risk plan for the cadmium contaminated area (**Figure 6**), such as the environmental sampling of the Department of Agriculture (DOA), the Land Development Department (LDD), the Department of Pollution Control (DPC) and the Department of Primary Industries and Mines (DPIM), and the individual sampling of the Mae Sot hospital for surveillance (Padungtod et al., 2017). Several studies have been conducted to determine Cd levels in soils and identify the origin of Cd in the vicinity of the mine. They found that the soil samples from the agricultural areas around the Pha Te village, the Mae Sot District have Cd accumulation. The upper-paddy soils receive irrigation water through a canal from the Mae Tao creek which flows into the lower-paddy soils which showed high Cd and Zn concentrations. Mae Tao creek originates in the mountains of Northwestern Thailand and is directly influenced by mining activities. Soil sample from the Mae Tao creek were found to have low Cd levels upstream (8.45 mg Cd kg^{-1}), increasing to 22.5 mg Cd kg^{-1} at Mae Tao Mai Village. Mae Ku creek, on the other side of the mountain with Zn mining, showed high Cd levels (7.55 to 34.95 mg Cd kg^{-1}). The Mae Tao Ngae Sai and Nong Khiao creeks in the northeastern and southwestern highlands of the mine area had Cd levels of 3.05 mg Cd kg^{-1} and 1.1 mg Cd kg^{-1}, respectively. The data indicate that these soils are contaminated with Cd and Zn, and the source of contaminant is located upstream from the Mae Tao creek (Akkajit, 2015; Unhalekhaka, & Kositanont, 2010). When Cd in surface water was surveyed by Moolthongnoi, & Arunlertaree, 2008, Cd levels in surface water from the Mae Tao creek (which passed through the Zn mining area) was higher during the rainy season (0.028 to 0.032 mg Cd L-1) than in the dry season (0.005 to 0.006 mg Cd L-1). They suggested that the paddy fields receive Cd mainly via suspended sediment transported from Mae Tao creek (Akkajit, 2015). In 2008, Cd levels in home-consumed rice grains collected from the Cd-polluted paddy fields around Pha Te village, ranged from 0.12 to 1.27 mg Cd kg^{-1} (Sriprachote et al.,2012; Akkajit, 2015). Research conducted over the past 5 years has identified serious health risks with the prolonged consumption of rice grown in this Cd contaminated area (Akkajit et al., 2015; Swaddiwudhipong et al., 2012). Several hundred villagers in these areas were found to have high levels of Cd in their blood (average of 8.2 µg g-1 creatinine). This is in excess of a 16-fold of the national average of 0.5 µg g-1 creatinine and was attributed to the consumption of contaminated rice and other local crops as the main route of exposure (Akkajit, 2015).

The help solve the problem, the Thai government, purchased and burned all the rice produced from these contaminated paddy fields. In addition, the cultivated prohibition on contaminated lands and the promotion of non-food cultivation such as sugar cane, decorative palms and rubber plantations to replace rice cultivation were conducted (Padungtod et al., 2006; Phenrat, & Otwong, 2015). However, those processes were a short-term solution and in time villagers returned to rice cultivation for local consumption after finding that sugarcane did not suit their land or their lifestyle. The consumption of contaminated rice affected the cadmium level in their urine and gave a greater than normal risk of kidney disease (Phenrat, & Otwong, 2015). Therefore, remedial plan is important for their future well-being.

Furthermore, the villagers sued to the Nation Environmental Broad for negligence, asked to declare the area protected under the 1992 Environmental Quality Promotion and Protection Act, which stipulates that contaminated area are automatically rehabilitated, and hoped to gain for suitable restoration in harmony amid traditional rice culture (Phenrat, & Otwong, 2015).



- **IWMI&DOA (phase2) (2001-2003)**: The examination of soil & rice samples
- **LDD (2001-2002)**:The solution from government and individual

- **DPIM (2003-2004):** The examination of environmental samples

- **IWMI&LDD (2004-2005), DGR (2004), Mahidol (2004), DWR (2004), Fisheries (2004), DMR (2004-2005), HSM.CHULA (2004), PCD (2004-2009) & W. Chantarachot et al.(2005)** :The examination of environmental samples
- **CUP of Mea sot & Mae Sot Hospital (2004-2005):** The examination of urine samples
- **Tak (2004-2006), DPIM (2004-2005), ONEP (2004-2005), PDI (2004-2005):** The solution from government and individual.

- **DOAE (2005-2012), DDC (2005):** The solution from government and individual.
- **S. Chunpho (2005), P. Maneewong (2005):** The examination of environmental samples
- **MOPH (2005):** The examination of urine samples

- **A. Sripachot (2006), K. Oraphin et al. (2006)** :The examination of environmental samples

- **K. Chuntawong (2007)** : The examination of environmental samples

PDI (2008-2009), Center of Mae Tao watershed development project (2008-2010):
The examination of environmental samples

- **DPIM Region 3 (2009):** The examination of environmental samples.
- **CUP of Mea sot & Mea Sot Hospital (2009):** The examination of urine samples

Ref : IWIM report (2000-2004)

Ref : DPIM report (2006)

Ref : Enlawfoundation.org (2011)

Ref : radio.prd.go.th (2013)

Ref : phitsanulokhotnews.com (2013)

Figure 6 Timeline of the attempt to investigate and solve environmental and health problems after discovery of Cd contamination in soil at Mae Sot, Tak Province, Thailand

Cadmium

1. Properties and application of Cd

Cadmium (Cd) is a naturally occurring metal that belongs the group IIb in the periodic table between zinc (Zn) and mercury (Hg). Cd chemical behaviour is similar to Zn. It generally exists as a divalent cation or complexed with other elements (e.g., CdCl2). The characteristics of Cd are presented in **Table 1**. Cd levels in the earth's crust are 0.1 ppm and associated with Zn, lead (Pb) and sulfide deposits, therefore being produced primarily as a byproduct of Zn or Pb smeltin (Bernhoft, 2013). The most common Cd mineral is greenockite (CdS) which is rarely found in a pure state. Cd is also a natural constituent of ocean water with average levels between <5 and 110 ng L^{-1}. Furthermore, it was found in higher levels near coastal areas and in marine phosphates and phosphorites (Faroon et al., 2012; Sharma, Rawal, & Mathew, 2015). Cd can form a number of salts. Its mobility in the environment and effects on the ecosystem depends to a great extent on the nature of these salts. Cd has a relatively high vapor pressure. The vapor is oxidized quickly to produce Cd oxide in the atmosphere. When reactive vapor or gases, such as carbon dioxide, water vapor, sulfur dioxide, sulfur trioxide or hydrogen chloride, are present, the vapor reacts to produce Cd carbonate, Cd hydroxide, Cd sulfite, Cd sulfate or Cd chloride, respectively. These salts may be formed in stack and distributed to the environment. Some Cd salts are practically insoluble in water. On the other hand, these can be dissolved in water under the influence of oxygen and acids, the sulfate, nitrate, and halogenates (as shown in **Table 2**).

Commercially, Cd has become of increasing industrial importance since the early 1900s. Cd is used in the electroplating and galvanizing industries, although it also has the application in color pigments for paints, pigments and stabilizers for plastics, cathode materials for nickel-cadmium batteries, and as alloys that lend temperature and pressure stability to industrial equipment. In **Figure 7** presented an increasing part of the global cadmium consumption is used for nickel-cadmium (NiCd) batteries, which in 2005 accounted for 82 percent of the total Cd consumption. Other major uses are pigments for plastics, ceramics, and enamels; stabilizers for plastics, in particular polyvinyl chloride (PVC); plating on iron and steel; and as an alloying element of some lead, copper and tin alloys. Since 1990, the Cd consumption for pigments, stabilizers, alloys and other uses has decreased significantly (Gwaltney-Brant, 2013; UNEP, 2010).

Cd is produced mostly as a by-product of zinc and lead mining, smelting and refining, and to a lower level as a by-product of lead and copper production. Moreover, it is sometimes present in large quantities in sewage sludge used as fertilizer (Gwaltney-Brant, 2013).

Table 1 Properties of cadmium

Physical properties	Chemical properties	Geochemical properties
• Silvery-white, soft, ductile chemical metal • Insoluble in water • Inflammable • Density is 8.645 g/cm^3 • Vapor pressure at 400°C is 1.4 mm and at 500°C is 16 mm. • Form CdO in air as vapor is very reactive. • Melting point is 321.069°C, 609.924°F and 594.219K • Boiling point is 767°C,1413°F and 1040K • CAS number-7440-43-9	• atomic number 48 • atomic weight 112.40 g/mole • has 8 isotopes (natural abundance) ^{106}Cd (1.22%), ^{108}Cd (0.88%), ^{110}Cd (12.39%), ^{111}Cd (12.75%), ^{112}Cd (24.07%), ^{118}Cd (12.26%), ^{114}Cd (28.86%) and ^{116}Cd (7.58%). • Transition metal in Group IIb of the periodic table • Form more stable compound due to the presence of 14 additional electrons in fourth orbital. • Oxidation state is +2 but few compounds show +1 oxidation state. • Have greater tendency to form covalent bonds with sulphur • With cyanine's and ammine form soluble complexes. • For 4-fold coordination, cadmium ionic radius is 0.88A° • For 6-fold coordination, cadmium ionic radius is 1.03A°	• Strong chalcophile element. • Abundance of cadmium in earth crust is 0.15 - 0.2 ppm • Low concentration in igneous rocks. • Ratio of Zn/Cd varies in all igneous rocks • Cadmium level occurrence is high in oceanic, shale's, and lacustrine sediments, oceanic manganese and phosphorites nodules

Source: Sharma et al., 2015

Table 2 Physical and chemical properties of cadmium salts

Cd salts	Cd chloride	Cd acetate	Cd oxide	Cd hydroxide	Cd sulfide	Cd sulfate
Formula	$CdCl_2$	$C_4H_6CdO_4$	CdO	$Cd(OH)_2$	CdS	$CdSO_4$
Relative atomic	183.32	230.50	128.40	146.41	144.46	208.46
Density	4.047	2.341	6.95	4.79	4.82	4.691
Melting point (˚C)	568	256	<1426	300 (decomposes)	1750	1000
Boiling point (˚C)	960	decomposes	900-1000 (decomposes)			
Water solubility (g/L)	1400 (20 ˚C)	Very soluble	insoluble	0.0026 (26 ˚C)	0.0013 (18 ˚C)	755 (0 ˚C)

Source: WHO, 1992

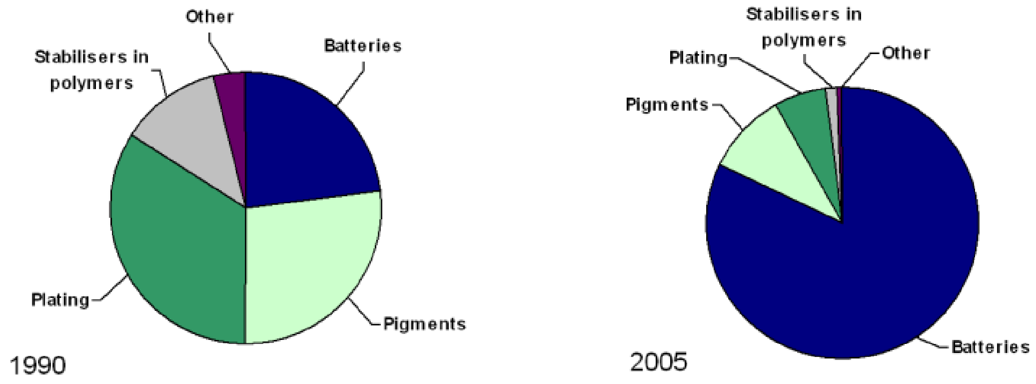


Figure 7 Consumption of primary cadmium by end-uses in 1990 and 2005

Source: UNEP, 2010

Normally, Cd release to the environment due to the natural mobilization of cadmium from the Earth's crust and mantle such as volcanic activity, weathering of rocks and minerals, forest fires, generation of sea salt aerosols, or other natural phenomena. The anthropogenic effect from the mobilization of Cd impurities in raw materials such as phosphate minerals, fossil fuels and other extracted, treated and recycled materials particularly zinc and copper. In addition, the anthropogenic is intentionally Cd releases in both products and processes from manufacturing, using, disposal or incineration of products. Besides these categories, remobilization of historic anthropogenic Cd releases previously deposited in soils, sediments, landfills and waste/tailings piles may be considered (UNEP, 2010).

Cd may be released into the environment, including the atmosphere, aquatic environments (fresh and salt water environments) and the terrestrial environment (soil and biota) (see figure 8). Within the environment, Cd will flux between these compartments. Cadmium released into the atmosphere will be redirected to the terrestrial and aquatic environments as atmospheric deposition, whereas some Cd released to soil over time will be washed out to the aquatic environments. It is also important to assess the bioavailability of Cd in soils or sediments, (see in **Figure 8**), where it was indicated that the Cd is released into the environment as an anthropogenic pollutant while emission from natural sources such as volcanic activities, weathering of rocks, and soil erosion are locally limited (Sebastian, & Prasad, 2013).

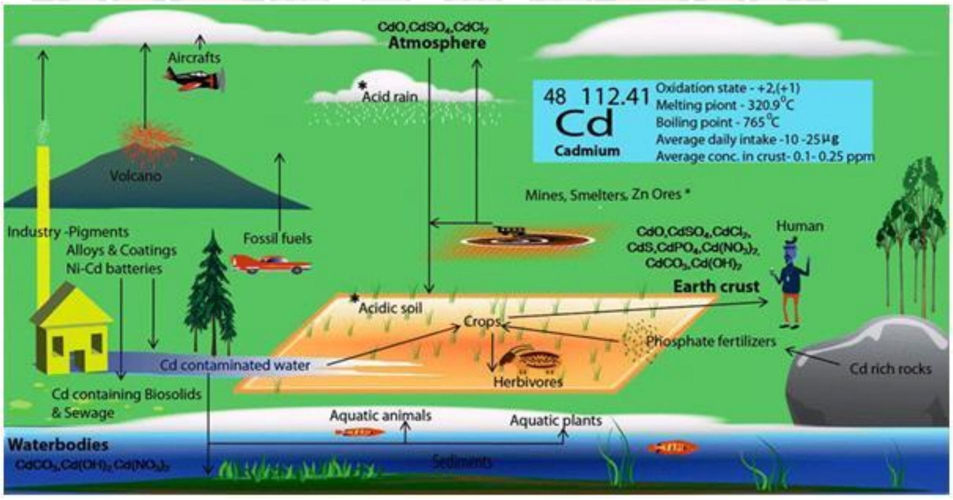


Figure 8 Biogeochemical cycle of cadmium in environment

Source: Sebastian, & Prasad, 2013

2. Cadmium in contaminated soils

Soil is the basic environmental element constituting an ecosystem, and the important material basis of human survival and development. The heavy metals essentially become contaminants in the soil environments because 1) their rates of generation via manmade cycles are more rapid relative to natural ones, 2) they were transferred from mines to random environment areas, where there is higher potential for direct exposure 3) the concentrations of these metals in waste form are relatively high compared to those in the receiving environment, and 4) the chemical form (species) in which a metal is found in the receiving environmental system may render it more bioavailable (Wuana, & Okieimen, 2011). Cd is one of the non-essential heavy metals. It can be released into the soil via both natural and anthropogenic activities. However, the total contribution of natural sources towards Cd contamination in soil counted for 10% as compared to the total release from all sources. Over 90% (5.6– 38 × 106 kg year^{-1}) of Cd is released into the environment from anthropogenic sources including the use of phosphate fertilizers, fossil fuel combustion, metallurgical works, industrial waste and/or agricultural waste, sewage sludge, and mining, smelting and metal ore processing (Khan et al., 2017; McLAUGHLIN, & SINGH, 1999).

Urban soil is mainly polluted with Cd from industrial processes and vehicular emission (Khan et al., 2016; Khan et al., 2017) A large amount (67%) is used in the production of metallic Cd electroplate used in nickel-cadmium batteries (Greenwood, & Earnshaw, 2012; Khan et al., 2017). Nriagu, & Pacyna (1988) reported that the worldwide estimated total input of Cd to soil through different anthropogenic sources was 5-38 × 10^6 kg year^{-1} with 12% from agriculture and animal wastes including fertilizers (Khan et al., 2017). In China, farmland area has been badly affected by Cd (27.86 × 10^4 km^2) (Cao et al., 1999; Khan et al., 2017). The Cd concentrations in mine-impacted paddy soil in Hunan is 0.26-37 mg kg^{-1} (Chen et al., 2016; Yin et al., 2017) and 99% of paddy soil samples from Nanxun county had Cd levels exceeding the natural background value indicating widespread Cd accumulation in local soils (Zeng et al., 2015). In Taiwan, over 100 ha of paddy areas had been contaminated by Cd and Pb as a result of the illegal discharge of wastewater from a plastic-stabilizer producing plant close to the fields (Hseu et al., 2010). Among different sources, the use of phosphate fertilizers is generally considered to be one of the major sources of Cd input to agricultural soil (Smolders, & Mertens, 2013). Concentrations in phosphate fertilizers used in Europe were observed in the range of 0.1 - 120 mg Cd (kg P_2O_5) $^{-1}$ (Nziguheba, & Smolders, 2008). In addition, the application of contaminated manure also adds Cd to agricultural soil. According to Nicholson et al. (2003), the input of Cd to agricultural soil from manure, when applied at a rate of Nequivalent to 250 kg Nha^{-1}-year^{-1}, ranged from 1.4 to 6.1 g Cd ha^{-1} year^{-1} (Khan et al., 2017).

In soils, Cd^{2+} may undergo hydrolysis, exchange, sorption, complexation and precipitation/occlusion/dissolution (Huang, Hayes, & Traina, 1998). The chemistry of Cd in the soil environment is to a great extent controlled by pH. The U.S. EPA (1999) reports that under acidic conditions, Cd solubility increases and adsorption of Cd with soil colloids, hydrous oxides, and organic matter decrease. At pH values greater than 6, Cd is adsorbed by the soil solid phase or is precipitated, and the concentrations of dissolved Cd are greatly reduced. Cd forms soluble complexes with inorganic and organic ligands, in particular with chloride ions. The formation of these complexes will increase Cd mobility in soils Adriano et al. (2005) argue that in general, chloride can be expected to form a soluble complex with Cd 2+ as CdCl+, thereby decreasing the adsorption of Cd2+ to soil particles. In contrast to inorganic ligand ions, Cd2+ adsorption by kaolinite, a variable-charge mineral, could be enhanced by the presence of organic matter via the formation of an adsorbed organic layer on the clay surface (UNEP, 2010). Although more than 99% of Cd is associated with the solid phase and 1% is found in the soil solution (McLAUGHLIN, & SINGH, 1999), Cd leachability and availability to plants conceptually are related to Cd in the soil solution and to pools of solid, which can be made available via the soil solution (McLAUGHLIN, & SINGH, 1999). Metals in the solution phases may exist as free, hydrated ions and as dissolved species complexes that have positive, negative or zero ion charge. The free ions and the complex species interact with the soil solid by precipitation-dissolution, adsorption-desorption, or ion-exchange phenomena (McLAUGHLIN, & SINGH, 1999). Plant roots can uptake of the dissolved species. Therefore, Cd leachability and availability are concerns when groundwater and food crops are considered.

3. Cadmium uptake into food crop

Cd availability is concerned to agriculture because consumption of Cd in contaminated food crops can lead to toxicities in animals and humans. The mechanisms of Cd accumulation in plant including the uptake of Cd from solution at the root surface, the transport of Cd^{2+} across root-cell plasma membranes, the intra- and inter-cellular movement of Cd, and the long-distance translocation and deposition of Cd in edible plant parts. **Figure 9** also shows the mechanisms Cd accumulation in the rice plant (Oryza sativa). The mechanism is started by root uptake into the root cell symplasm, which OsNramp5 (natural resistance-associated macrophage protein 5) was identified as the major Cd uptake transporter in rice. OsNramp5 is expressed in the plasma membrane at the distal side of exodermis and endodermis cells. In addition, other transports including OsIRT1 (iron regulated transporter1), OsIRT2 and OsNramp1 are potentially implicated in Cd uptake, in particular upon reaeration of soil after flooding. These are Fe^{2+} transporters with limited specificity and induced under Fe deficiency. When pond water is released, aerobic conditions arise which simultaneously decrease Fe availability as Fe^{2+} becomes oxidized and also increases Cd availability as Cd sulfides are oxidized to more soluble sulfates. OsNramp1 overexpression increases Cd sensitivity and Cd accumulation in leaves. However, because OsNramp5 was shown to account for most of the rice Cd uptake under different Fe supply conditions, OsIRTs and OsNramp1 appear to play only a minor role in Cd uptake from the soil. When Cd uptake by transporters existing in the root through vacuolar storage and xylem loading activity. The high Cd-accumulating cultivars carry mutations in OsHMA3 (Heavy Metal ATPase 3) that renders the protein non-functional, thereby inhibiting Cd retention in roots. A protein implicated in xylem loading is OsHMA2. It is predominantly expressed in the vascular bundles of roots and contributes to Cd accumulation in leaves and grain. The Cd transporter OsLCT1 mediates xylem-to-phloem transfer in node 1. Thus, a key process for the transfer of Cd to the grain is xylem-to-phloem transfer (Clemens et al., 2013).

For environmental Cd exposure via food crops including the consumption of Cd contaminated rice as a result of uncontrolled Cd discharge into the Jinzu River basin, in Japan (Kobayashi et al., 2008). The excessive concentration of Cd in cocoa (*Theobroma cacao*) in Peninsular Malaysia from phosphate fertilizers (Zarcinas et al., 2004). The Cd content of rice grain grown in metal-contaminated paddy soils near abandoned metal mines in South Korea was found to exceed safety guidelines (0.2 mg Cd kg^{-1}) set by the Korean Food and Drug Administration (KFDA) (Ok et al., 2011). Several cities in Southern China have Cd-contaminated rice from extensive metal contamination of paddies with the fast expansion of nonferrous metal mining and smelting activities (Hu et al., 2016). The Cd contamination of agricultural soils in the Mae Sot District, Tak Province, Northwestern Thailand because of the mining of zinc deposits in the area located uphill of the Mae Tao creeks, led to the motion of Cd and Zn along the creek to contaminate paddy soils downstream (Akkajit, 2015), etc.

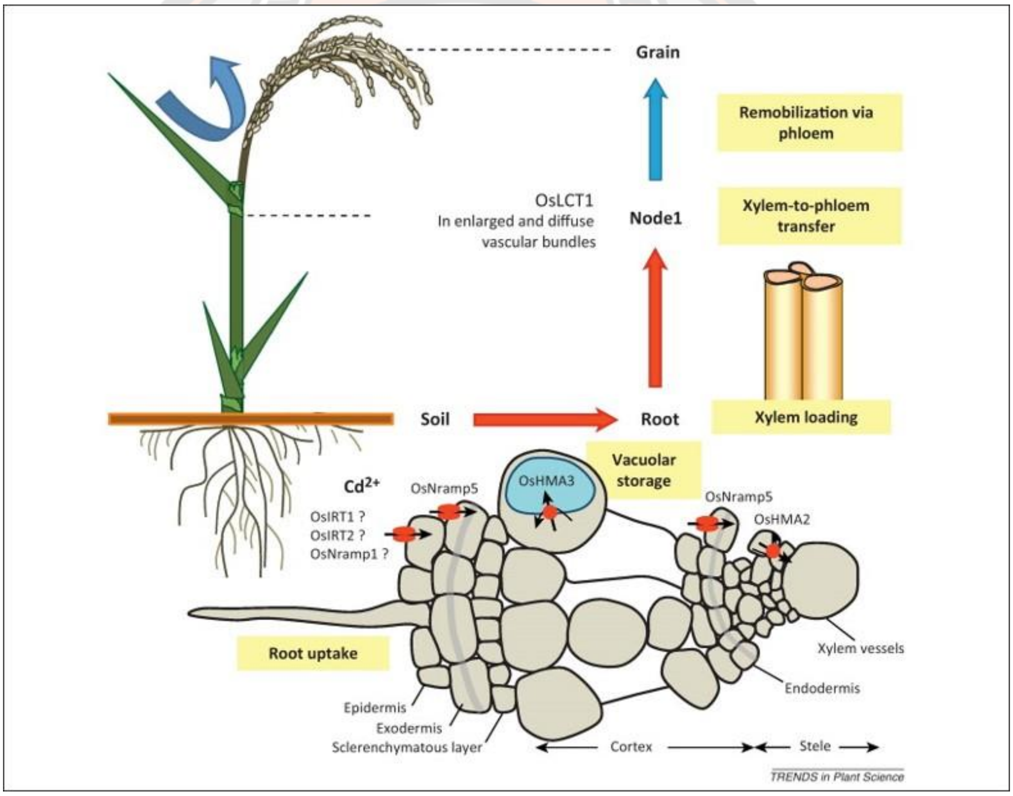


Figure 9 Mechanisms Cd accumulation in rice grain

Source: Clemens et al., 2013

4. Cadmium in people

From what is said above, it can be seen that Cd is mainly used in industrial and agriculture areas. Although Cd emissions in the environment have been reduced in most industrialized countries, Cd remains an area of concern for industrial workers and for populations living in polluted areas, especially in less developed countries. Cd is toxic via inhalation and ingestion. It can cause acute and chronic toxicity in people who are exposed to it. Human exposure to Cd occurs chiefly through food and tobacco smoking. The consumption of staple foods such as wheat and rice significantly contribute to human exposure. For those in industry, Cd exposure is mainly by inhalation. The amount of Cd ingested daily with food in most countries are in the range of 10 to 20 µg day^{-1}, where Cd was absorbed by the oral route around 5% but can increase up to 15% in someone who has low iron reserves. Intestinal absorption is greater in persons with iron (Fe), calcium (Ca), or zinc (Zn) deficiency. For inhalation, human absorbed Cd between 10 – 50% depending on the particle size and the solubility of Cd compounds. For instance, tobacco smoke (mainly in the form of CdO), Cd was absorbed an average of 10% (Bernard, 2008; Bernhoft, 2013).

Acute toxicity for Cd exposure occurs by the inhalation of Cd contaminated air. An initial sign of Cd inhalation is slight irritation of the upper respiratory tract, although symptoms may be delayed for 4-8 hours. The inhalation of Cd may also cause a metallic taste, headache, dyspnoea, chest pain and muscle weakness. The intake of Cd contaminated food causes acute gastrointestinal effects, such as vomiting and diarrhoea (Bull, 2010; Godt et al., 2006). The acute toxic effects following inhalation and ingestion are summarized in **Table 3**.

Table 3 Summary of acute Cd toxic effects by inhalation and ingestion

Dose	Signs and symptoms
	Inhalation (mg m^{-3}; unit of dose)
0.01-0.15	Cough, irritation of the throat, gastroenteritis symptoms - vomiting, abdominal cramps, diarrhoea (expose for nine hours)
0.5	Threshold for respiratory effects after 8-hour exposure
1-5	Immediately dangerous to health - facial oedema, hypotension, dysrhythmias, confusion, oliguria, metabolic acidosis and acute centrilobular necrosis of the liver, pulmonary oedema, tracheobronchitis, pneumonitis
5	Lethal after 8 hours

Dose	Signs and symptoms
39	Lethal after 20 minutes
250	Lethal after 10 minutes
2500	Lethal after 1 minute
	Ingestion (mg kg^{-1} bw; unit of dose)
0.07	Nauseating
>15	Gastrointestinal symptoms – vomiting, abdominal cramps, diarrhoea
20-30	Extensive fluid loss, shock, pulmonary oedema, hypotension, oliguria, multiorgan failure, death

Source: Bull, 2010

Cd is efficiently retained in the organism and remains accumulated throughout life. **Figure 10** shows the mechanism responsible for the selective accumulation of Cd in the liver and the kidneys (Bernard, 2008). Cd is taken up by the blood, the majority of the Cd is transported bound to proteins, such as albumin and metallothionein. The first organ reached after Cd uptake into the plasma is the liver. In liver, Cd induces the production of metallothionein. After that hepatocyte necrosis and apoptosis, Cd-metallothionein complexes are washed into sinusoidal blood. From here, parts of the absorbed Cd enter the entero-hepatical cycle via secretion into the biliary tract in the form of Cd-Glutathione conjugates. Enzymatically degraded to Cd-cysteine complexes in the biliary tree, cadmium re-enters the small intestines (Godt et al., 2006). For Cd accumulation in kidney, metallothionein is rapidly cleared from plasma by glomerular filtration before being taken up by the proximal tubular cells. This glomerular filtration pathway is at the origin of the selective accumulation of Cd in proximal tubular cells and thus in the renal cortex where this segment of the nephron is located. The main organ for long-term Cd accumulation is the kidney. Here the half-life period for Cd is approx. 10 years. A life-long intake can therefore lead to a Cd accumulation in the kidneys, consequently resulting in tubular cell necrosis (Bernard, 2008; Godt et al., 2006). Metabolism, storage and the excretion of Cd in the human body are presented in Figure 11. Therefore, long-term Cd exposure into body directly effects the liver and kidneys and can cause serious damage. The “threshold” level of cadmium above which renal damage may occur is generally considered to be 200 mg g^{-1} of renal cortex (EFSA, 2009).

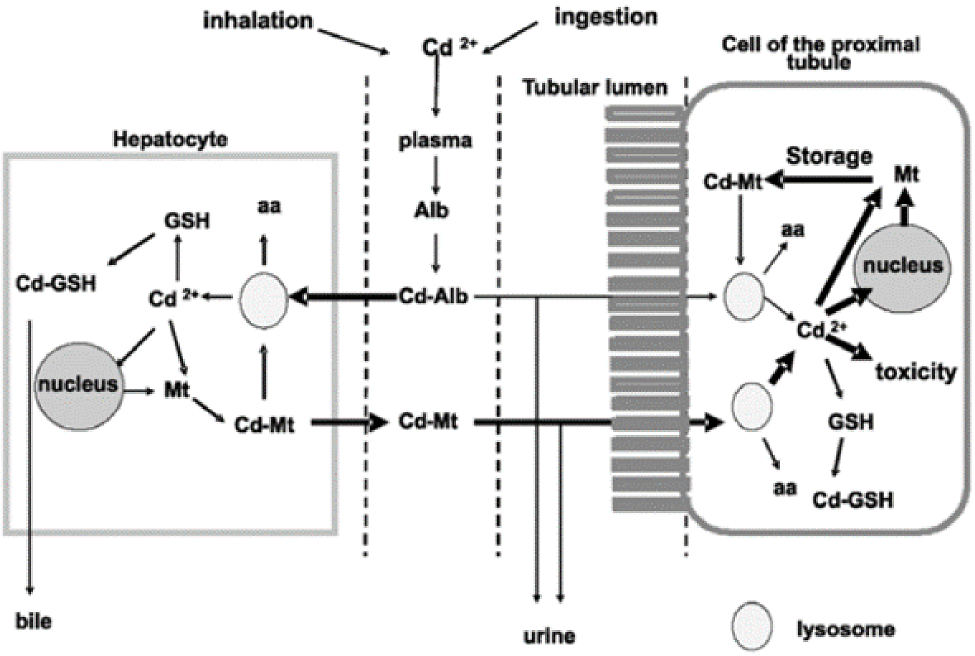


Figure 10 Scheme illustrating the mechanism responsible for the selective accumulation of Cd in liver and kidney

Source: Bernard, 2008

Alb, albumin; Mt, metallothionein; GSH, glutathione; aa, amino acid.

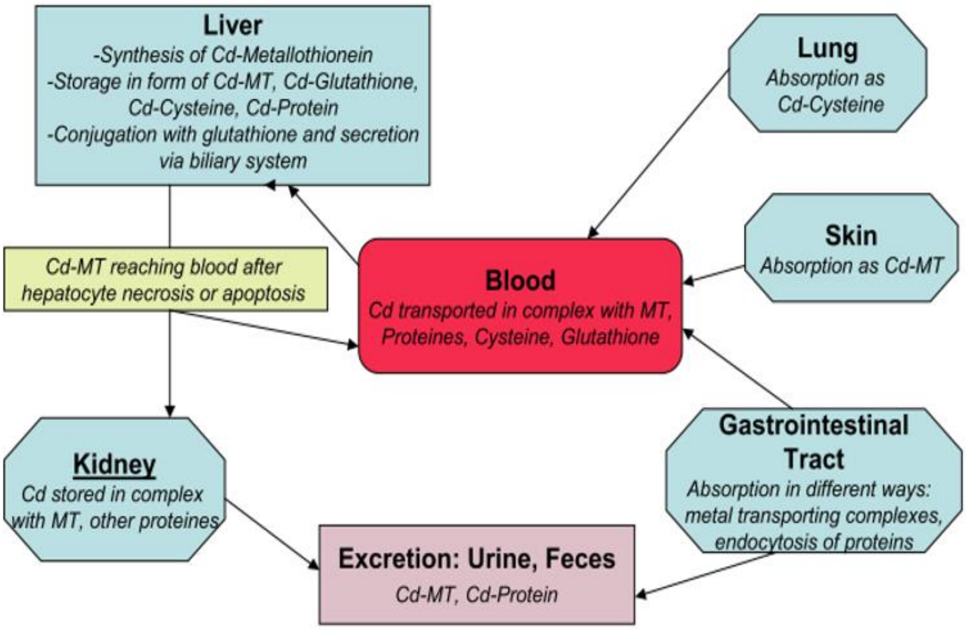


Figure 11 Metabolism, storage and excretion of cadmium in human body

Source: Godt et al., 2006

In addition, long-term exposure to Cd, both environmental and occupational, may cause severe damage to the bone. Cd toxicity is reduced bone density resulting from prolonged exposure. The first reports about bone disease related to cadmium exposure is the Itai-Itai disease, which it was found in Japan due to a heavily Cd-polluted area of the Jinzu River basin (Jarup, & Akesson, 2009). The results of recent European studies: OSCAR (Alfven et al., 2000), WHILA in Sweden (Akesson et al., 2006) and CadmiBel in Belgium (Staessen et al., 1992) as well as the findings of a Japanese study (Honda et al., 2003) indicate that low-dose Cd exposure increases the risk of osteoporosis; this referring to a lower, Cd concentration than previously expected (Trzcinka-Ochocka et al., 2010). In addition, Nordberg et al., 2002 have found decreased bone mineral density in Chinese farmers exposed to Cd from contaminated rice for more than 20 year (Bernard, 2008). The mechanism of bone damage by Cd has not been completely elucidated. Three main pathways of Cd having impact on bone mass have been assumed: 1) a disturbance of the normal activation process of vitamin D following renal tubular injury, 2) the action of Cd within the digestive tract interfering with calcium absorption, 3) direct action of Cd on bone metabolism which does not cause renal injury (Trzcinka-Ochocka et al., 2010).

Some studies have suggested that there is a direct link between exposure to Cd and loss of bone density. This effect is thought to occur at Cd exposure levels that do not affect the renal function but can directly target the bone cells, causing an early bone loss. Cd can decrease bone formation and increase bone resorption in vivo. The maintenance of bone mass depends on the equilibrium between bone formation due to osteoblastic activity and bone resorption due to osteoclastic activity (Bhattacharyya, Whelton, Stern, & Peterson, 1988). Bone loss is the result of the uncoupling of these two processes (Trzcinka-Ochocka et al., 2010). However, Cd has also been identified as a possible cause of cancer. There is sufficient evidence that long-term occupational exposure to Cd (e.g. through Cd fume) contributes to the development of lung cancer. In addition, there is limited evidence that cadmium may also cause cancers of the kidney and prostate. The International Agency for Research on Cancer (IARC) has classified Cd and Cd compounds as carcinogenic to humans (Group 1), meaning that there is sufficient evidence for their carcinogenicity in humans (WHO, 2010).

5. Minimal risk to humans (MRLs) of Cd

Estimates of exposure levels posing minimal risk to humans (MRLs) have been made for cadmium. An MRL is defined as an estimate of daily human exposure to a substance that is likely to be without an appreciable risk of adverse effects (noncarcinogenic) over a specified duration of exposure. MRLs are derived when reliable and sufficient data exist to identify the target organ(s) of effect or the most sensitive health effects for a specific duration within a given route of exposure. MRLs are based on noncancerous health effects only and do not consider carcinogenic effects. MRLs can be derived for acute, intermediate, and chronic duration exposures for inhalation and oral routes (Faroon et al., 2012).

Acute duration inhalation MRL of $3x10^{-5}$ mg Cd m^{-3} (0.03 µg Cd m^{-3}) has been derived for acute-duration inhalation exposure (<14 days) to cadmium. While chronic duration inhalation MRL of An MRL of 0.01 µg Cd m^{-3} has been derived for chronic-duration inhalation exposure (≥1 year) to cadmium.

Acute duration oral MRL of >10 mg Cd $kg^{-1}day^{-1}$ have been observed from high exposures to cadmium chloride administered via gavage or drinking water. Although the Baranski (1985) study identified the lowest observed adverse effect level (2 mg Cd $kg^{-1}day^{-1}$) following acute duration exposure, this study was not considered suitable for derivation of an MRL. While chronic duration oral MRL of 0.1 µg Cd $kg^{-1}day^{-1}$ has been derived for chronic-duration oral exposure (≥1 year) to cadmium.

Zerovalent Iron (ZVI)

Zero-valent iron (ZVI) is an effective material, non-toxic, abundant, cheap, easy to produce and its reduction process requires little maintenance (Fu et al., 2014). ZVI is reactive metal with standard redox potential ($E^0 = -0.44$ V). Therefore, it is an effective reductant when reacting with oxidized contaminants such as chromium (Cr) (VI). The removal mechanism of contaminants by ZVI concerns the directional transfer of electrons from ZVI to the contaminants which transforms the latter into non-toxic of less toxic species. On the other hand, ZVI can degrade and oxidize a series of organic compounds in the presence of dissolved oxygen (DO) because of ZVI transfers two electrons to O_2 to produce H_2O_2. When ZVI produce H_2O_2, H_2O was generated by another two-electron transfer from ZVI. However, the combination of H_2O_2 and Fe^{2+} as fenton reaction can create hydroxyl radicals (·OH) which possess strong oxidizing capability towards a variety of organic compounds as in equation 1-4 (Fu et al., 2014).

$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \qquad (1)$$

$$Fe^0 + 0.5O_2 + H_2O \rightarrow Fe^{2+} + 2OH^- \qquad (2)$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2HO^- + H_2 \qquad (3)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + HO^- \qquad (4)$$

ZVI has been successfully applied to groundwater remediation / wastewater treatment, which was contaminated with chlorinated organic compounds (COCs), nitroaromatic compounds (NACs), arsenic (As), nitrate, dye, and phenol. However, ZVI was modified for pollutant remediations. For example, ZVI was investigated to be permeable reactive barriers (PRBs) for the remediation of groundwater contaminated COCs, nitrates and heavy metals. ZVI improvement with Fenton-based oxidation was investigated for the primary treatment of 2,4 - dinitroanisole producing wastewater or for the treatment of 2,4,6-trinitrotoluene (TNT) industry wastewate (Fu et al., 2014). The ZVI was adapted to more surface area and reactivity, which it is zero-valent iron nanoparticles (nZVI), to remove many kinds of contaminants. In addition, ZVI was applied for reducing the mobility and bioavailability of heavy metals in contaminated soils. Several studies of ZVI have shown that it immobilized heavy metals in contaminated soil. For instance, (Kumpiene et al.,2006) specified that ZVI effectively reduces the mobility and bioavailability of As and Chromium (Cr). (Ok et al.,2011) specified that ZVI can inhibit Cd contamination of rice plants by as much as 42%. (Feng et al., 2016) explained that Cu immobilization by ZVI in contaminated soil reduces the bioavailability of Cu. ZVI can also remove contaminants by magnetic separation from soil.

When ZVI was applied in soils, ZVI can be rapidly transformed onto iron (hydr)oxides (e.g. ferrihydrite) with high surface area and sorption capacity. ZVI can adsorb both anions and cations because of they have a variable surface charge and large number of reactive terminal hydroxyl groups. The stronger sorption of anions generates at low pH (higher net positive surface charge), while stronger sorption of cations produces at high pH. At intermediate pH values both cations and anions may be strongly sorbed. Further, metals can be co-precipitated with newly-formed iron (hydr)oxides (Komarek et al., 2013). The mechanisms of ZVI for the removal of the contaminants was shown in **Figure 12**. Critical factors that affect the immobilization capacity of oxidized ZVI include pH and redox conditions, the volume of infiltrating water and microbial activity (Kumpiene et al., 2008), as well as the rate of crystallization of the formed iron (hydr)oxides (Cundy et al., 2008).

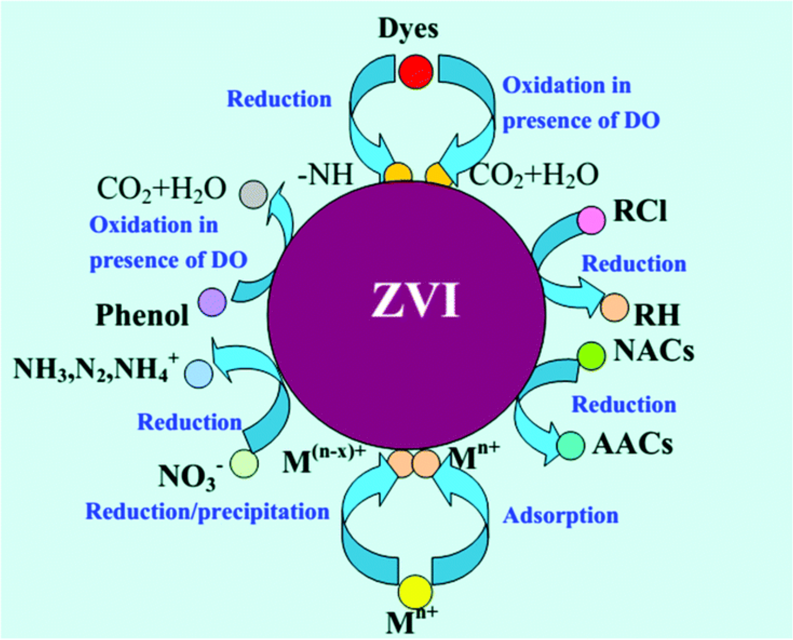


Figure 12 Schematic model of reaction mechanisms of ZVI for remove the different contaminants

Source: Fu et al., 2014

Soil remediation

Once metals are introduced into and contaminate the environment, they may persist for long time depending on the type of metal and soil. Heavy metals are reported to cause several disorders in humans including cardiovascular diseases, cancer, cognitive impairment, chronic anemia, damage of kidneys, nervous system, brain, skin, and bones (Jarup, 2003). Because of potential toxic effects associated with heavy metal exposure, there is a global concern to the heavy metal content of agricultural soil and the crops cultivated. Moreover, people are becoming more aware of the inferences of heavy metal contaminated soils on human and environmental health, resulting in the improvement and development of technologies for remediation of heavy metal contaminated sites.

The conventional remediation technique used for clean-up of heavy metals contaminated soils may be in-situ or ex-situ, on-site or off-site, and biological, physical and chemical as show in **Figure 13**. Soil remediation methods can be broadly divided into three categories: physical, chemical and biological. Physical remediation includes soil replacement, soil isolation, vitrification, and electrokinetic. Biological methods generally include phytostabilization, phytoevaporation and phytoextraction. while chemical methods contain immobilization and soil washing (Khalid et al., 2017). These techniques are often applied in combination for more efficient remediation of pollutants. Each technique has a different advantage and disadvantage. Physical remediations can be applied to highly contaminated sites but are laborious and costly. Chemical techniques, can rapidly manage and effectively remedy the situation. How effective they are, depends on the type of soil, types of chemicals used and the heavy metals to be remedied. Although the biological method is economical and eco-friendly, it is time consuming and limited to moderately contaminated soils. This study reviews some of the available technologies including soil amendment, soil washing and electrokinetic for supporting the feasibility and the evaluation of Cd contaminated soil under consideration.

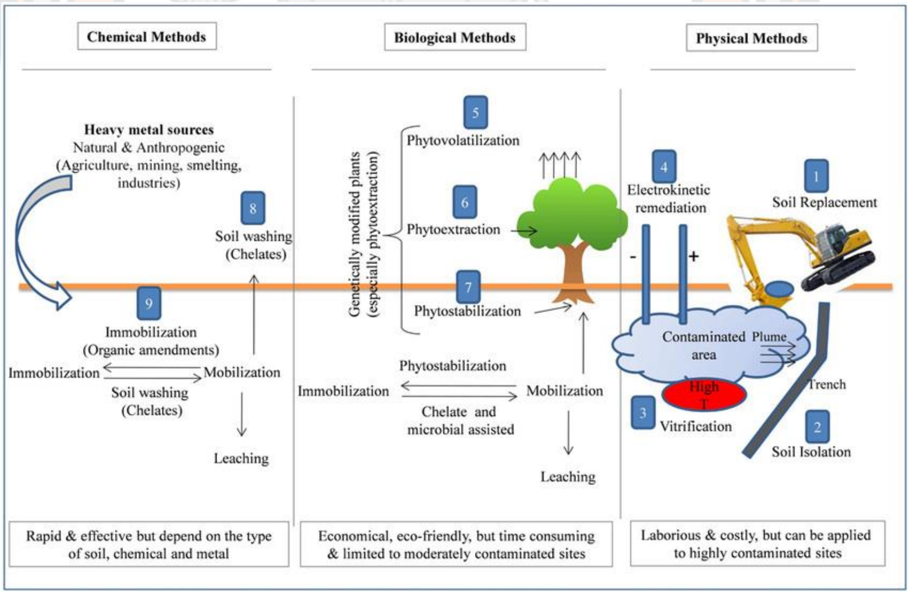


Figure 13 Comparison of different soil clean-up techniques.
Soil remediation methods can be broadly divided into three categories:
Physical, chemical and biological

Source: Khalid et al., 2017

1. Soil amendment

Soil amendment is a chemical technique which refers to a decrease in the mobility, bioavailability and bio-accessibility of heavy metals in soil. Soil amendment techniques can use either to mobilize or immobilize heavy metals in soils. The mobilization technique is conducted by adding mobilizing agents for the release of metals in soil solution through solubilization, desorption, chelation, and/or complexation reactions, which are subsequently removed using higher plants. In contrast, the immobilization technique uses immobilizing agents to immobilise heavy metals in contaminated soils. Heavy metals can be immobilized in soil by complexation, precipitation and adsorption reactions. These processes cause dispersion of heavy metals from soil solution to solid particles, thus limiting their transport and bioavailability in soil (Bolan et al., 2014; Khalid et al., 2017). In this study, the soil amendments involved in the immobilization of metals will be discussed in terms of the growth of rice crops. The immobilization of heavy metals in soil is generally carried out by using organic and inorganic amendment of soils. The more common heavy metal amendment is immobilization including phosphate compounds, liming materials, organic matter, and metal oxides (**Table 4**).

1.1 Phosphate compound

Phosphate (P) compounds enhance the immobilization of metal in soil through various processes including direct metal adsorption/substitution by P compounds, P anion-induced metal adsorption, and the precipitation of metals with solution as metal phosphates. The generation of those processes depends on the source, such as the application of P compounds which can cause direct adsorption of metals into these compounds via increased surface charge and enhanced anion-induced metal adsorption (Bolan et al., 2014). Precipitation with P as metal–P has been proved one of the main mechanisms for the immobilization of metals, such as Pb and Zn, in soil. These fairly stable metal-P compounds have extremely low solubility over a wide pH range, which makes P application an attractive technology for managing metal contaminated in soils. In typical arable soils, precipitation of metals is unlikely, but in modest metal contaminated soils, this process can play a major role in the immobilization of such metals (Bolan et al., 2014).

In previous study, the ability of apatite to immobilize Pb in solution or Pb in contaminated soils through precipitation as Pb–P has been well documented (e.g., (Bolan et al., 2014; Chrysochoou et al., 2007)). Two processes for the reaction of dissolved Pb with apatite have been proposed. Firstly, Pb^{2+} can substitute for Ca^{2+} in apatite. Thus (Ca, Pb) apatite could be potentially formed by adsorption of Pb or by dissolution of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) followed by coprecipitation of mixed apatites. Secondly, Pb^{2+} can react with apatite through hydroxyapatite dissolution, followed by precipitation of pure hydroxy pyromorphite ($Pb_{10}(PO_4)_6(OH)_2$). The addition of P in Zn contaminated sediments resulted in the precipitation of hopeite (Bolan et al., 2014; Ndiba et al., 2008). It has often been shown that the adsorption of specifically sorbent ligands such as HPO_4^{2-} in strongly weathered and variable charge soils can induce Cd adsorption through increased negative surface charge (Bolan et al., 2014; Bolan et al., 1999; NAIDU et al., 1994). The efficiency of P-induced metal in soil can be enhanced by increasing solubility of P compounds. Co-application of phosphoric acid phosphoric acid and rock phosphate effectively immobilized Pb and Zn (Bolan et al., 2014; Cao., 2003). In addition, phosphate solubilizing bacteria were employed to increase Pb immobilization in soil by slowly releasing P from insoluble P rock (Bolan et al., 2014; Park et al., 2011).

1.2 Liming materials

Liming, is primarily aimed at ameliorating of soil acidity, has often been shown to reduce the concentration of Cd, lead (Pb), and other metals in edible parts of crops. Liming enhance sorption of heavy metals by reducing the H+ concentration and increasing negatively charged sites. The addition of alkaline materials such as red mud and lime in a contaminated soil increased the concentration of the residual fraction of Pb and Cd. The pH increase induced by red mud and lime resulted in the precipitation of heavy metals (Bolan et al., 2014; Garau et al., 2007). Similarly liming can alleviate the phytotoxic effects of nickel (Ni) in soil. However, the effect of liming materials in reducing metal uptake by plants has been attributed to decreased mobility in soils via adsorption or precipitation and to the competition between calcium Ca^{2+} and metals on the root surface. Field scales of in situ remediation of heavy metal contaminated soil, the addition of lime and red mud increased soil pH and reducing the availability of metals. (Bolan et al., 2014; Gray et al., 2006).

Lime can be used as a co-amendment to reduce the availability of heavy metals in soil amendments. Lime increased pH and decreased electrical conductivity (EC) through precipitation of soluble ions when it was mixed with biosolids. Water-soluble and DTPA-extractable Cu, Mn, Zn, and Ni were reduced in lime-amended biosolids (Bolan et al., 2014; Fang, & Wong, 1999). Lime treatment in composting significantly reduced the bioavailability and leachability of heavy metals by effectively increasing pH (Bolan et al., 2014; Singh, & Kalamdhad, 2013). In addition, lime or magnesium oxide was used for removal of chromium (Cr (III)) from industrial effluent through precipitate as chromic hydroxide. Precipitation is reported to be most effective at pH 8.5-9.5 due to the low solubility of chromic hydroxide in that range. This method can reduce Cr concentrations to very low levels and hence the precipitation systems are widely used in the tanning process. However, caution should be taken when using lime in Cr concentration soil. Increased soil pH as a base condition enhances the oxidation of Cr (III) to the more mobile and toxic Cr (VI) (Bolan et al., 2014; Bourotte et al., 2009; Pantsar-Kallio et al., 2001), which can negatively affect vegetation and ecosystem health.

1.3 Organic materials

The major sources of organic composts include biosolids, animal manures, zeolites, compost and humus. Immobilization of metals by organic amendments is achieved through adsorption due to increase the cation exchange capacity of soils, such as typical municipal biosolids. Metals form both soluble and insoluble complexes with organic constituents in soils, which the processes apparently depend on the nature of the organic matter. The organic component of soil has a high affinity for metal cations because of the presence of ligands or functional groups that can form chelates with metals. When soil pH increase, the functional groups such as the carboxyl, phenolic, alcoholic, and carbonyl in soil organic matter will dissociate. Therefore, the affinity of ligand and ions for metal cations will increase. In addition, manure application can decrease Cu, Zn in shoot and concentrations in contaminated soil with pyritic waste from mine spill by increasing of soil pH, which it prevents sulfide oxidation/hydrolysis (Bolan et al., 2014; Walker et al., 2004). Similarly, the high metal binding capacities of compost amendment was attributed to high compost humic and fulvic acid concentrations led to enhance the growth of white lupin (*Lupinus albus*) and reduce uptake of Pb and Zn in the soils (Alvarenga et al., 2009; Bolan et al., 2014; Perminova, & Hatfield, 2005). A number of studies have been carried out concerning organic soil amendments decreasing the amount of heavy metals such as Chromium (Cr) and selenium (Se) in the soil. For example, the adding of cattle manure has resulted in the reduction of Cr (VI) to less toxic and less mobilize Cr (III) via both chemical and biological processes (Bolan et al., 2003).

Table 4 Example of using organic and inorganic amendment in soils

Amendment	Metals	Observations	Reference
Phosphate compounds			
KH_2PO_4	Cd	Enhanced immobilization and decreased plant availability.	(Bolan et al., 2003)
Apatite, zeolite, Fe-oxide	Cd, Pb	Reduced the transport and uptake by plant	(Chlopecka, & Adriano, 1997)
Phosphate rock, diammonium phosphate	Cd, Pb, Zn	Reduced metal releasing	(Basta, & McGowen, 2004)
H_3PO_4, Ca ($H_2 PO_4$), phosphate rock	Pb, Zn, Cu	Increased residual fraction of heavy metal, and reduced metal translocation from root to shoot of plant	(Cao et al., 2003)
Liming materials			
$Ca (OH)_2$	Cd	Transformed to less mobile fractions, reduced phytoavailability.	(Bolan et al., 2003)
Lime	Cd, Ni, Zn	Reduced Cd uptake by lettuce and by radish Reduced uptake of Cd, Ni, Zn	(Brallier, Harrison, Henry, & Dongsen, 1996; Han, & Lee, 1996)
Red mud, natural zeolite, lime	Pb, Cd, Zn	Reduced solubility of Pb, Cd and Zn, Changes in microbial communities.	(Garau et al., 2007)
Cyclonic ashes, lime	Zn, Cd	Decreased metals accumulation in plant and Zn, Cd levels in soil pore water	(Ruttens et al., 2010)

Amendment	Metals	Observations	Reference
organic materials			(Bolan et al., 2003)
Biosolid	Cd, Cu, Zn	Reduced the bioavailability, the phytotoxic effect	(Bolan et al., 2003)
Manure	Cu, Cr	Decreased the phytotoxicity	(Bolan et al., 2003)
Compost	Cr, Zn, Cd	Decreased the phytotoxicity, Zn and Cd leaching	(Bolan et al., 2003; Ruttens et al., 2006)
Humus	Cd	Reduced Cd uptake by rice	(Ok et al., 2011)
Hard wood biochar	Cd, Zn	Biochar immobilized metals due to enhanced pH	(Beesley, Moreno-Jiménez, & Gomez-Eyles, 2010)
biochar	As, Cd	The single biochar amendment significantly reduced the bioavailability of Cd	(Qiao et al., 2018)
Metal oxides			
Hydrous Mn oxides	Cd, Zn, Pb	Reduced mobility of Cd, Zn and Pb, and uptake by ryegrass	(Mench, Vangronsveld, Didier, & Clijsters, 1994)
Mn oxides	Pb, Cd	Reduced bioavailable Pb, exchangeable fraction of Cd and Pb, and uptake by Chinese cabbage.	(Cheng, & Hseu, 2002; Hettiarachchi et al., 2000)
Fe-rich waste (Fe(hydr)oxides) with redox cycles	Cd, Cu, Ni, Pb, Zn	Reduced exchangeable Cd, Cu, Zn, and Pb	(Contin et al., 2007)
Fe oxide waste by product	Cd, Pb	Reduced uptake of Cd and Pb by maize and bariey	(Chlopecka, & Adriano, 1996)
ZVI	Cu, As	Decreased As bioavailability, the bio-accessible fraction of Cu	(Feng et al., 2016; Qiao et al., 2018)

Source: Bolan et al., 2014

In addition, biochar, one of organic or carbonaceous materials, that can stabilize heavy metals in contaminated soils, improve the quality of the contaminated soil and has a significant reduction in crop uptake of heavy metals (Zhang et al., 2013). Biochar produced at a lower pyrolysis temperature (<500 °C) usually has attractive attributes for the remediation of inorganic pollutants due to high organic carbon content (at non-carbonized fraction), specific porous structure and numerous functional groups, interact with heavy metals in several ways (Oliveira et al., 2017). Immobilization of heavy metals in soils with the application of biochar could involve a number of possible mechanisms, as illustrated in **Figure 14** (Oliveira et al., 2017). The removal of heavy metals by biochar are mainly via surface interactions through ion-exchange and complexation between biochar functional groups (e.g., OH, COOH, R-OH) and heavy metal ions (Cao et al., 2009; Zhang et al., 2013). Moreover, formation of metal precipitates with inorganic constituents (Cao et al., 2009; Lu et al., 2012) and coordination of metal ions with π electrons (C=C) of biochar (Uchimiya, Wartelle, Lima, & Klasson, 2010). For instance, the mechanisms for Pb2+ sorption by sludge-derived biochar that could include (i) heavy metal exchanges with Ca^{2+}, Mg^{2+}, and other cations associated with biochar, attributing to coprecipitation and innersphere complexation with complexed humic matter and mineral oxides of biochar, (ii) the surface complexation of heavy metals with different functional groups, and innersphere complexation with the free hydroxyl of mineral oxides and other surface precipitation, and (iii) the physical adsorption and surface precipitation that contributes to the stabilization of Pb^{2+} (Lu et al., 2012). In the case of acidic contaminated soils, depending on the type of biochars and exchangeable cations (Na, Mg, K, and Ca) present in it, could hold the key for the release of some of these cations during the sorption process with the heavy metal, and thus may enrich the stabilization process. Lu et al. (2012) further demonstrated that the heavy metal exchange with Ca^{2+}, Mg^{2+}, and other cations (Na^+ and K+) associated with sludge-derived biochar was the main mechanism responsible in their study. However, contribution of monovalent (Na^+ and K^+) cations for heavy metal exchange was found to be negligible. Therefore, it is conceivable that under realistic field situations, sorption mechanisms for metal contaminated soils by biochar could be dependent on the type of soils and the cations present in both soils and biochar. In previous study, biochar application can reduce the bioavailability of heavy metals in contaminated soils (**Table 5**).

Moreover, biochar did have a positive impact on Cd migration due to its greater surface area, alkaline pH, strong sorption capacity and high cation exchange capacity (Qiao et al., 2018; Zhang et al.,2013). Biochar can lead to the raise soil pH, which can greatly reduce the mobility and bioavailability of Cd, mainly by increasing the net negative charge of soil constituents and the capacity of cation exchange sites

(Houben, Evrard, & Sonnet, 2013). This reason promotes the metal precipitation, decrease metal solubility and promote metal adsorption on the biochar particles.

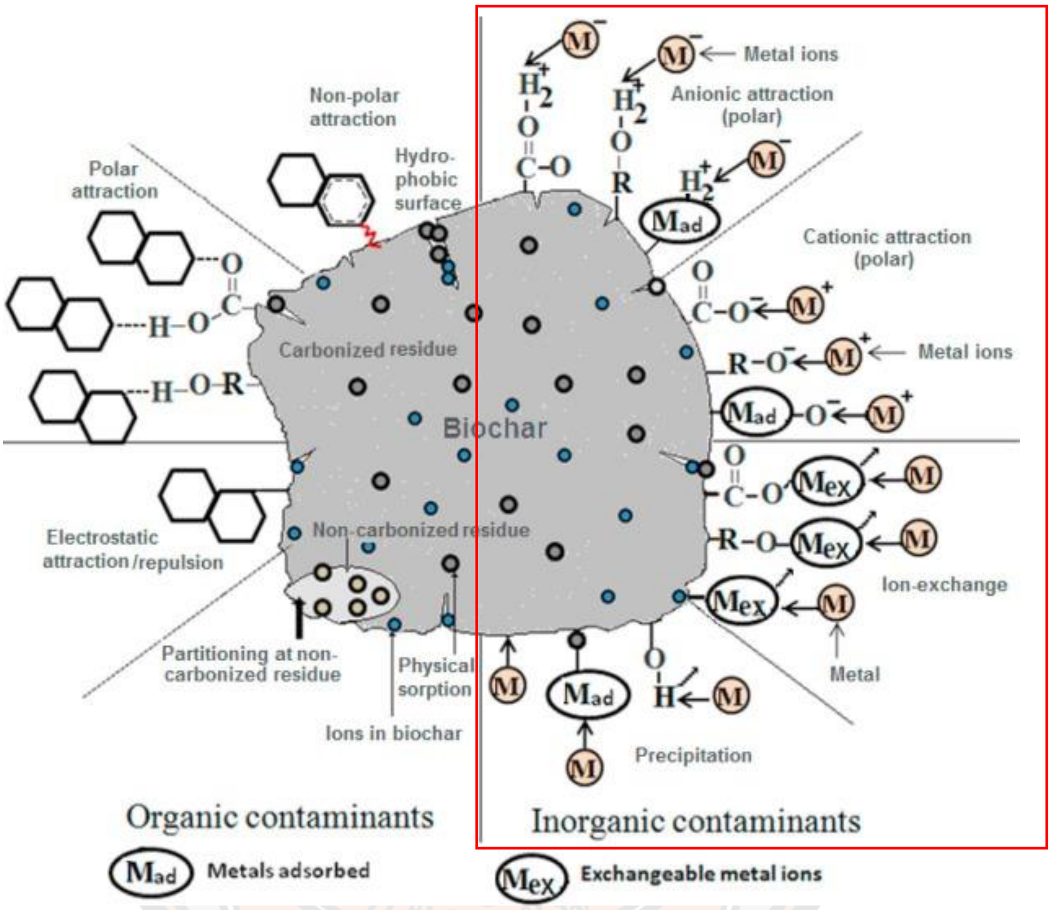


Figure 14 Conceptual illustration of possible mechanisms of organic and inorganic contaminants on biochar

Source: Oliveira et al., 2017

Table 5 Material application of biochar on the bioavailability of heavy metals in soils

Feedstock	Contaminant	Effect	Reference
Cotton stalks	Cd	Reduction of the bioavailability of Cd in soil by adsorption or co-precipitation	(Zhou et al., 2008)

Feedstock	Contaminant	Effect	Reference
hardwood	As, Cu, Cd, Zn	Cd and Zn were immobilized, Cu and As were mobilized	(Beesley et al., 2010)
Orchard prune residue	Cd, Cr, Cu, Ni, Pb, Zn	Significant reduction of the bioavailable Cd, Pb, and Zn, with Cd showing the greatest reduction; an increase in the pH, CEC, and water-holding capacity	(Fellet et al., 2011)
Chicken manure and green waste	Cd, Cu, Pb	Significant reduction of Cd, Cu, and Pb accumulation by Indian mustard	(Park et al., 2011)
broiler litters	Cu	The electrostatic attraction between positively charged Cu and negatively charged biochar is the prevailing mechanism of soil Cu immobilization	(Uchimiya et al., 2011)
Chicken manure	Cr	Enhanced soil Cr (VI) reduction to Cr (III)	(Choppala et al., 2012)
Sewage sludge	Cu, Ni, Zn, Cd, Pb	Significant reduction in plant availability of the metals studied	(Méndez et al., 2012)
Rice straw	Cu, Pb, Cd	Significant reduction in concentrations of free Cu, Pb, and Cd in contaminated soils; identification of functional groups on biochar with high adsorption affinity to Cu	(Jiang et al., 2012)
Quail litter	Cd	Reduction of the concentration of Cd in physic nut; greater reduction with the higher application rates	(Suppadit et al., 2012)

Feedstock	Contaminant	Effect	Reference
Oak wood	Pb	Bioavailability reduction by 75.8 %; bioaccessibility reduction by 12.5 %	(Ahmad et al., 2012)

Source: Zhang et al., 2013

1.4 Metal Oxides

Oxides of metals, such as Fe, Aluminium (Al), and Manganese (Mn), play an important role in metal geochemistry in soils. Because of large, active surface areas and the amphoteric nature of oxides make them suitable for removal/reduction of a wide range of soil contaminants (Bolan et al., 2014) (**Table 4**). Metal oxides can strongly bind metals through specific sorption, co-precipitation, and by forming innersphere complexes. Naturally occurring oxides, synthesized oxide particles, as well as industrial by-products, have been studied for their suitability for use in soil remediation (Kumpiene, 2010) . Normally, metal oxides occur in the soil, such as iron oxides (hematite, maghemite, and magnetite), oxyhydroxides (ferrihydrite, goethite, akaganeite, lepidocrocite, and feroxyhite), and Mn oxides (phyllomanganates and birnessite group of minerals). Zn, Cd, and Pb form mononuclear complexes on goethite and ferrihydrite surfaces, and AsO_4^{3-} and Pb (II) form innersphere surface complexes with hydrous ferric oxide (Bolan et al., 2014; Knox, Seaman, Mench, & Vangronsveld, 2001). Surfaces of iron hydrous oxides play an important role in the retention of Arsenic (As) anions. Positive surface charge leads to adsorption of As anions, and adsorption of As increases at low pH because the surfaces of many oxides are positively charge. Goethite, iron grit, leachates from contaminated soils through a series of leachate extraction tests. Pb and Cd were immobilized with the incorporation of iron (II) and (III) sulfates. In addition, the reuse of iron oxide-based drinking water treatment residuals shows a very effective retention of As. Mn oxide minerals, birnessite showed the greatest adsorption capacity on Pb, Cu, Cobalt (Co), Cd, and Zn, which the maximum sorption capacity by birnessite was Pb (II). The adsorption of metals by birnessite was related to the hydrolysis constants, which indicates that metal adsorption by Mn oxide occurs mainly in the form of hydroxylation cations

(Bolan et al., 2014; Feng et al., 2007). Mn (IV) oxides are known to specifically adsorb Pb. Furthermore, biogenic Mn oxides have a high sorption capacity for metals and also can oxidize metals. Bacteria and fungi enzymatically oxidize Mn (II) and produce insoluble Mn (III, IV) oxides. Metals sorption of Mn oxides occurs by complexation below or above the structural vacancies and at structural sheet edges, and incorporation into the vacancies by isomorphical substitution for Mn. Biogenic Mn oxide produced by bacteria led to Pb, Zn, Ni, and As (V) sorption and As (III) and Cr (III) oxidation (Bolan et al., 2014; Miyata et al., 2007). In addition, nanosized metal oxide such as ferric oxides, Mn oxides, Al oxides, titanium (Ti) oxides, Mg oxides, and cerium (Ce) oxides are considered as adsorbent materials for metal removal from the environment due to large surface areas and high activities (Bolan et al., 2014; Hua et al., 2012). Nanosized alumina synthesized by ammonium acetate fuel was effective in the adsorption of Pb, Ni, and Zn from aqueous solutions. One potentially effective immobilizing agent of metal oxides is zero-valent iron (ZVI), which ZVI is a one of effective, non-toxic, and cheap amendment for reducing the mobility and bioavailability of heavy metals in contaminated soils (Kumpiene et al., 2006). In previous studies, Ok et al., 2011 used ZVI, lime, humus, compost and combination of these compounds to inhibit Cd from rice plant. (Feng et al., 2016) studied the Cu immobilization in contaminated soil with ZVI. In addition, Qiao et al., 2018 presented that ZVI can easily be oxidized by the O_2 in the paddy soils and transformed them into amorphous iron oxyhydroxides (Eq. 5). The reactions of ZVI and H^+/H_2O will generate Fe^{2+} (Eq. 6 and 7), which can be next oxidized via biotic or abiotic processes followed by the formation of amorphous iron oxyhydroxides, such as ferrihydrite (am-FeOOH) (Eq. 8 and 9). The newly formed iron minerals from the above corrosion processes of ZVI can provide many new surface adsorption sites for Cd adsorption and resulting in an increase in Cd immobilization.

$$4Fe^0 + 3O_2 + 2H_2O \rightarrow 4\text{am - FeOOH} \qquad (5)$$

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \qquad (6)$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2 \qquad (7)$$

$$Fe^{2+} + 1/4O_2 + 3/2\ H_2O \rightarrow \text{am-FeOOH} + 2H^+ \qquad (8)$$

$$Fe^{2+} + 1/5NO^-_3 + 7/5H_2O \xrightarrow{\text{FeOBs}} \text{am-FeOOH} + 1/10N_2\ (g) + 9/5H^+ \qquad (9)$$

2. Soil washing

Soil washing is an ex situ process employing physical and/or chemical procedures to extract and separate of organic, inorganic, and radioactive contaminants, including petroleum and fuel residues, radionuclides, heavy metals, polychlorinated biphenyls (PCBs), pentachlorophenol (PCP), pesticides, cyanides, creosote, semi volatiles and volatiles, from soils. The ordinary process procedures excavation of the contaminated soil, mechanical screening to remove various oversize materials, separation processes to generate coarse- and fine- grained fraction, treatment of those fraction (soil washing), and management of generated residuals. It is a separation and quantity reduction process, typical used in combine with other technologies. **Figure 15** presents a schematic diagram of typical options used in soil washing processes for metal contaminated soils: 1) physical separation; 2) chemical extraction; 3) combination of both. Physical separation (PS) concentrates metal contaminants into a smaller volume of soil by exploiting of difference physical characteristics between the metal bearing particles and soil particles (size, density, magnetism, and hydrophobic surface properties). Chemical extraction relates to techniques that try to solubilize the metal contaminants from the soil with an extracting aqueous fluid containing chemical reagents such as acids or chelating agents. In general, physical separation is primarily applicable when metal contaminants are under particulate forms (ideally liberated particle), while chemical extraction is primarily suitable for ionic forms adsorbed on soil or non-detrital metals (Dermont et al., 2008).

Soil washing was applicated on full-scale, significant pilot/field demonstrations and laboratory investigations. Most of the soil washing projects conducted in the US and Canada were for treating metal contaminants in soil. Also, some pilot projects performed in Europe and Korea are gathered. **Table 6** recapitulates laboratory investigations and field application case studies about soil washing including projects involved PS technologies, projects involved CE procedures, and projects involved both PS and CE processes. Most metals frequently treated are Pb (78% of the projects), Cu (43%), Zn (41%), and As (27%) (Dermont et al., 2008).

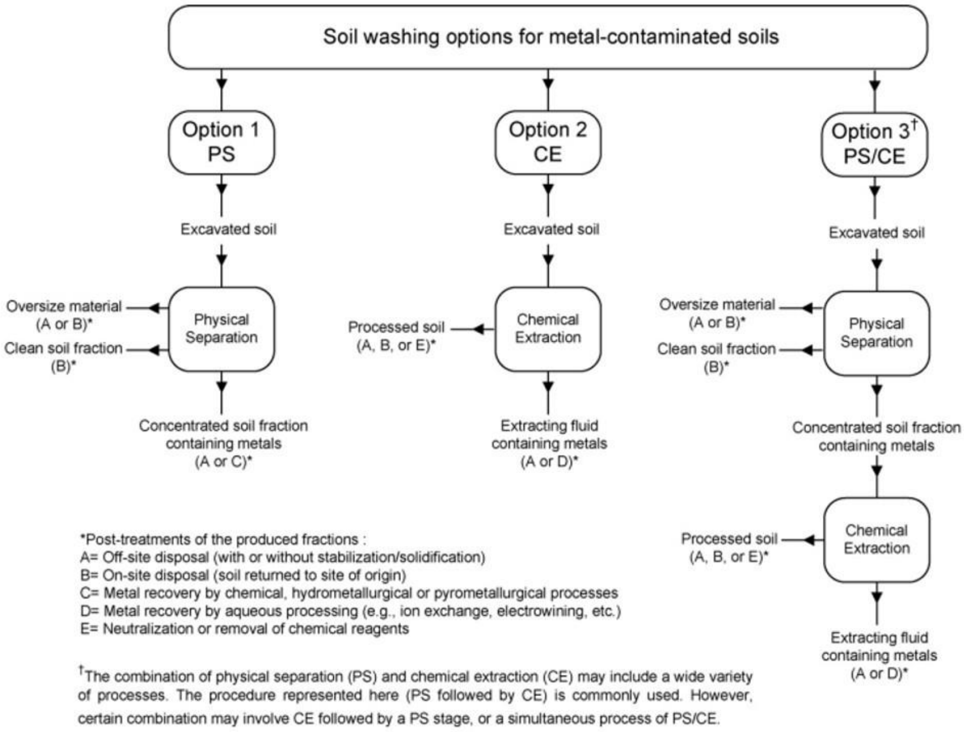


Figure 15 Schematic diagram of typical options used in soil washing processes for metal contaminated soils

Source: Dermont et al., 2008

Table 6 Summary of laboratory investigations and field application case studies about soil washing, modified from

Examples of studies	Metal	Effect	Ref.
Magnetic separation (HIMS) on six soils in the Netherlands (results with soil “L”)	Cu Cr Pb Zn	Use of high intensity magnetic separation (HIMS) with dry and wet separators (63–2000 µm), which removal efficiency range 46-96 % and volume reduction of contaminated soil range 87-93 %	Rikers et al., 1998
Evaluation of physical separation technologies for	Cu Pb Zn	Using gravity concentration technology and spiral concentrator; shaking table (63-850µm), jig (850-	Mercier et al., 2001

Examples of studies	**Metal**	**Effect**	**Ref.**
remediation of six brownfield soils (polluted by landfilling of various wastes in Quebec City, QC, Canada (results with soil "A1", 90% of sand)		2000 μm) show that remove Cu 52% jig and 89% shaking table, remove Pb 61% jig and 67 % shaking table, and remove Zn 58% jig and 54 % shaking table	
Using EDTA for removal artificially contaminated sandy soil	Cu	80–90% of Cu was removed within 5 h of the leaching. Cu removal strongly depended on liquid/solid (L/S) ratio and EDTA/Cu ratio. Best results were obtained with L/S = 12.5 and EDTA/Cu = 12.5	Di Palma et al., 2005
*Using of surfactants improved EDTA leaching for removal Soil contaminated by metals and PCB in Montreal, Canada	Cd Cr Cu Ni Pb Zn	removal efficiency with EDTA + surfactant (non-anionic) was effective for Pb (73%) and moderately effective for Cu (49%), Cd (36%) and Zn (44%). removal efficiency was ineffective for Cr and Ni (mainly associated with residual soil fraction)	Mulligan et al., 1999
*Using EDTA with HCL for two urban soils in Montreal, Canada	Cd Cu Pb Zn	Acid washing with low HCl conc. was ineffective because the soils had high buffering capacity. EDTA was more effective. RE depended on EDTA dosage (best result with high conc.). High silt/clay content affected metal removal efficiency	Tejowulan, et al.,1998
Using HCl and $CaCl_2$ for two contaminated rice soils in Taiwan	Cd Cr Cu Ni Pb Zn	the use of CaCl2 increased removal efficiency in diluted HCl (<0.01 M) for Cd removal. Fe–Al oxides are attacked by HCl with dosage >0.01 M	Kuo., et al., 2006

Examples of studies	Metal	Effect	Ref.
Using NaCl/HCl/EDTA for two soils from abandoned Pb-battery recycling sites, TX and FA	Pb	Best results (RE = 97%) were obtained with successive two-step extraction (L/S = 7, time = 1 h) using acidified (pH 4) NaCl solution (4.3 M to saturated 6 M). Kinetic study suggested that Pb removal mechanism is composed of three stages: (1) extraction of free-Pb precipitates (quick process: <1 min); (2) cation exchange of Pb located on soil surface (30 s to 5 min); (3) removal of Pb located within soil structure (slow process Pb after 5 min)	Nedwed et al., 2000
Pilot-scale demonstration (Environment Canada program) of Tallon's physical separation unit (mobile system) at Dickson site, Montreal, QC, Canada (1993)	As Cu Pb	It can remove 50-60% of As, <25 % of Cu and Pb	CCME, 1995
**Pilot-scale demonstration of the physical separation process in fixed facility (INRS and Dragage Verreault Inc.) for remediation of brownfield soils from Montreal, QC, Canada (2000)	Cu Pb Zn	It can remove 52-56% of Cu, 26 - 60 % of Pb, and 21-22% of Zn.	Bergeron, 2005

Examples of studies	Metal	Effect	Ref.
**Pilot-scale demonstration of BESCORP's Particle Separation System (mobile system) at the SAFR site, Fort Ord, CA (period 2001–2005)	Pb Cu	It can remove 95% of Pb	BESCORP, 2005; NJDEP, 2001
**Pilot soil washing/leaching test (combine of physical & chemical process) for remediation of soils from battery-breaking site in Fairbanks, AK (2001)	Pb	The size separation; density separation by jig can remove 84-88% of Pb and leaching with chloride solution (NaCl, 2 M; HCl, pH 2) and oxidant (NaOCl) can remove 96% of Pb	Lin et al., 2001
**Pilot-scale study (combine of physical & chemical process) for remediation of contaminated soils from mining area, Seoul, Korea (2006)	Cu Pb Zn	The size separation (screening, spiral, hydro cyclone) and acid leaching (HCl, pH 2–3) can remove 44-60 % of metals	Mercier, et al., 2007

Note: * the process was supported with leachate treatment

** the process was supported with management of the processed soil and washing residuals.

Table 7 The advantages ang disadvantages of soil washing

Type	Advantages	Disadvantages*
physical separation	- can treat both organic and metal contaminants in the same system - reduce the volume of soil to be further treated (for metal recovery) or to be disposed of off-site - the treated soil can be returned to the site at low cost - the recovered metal may be recycled in certain cases (e.g., sent to smelting facility) - the treatment train systems and some mobile unit systems are available at full-scale for onsite remediation - they are well established in the mineral processing industry and the operational costs are usually low.	- this treatment system requires a large equipment outlay and large spaces for soil treatment - the volume of soils to be treated must be large to be cost effective - wash-water treatment and off-site disposal of residual solids may be required, which significantly increases the cost
chemical extraction	- sorbed metal forms can be treated - some metal compounds can be dissolved - the fine-grained soils may be treated (certain cases) - the extracted metals may be easily recovered by a wide variety of methods	- using chemical agents can increase processing costs - the processed soil may be inappropriate for cultivation and on-site disposal because physicochemical and microbiological properties have been affected

Type	Advantages	Disadvantages*
		- toxic chemical agents in the final soil or the residual sludge may be problem for disposal - certain chemical agents in the wash fluid can complicate recycling and treatment, thus increasing the cost of this process - the treatment of sludges rich in metal can be difficult.

Note: *the disadvantages of systems are due to large-scale application

3. Electrokinetic

Electrokinetic (EK) remediation is a well-studied technology for the remediation of contaminated soils, sludges, and sediments. It has attracted increased interest among scientists and governmental officials in the last decade. This method aims to remove contaminants from low permeability contaminated soils. The contaminants removal is based on the application of a low levels electric field (1 DCV/cm is generally accepted) via two electrodes (anode and cathode) directly inserted in the soil specimen, thus forming an electric field in the targeted soil area. When an electric field is applied to soil, it stimulates to occur several physical and/or chemical mechanisms, such as the migration of electricity, pore fluid, ions and fine particles across the soil towards the oppositely charged electrode, which have the efficiency to support to the mobilization and transportation of the contaminants from soil (Cameselle, & Gouveia, 2018; Nasim et al., 2012; Virkutyte et al., 2002). The EK technique has widely been used to remediate contaminated soils, contaminants in the aqueous phase or contaminants desorbed from the soil surface are transported towards electrodes depending on their charge.

Heavy metals are one of the main contaminants that are removed by the EK process. Heavy metals and other positively charged species are highly attracted and sorbed on the negatively charged clay surfaces. The migrated species can then be removed by several different methods, such as electroplating, adsorption onto the electrode, precipitation and co-precipitation at the electrode or pumping near the electrode. EK soil treatment induces the many changes in the pore fluid chemistry, diffuse double layer (DDL), soil fabric and the hydraulic conductivity. In fact, the presence of DDL of clay minerals gives rise to several EK phenomena in soil (Nasim et al., 2012).

The direction and quantity of pollutant movement is influenced by the pollutant concentration, soil type and structure, and the mobility of pollutant ions, as well as the interfacial chemistry and the conductivity of the soil pore water (Virkutyte et al.,2002). Electrokinetic technique is possible in both saturated and unsaturated soils. Electrokinetic treatment relies on several interacting mechanisms, including electrolysis, electro-osmosis, electrophoresis and electro-migration **(Figure 16)**. Electrolysis stands for chemical reactions associated with the electric field which generate H_2 and OH^- at the cathode (reduction) and O_2 and H^+ at the anode (oxidation) as follows:

Anode: $2H_2O - 4e^- \rightarrow O_2\uparrow + 4H^+$ $E_0 = -1.229$ (10)

Cathode: $2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^-$ $E_0 = -0.828$ (11)

The acid front generated near the anode and a base front produced near the cathode and that migrate towards each other. The acid front moves faster than the base front due to the higher mobility of H^+ than OH^- lead to the acid front carries toward the cathode. Electroosmosis is the movement of the pore fluid from anode to cathode through the capillary influence of an electric field. Electrophoresis is the motion of charged particles (usually micelles or colloids) relative to a fluid under an electric gradient, while electromigration is the transport of the ions or charged electrical species under an electric gradient (Nasim et al.,2012; Virkutyte et al.,2002). The rate of movement and direction of an ionic species is dependent upon its charge, both in magnitude and polarity, plus the magnitude of the electro-osmosis-induced flow velocity. While non-ionic species, both inorganic and organic, will also be carried along with the electro-osmosis induced water flow (Nasim et al.,2012). Several investigations applied and improved the removal of pollutants from soil by EK process as show some investigated in **Table 8**. Compared to other remediation technologies, EK has several advantages, such as being less expensive (cost-effective), being applicable both in-situ and ex-situ, rapid installation and easy to operate (simplicity), having silent operation, having the advantage of not disturbing the site activities, and relatively short treatment duration. On the other hand, it has some limitations, such as the surface of the electrode attracts the gas generated from the electrolytic dissociation process and increases the resistance lead to significantly slows down the remediation process, OH^- ion are formed react with cations and form a sediment, which plugs the spacing between soil particles, subsequently hindering the electrical current and decreasing the diffusive flow over time when the voltage is applied, and enhancement the efficiency of EK with alternative technique, example injection of appropriate chemical stabilizers or optimize all variables (e.g. current and voltage levels, processing time, installation and operation costs, etc.) (Nasim et al., 2012; Virkutyte et al., 2002).

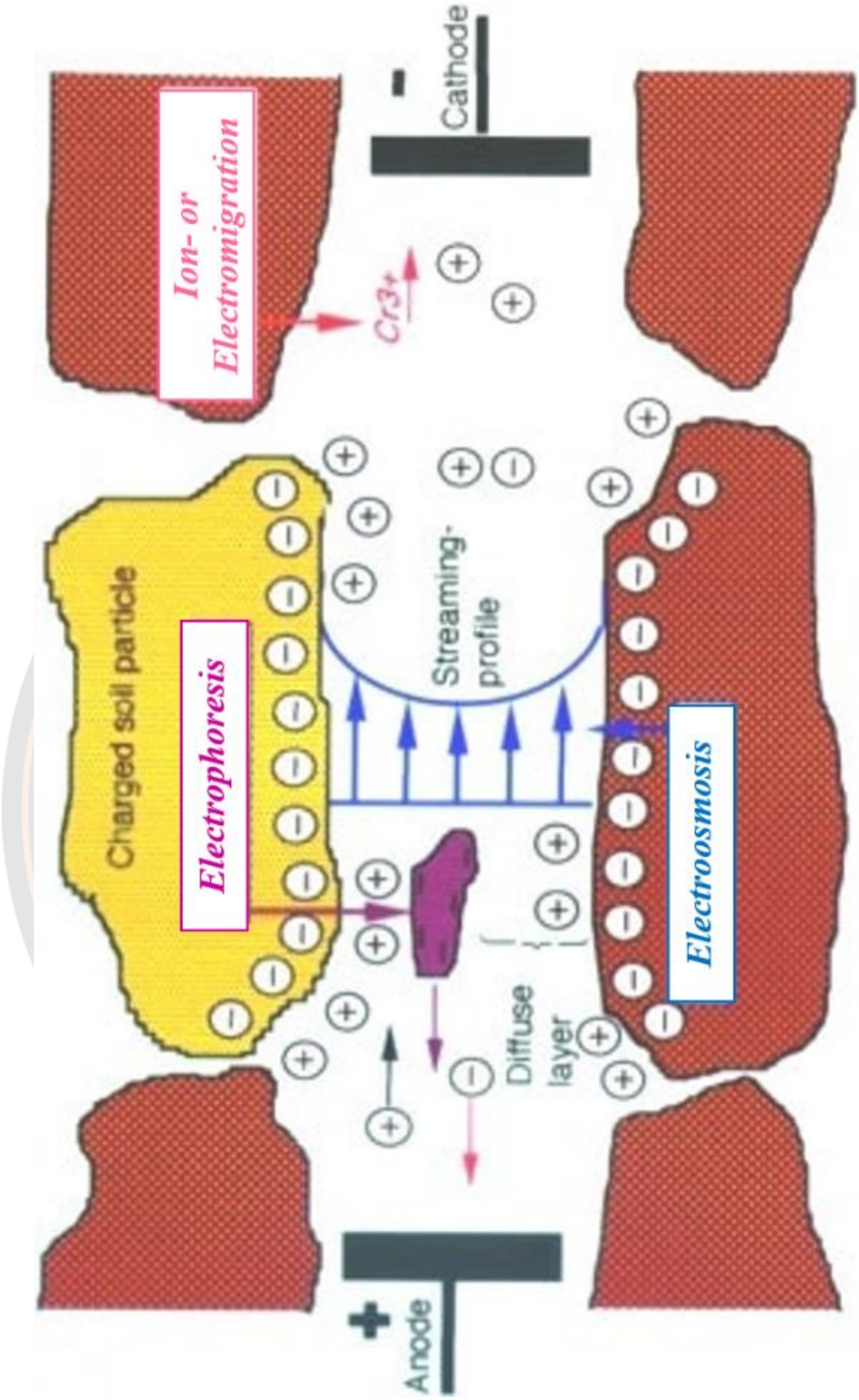


Figure 16 Present The 4 mechanisms in an electrokinetic treatment

Source: Nasim et al., 2012

Table 8 The electrokinetic remediation technologies for the removal of contaminants in soil

Technology	pollutants	results	Ref.
EK & bipolar electrode	Cu	removal increased to 42% when using bipolar electrode	(Hansen, Rojo, & Ottosen, 2007)
EK & solar cell	Cd	solar cell could be used to drive the electromigration of cadmium in contaminated soil, and removal efficiency achieved by solar cell was comparable with that achieved by DC power supply.	(Yuan et al., 2009)
EK & ion exchange cathode	Cr, Cu, Zn	Occurred metal accumulation in cathode. This was a result of metal cation complexation with Cl^- released from the anion exchange resin that changed the direction of metal migration.	(Rajić et al., 2013)
EK & chelate agents	Cd, Pb Cu	removal efficiency for Cd was 65–95%, for Cu 15–60%, but for Pb was less than 20%	(Giannis, Nikolaou, Pentari, & Gidarakos, 2009)
EK & sodium salt coated nZVI	Cr (VI)	enhance the delivery of nZVI for the reduction of Cr (VI) to the less toxic trivalent chromium.	(Gomes et al.,2012)
EK & Co-solvents	Petroleum hydrocarbons	70% ethanol in water as processing fluid favored the large electroosmotic flow and hydrocarbon removal	(Karkush, & Altaher, 2017)
EK & Surfactant	Phenanthrene Heavy metals	61% removal of phenanthrene with Brij 35	(Saberi, Aghababaei, Ostovar, & Mehrnahad, 2018)

Technology	pollutants	results	Ref.
EK & Biosurfactant nZVI	Phenanthrene Trichlorophenol	Enhanced mobility of contaminants with rhamnolipid Removal: 50% Phenanthrene, 65% trichlorophenol	(Sun, Gao, Zhang, & Zou, 2017)
EK & nZVI	HOCs	Iron nanoparticles resulted in the 22–98% removal of HOCs.	(Jiang et al., 2018)
EK & Bioremediation	Diesel hydrocarbons	36% removal of diesel hydrocarbons at 1.5 DCV/cm. 10days. Enhanced biological activity in soil	(Mena, Villaseñor, Rodrigo, & Cañizares, 2016)
EK & Phytoremediation	Heavy metals PAHs	AC electric current enhanced plant growing and slightly enhanced contaminants removal	(Chirakkara, Cameselle, & Reddy, 2016)

Source: Cameselle, & Gouveia, 2018

Cost-benefit analysis

Cost-benefit analysis (CBA) is a basis for an environmental policy which was applied by a decision-makers. CBA is applied to environmental policies in order to compare the social costs and benefits (Feuillette et al., 2016; Hansson, 2007). In the 1980s and early 1990s, most of the environmental policy was developed, reducing health risks for humans and for the environment was the major factor in setting environmental quality standards, and the precautionary principle played a large role (van Wezel, Franken, Drissen, Versluijs, & Van den Berg, 2008). Currently, people demand to exist with efficiency in environmental policies, i.e., how much reduce the risk with our money? CBA can play a role in answering that demand. In previous, CBA was applied for environmental contamination such as using CBA of phytoremediation for heavy metal contaminated soil (Wan, Lei, & Chen, 2016), application for health benefits in drinking water systems (Bergion, Lindhe, Sokolova, & Rosén, 2018), or evaluation of economic benefit of remediation in Norway or Netherlands (Barton, Navrud, Bjørkeslett, & Lilleby, 2010; van Wezel et al., 2008).

Assessment of values through monetary indicators is relatively easy when they are connected with market prices (e.g. material cost, the product of rice), but it is more complex to capture the non-market cost (e.g. health cost) (Feuillette et al., 2016). Monte Carlo Simulation (MCS) is one of the most common methods applied to accommodate the uncertainties associated with many risk-related problems or complex problems, and it has been recognized as a means of quantifying variability and uncertainty in risk assessments by the National Academy of Sciences and USEPA. MCS presents a great opportunity for estimating how the distribution of input parameters affects the distribution of the final result. This technique provides a quantitative way to estimate the probability distributions for exposure and health risks within the validity of the assessment model (Poulter, 1998; Qu et al., 2012; USEPA, 1997; Zupunski et al., 2010). In order to obtain more reasonable data and get the most significant factors, probabilistic models based on Monte Carlo simulation were applied in the previous research. For example, assessment of health risk of heavy metal soil pollution in China (Qu et al., 2012), simulation of the health risk level of 16 PAHs in soil in Shanghai, China (Tong, & Yang, 2017), the assessment of nitrate health risk in drinking water resources of the Iranshahr city, Sistan and Baluchistan province in Iran (Shalyari, Alinejad, Hashemi, RadFard, & Dehghani, 2019).

A concept of this study is an integrated economic decision analysis including the analysis of the expenses of health risk and remediation cost as well as other risk management activities in the past and in the future in order to make an appropriate decision on a remedial selection with maximum social benefit. For health risk, we will simulate with MCS to predict the expense of health outcome associated with Cd exposure base on the data in this study area. We will get a health outcome and health expense from this model. After that health expense was compared with remediation cost using the net present value (NPV). The NPV is the sum of discounted costs and benefits, using a social discount rate in order to account for time preferences and productivity of capital (Bergion et al., 2018).

Summery of knowledge

The problem of rice and paddy area at Phatat Pha Daeng and Mae Tao Mai sub-districts, Mae Sot, Tak Province, Thailand were accumulated with Cd. Irrigation is sourced from Mae Tao Creek the upper stretches of which pass through an actively mined Zn-mineralized zone. Mae Tao Creek is utilized for irrigation by the eight communities with a combined resident population of 5,796 and an annual combined rice production of 7,592 t year $^{-1}$. However, the total area under paddy rice for the 8 villages is 2,201 ha (Simmons et al., 2005). The residents in contaminated area required to remedial methods, which suit traditional rice culture and don't have the pollutants. Therefore, the restorations, including soil amendment, soil washing and EK, were selected to study for this area. ZVI material has a potential in heavy metal stabilization and its magnetic character (**see in topic "Zerovalent Iron (ZVI)"**), thus it was considered for those restorations. ZVI amendment technique will suit the low Cd level area and can remediate together with crop cultivation. While soil washing will use physical and chemical options by using ZVI for Cd-ZVI stabilization and then separated with magnetic separated machine or using electric field via two electrodes. Matching of these techniques is newly alternative method for remediation of Cd contaminated area in Thailand. Moreover, integrated economic decision analysis can predict the cost-benefit accuracy of each remedial technique, which helps in the consideration of appropriate restoration of Cd contaminated areas in the Mae Sot district, Tak province, Thailand.

CHAPTER III

RESEARCH METHODS

The processes of this study follow the plan outlined in **Figure 17**. The investigated scales of this study include experiments in the field as well as laboratory experiments. The field experiments comprised soil amendment and magnetic-assisted soil washing, which were tested in a Cd contaminated paddy field. The solar-powered electrokinetic separation was conducted to treat Cd contaminated soil in the laboratory. In addition, this study evaluated the cost-benefits of risk management from the alternative technique for Cd contaminated paddy soil in the Mae Sot district of Tak province, Thailand. In order to provide the results, we follow below steps:

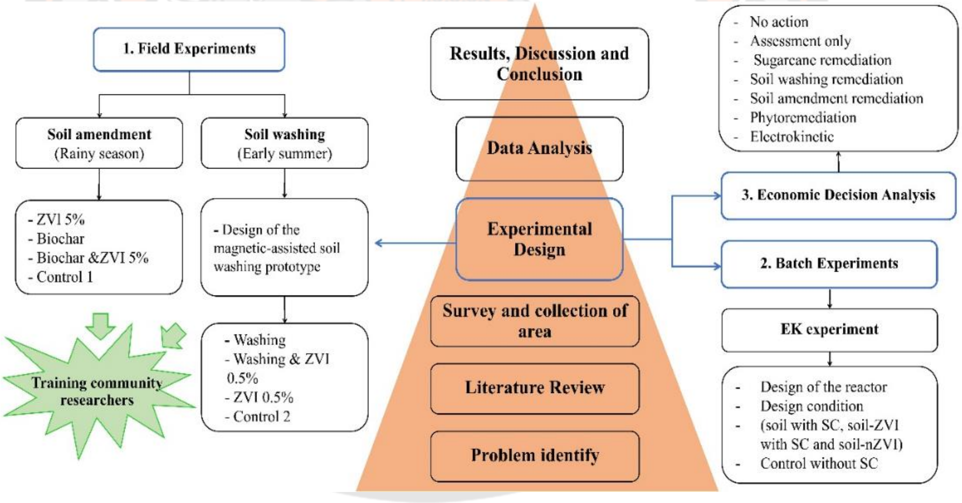


Figure 17 Conceptual Framework

Study area and Physicochemical Soil Properties

1. Survey and Collection of Study Area

Phatat Pha Daeng subdistrict, Mae Sot, Tak Province, Thailand was determined for both field and laboratory experiments. This area was found to be contaminated with cadmium as the rice fields were irrigated with water from the Mae Tao and Mae Ku creeks, which flow through zinc mining areas. See 8.1. below. The low land and up land in Phatat Pha Daeng were surveyed for consideration in the investigation. Cd concentration in soil samples from both areas were screened and it was found that Cd levels in lowlands ranged 23.21- 48.31 mg Cd kg^{-1} higher than in the up lands. Therefore, samples from the low-lying areas **(Figure 18)** were collected for investigation in this study. The location of this area is shown in **Table 9**.

2. Physicochemical Soil Properties

The heavy metal concentrations were determined from six random composite soil samples. The concentrations of Cd, Zn and Fe in the soil samples were determined using atomic absorption spectroscopy (AAS) (Hitachi High-Tech–Z-2000) after microwave-assisted acid digestion (Milestone Ethos Easy) with 10 mL of 65% nitric acid following the EPA method (3051a). Triplicate samples were done for each soil sample. Moreover, a five-step sequential extraction for Cd in the initial soil samples were determined according to the procedure described in **Table A1 (in Appendix)**. The selective extractions were conducted in centrifuge tubes (polypropylene, 50 mL) to minimize solid material loss. Between each successive extraction, separation was performed by centrifugation at 2500 rpm for 30 min. The supernatant was removed for the analytical step, whereas the residue was washed with 20 mL of deionized (DI) water and centrifuged for 30 min. This second supernatant was discarded prior to adding the extractant for the next step. The Cd concentration in extractants were quantified by AAS as discussed in this section. This will result in five chemical fractions of Cd: exchangeable, carbonate, Fe-Mn oxide, organic/sulfide, and residual fractions. Other physicochemical characteristics of paddy soil, including the pH, organic carbon, cation exchange capacity (CEC), exchangeable cations, and soil texture, were determined using appropriate methods. The soil pH was measured with pH meter by making soil slurry at the soil-to-DI water ratio of 1:5 (Rayment, & Higginson, 1992). The organic matter in soil was determined following the Walkley - black method (Schulte & Hoskins,2011). The cation exchange capacity (CEC) and exchangeable cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) was determined by the Kjeldahl distillation after saturating the samples with 1 M NH_4OAc. The concentrations of Ca^{2+}, Mg^{2+}, K^+ and Na^+ in each extractant were quantified using AAS (Stritsis, Steingrobe, & Claassen, 2014). In addition, the soil texture and particle size analysis were determined by hydrometer method and characterized based on the USDA textural triangle (Ashworth, Keyes, Kirk, & Lessard, 2001).

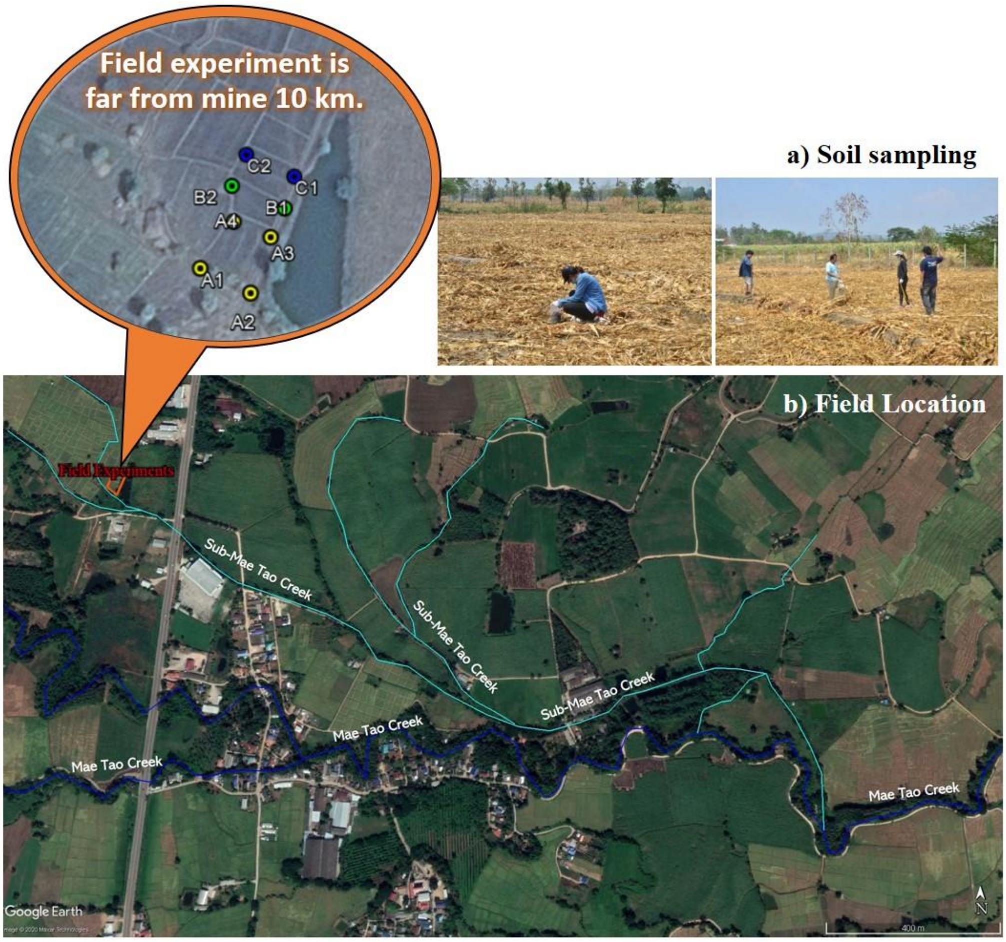


Figure 18 Survey and collection of study area in this research (picture a) taken in 2015)

Table 9 the location of the study area in this research

Station	**Level (m.)**	**Location**	
		N	E
A1	226	16° 40.549	098° 35.779
A2	228	16° 40.543	098° 35.791
A3	228	16° 40.556	098° 35.795
A4	226	16° 40.560	098° 35.786

Station	Level (m.)	Location	
		N	E
B1	227	16° 40.563	098° 35.798
B2	227	16° 40.569	098° 35.785
C1	227	16° 40.571	098° 35.800
C2	227	16° 40.577	098° 35.788

Field Experiments

1. ZVI and Biochar

The ZVI was a by-product from a bearing manufacturer. The ZVI was cleaned three times using detergent and water. Biochar was from the pyrolysis of chaff rice at 600°C. Physicochemical characteristics of ZVI and biochar, including particle size, morphology, mineralogy, and surface areas, were examined using sieve analysis, a scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (Philips Leo 1455 VP), X-ray diffraction (XRD; PW 3040/60, X'Pert Pro MPD), and a Brunauer–Emmett–Teller surface area analyzer (Micromeritics TriStar II), respectively.

2. Magnet-assisted Soil Washing

The magnet-assisted soil washing prototype was designed and assembled (**Figure 19**). It consists of two major parts: a magnetic separator and soil slurry mixing tanks. The magnetic separator consisted of a rotating cylindrical magnet (0.2 m. in diameter and 0.45 m. in length with the surface magnetic flux density around 3,000 ±500 gauss) and a rubber wiper to remove Cd-sorbed ZVI particles from the cylindrical magnet (**Figure 19a)**. On the other hand, the soil slurry mixing tanks were 200-litre plastic tanks with the diameter of 0.58 m and the height of 0.90 m (**Figure 19b**). The total volume of each tank was 0.71 m^3. Each tank had a mixing paddle with the diameter of 0.31 m which was driven by a motor at 600 rpm.

The washing process starts with mixing soil, water, and ZVI in the tanks for 6 hrs to promote Cd adsorption to ZVI from the soil. In the mixing tanks, Cd adsorption to ZVI from the soil via surface complexation occurred, as proven by a recent laboratory experiment (Phenrat, Hongkumnerd, Suk-in, & Khum-in, 2019). Next, the soil slurry was drained from the mixing tanks to the magnetic separator to separate Cd-adsorbed ZVI from the slurry. In this process, Cd-adsorbed ZVI was magnetically attached to the magnetic core and wiped out to another tray using a rubber wiper. In this process, the soil slurry after ZVI removal was discharged to a sedimentation tank. The washed and sedimented soil particles were delivered back to the paddy field for rice cultivation.

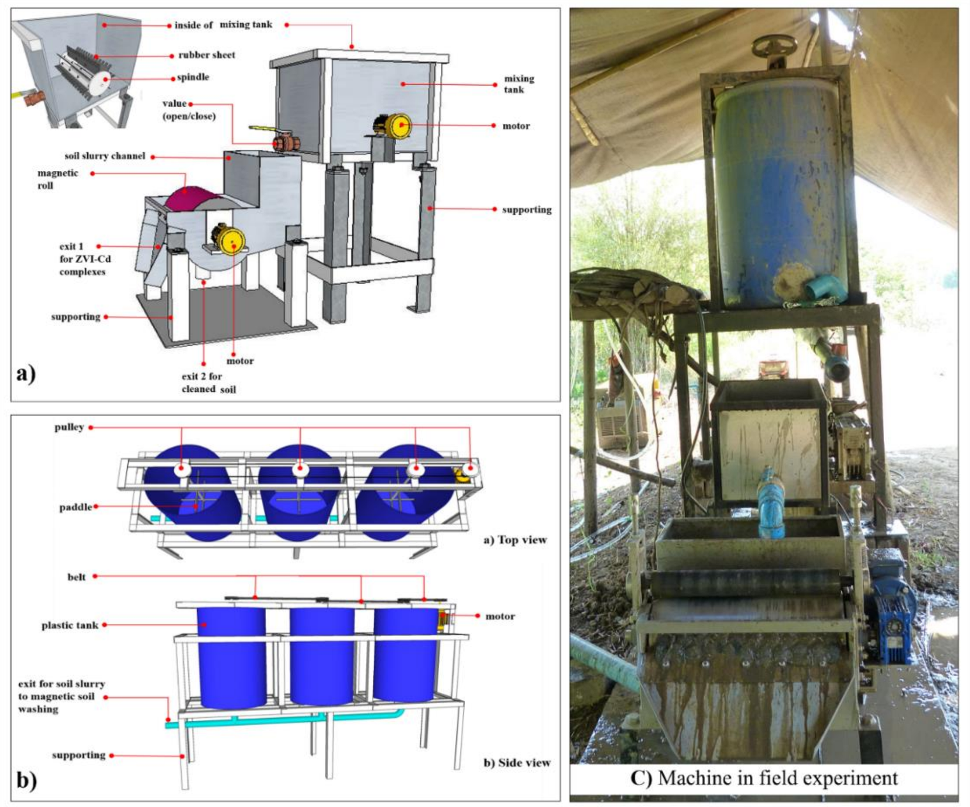


Figure 19 The magnetic-assisted soil washing prototype for Cd removal from soil (picture c) taken in 2015)

3. Field Experiments

The field experiments involved two steps. First, Cd-contaminated paddy soil (from the surface to 15 cm deep) was treated using soil amendment, soil washing, or bot (**Table 10**). Second, rice plantlets were cultivated in treated paddy soil. In this step, soil and plant samples were collected to quantify Cd, Zn and Fe concentrations at different rice-growth stages. The main indicator for successful remedial actions was lowering the Cd accumulation in rice to meet the maximum allowable Cd level in polished rice. Each experiment was conducted in duplicate in the pilot plants (2 m x 4 m; **Figure 20** and **Figure 21**).

Two rounds of field-scale experiments were performed. First, the soil restoration was evaluated using soil amendment including biochar, ZVI, and BZVI. This was performed in the rainy season (i.e., from August 2016 to November 2016). Soil curbs (30 cm high) were made at each field boundary to store water (**Figure 20b**) and avoid mixing treatments. For the first experiment round, the field was flooded to match the practice of local farmers during this season. The irrigation water was from rain and Mae Tao Creek. The amendment doses for different treatments are summarized in **Table 10**. A control experiment (CE) without soil amendment was also performed (CE 1).

Second, soil restoration was evaluated using magnet-assisted soil washing. From winter to the beginning of summer (i.e., from November 2016–March 2017), fields with soil curbs similar to the first round were used. Nevertheless, the field was unflooded most of the time because of seasonal conditions, matching the practice of local farmers who cultivate rice during this period. The irrigation water was from Mae Tao Creek. Magnet-assisted soil washing was performed as described in **Section 2 Magnet-assisted Soil Washing** with soil slurry (soil-to-water ratio: 1:2) at the ZVI dose of 10 g kg^{-1} for 6 hrs. Two soil washing experiments were examined (**Table 10):** one applied magnet-assisted soil washing alone and the other also applied ZVI to the washed soil **(see Figure 21)**. These two experiments were compared to examine whether soil amendment is needed after soil washing for irrigation water, upgradient soil, and run-off that are still contaminated with Cd. However, the ZVI concentration (0.5%) in this combined treatment was 10 times lower than the soil amendment using ZVI alone (5%) in the first round because using ZVI after the washing experiment was only to sequester additional Cd from the irrigation water or contaminated run-off. A CE without soil washing or amendment was also performed (CE 2).

More importantly, we trained community researchers to perform experimental field procedures including soil washing, soil amendment, and rice and soil sampling. The samples collected by the community researchers were shipped to our laboratory for chemical analyses.

Table 10 Amendment dose in each treatment

Treatment	Soil Amendment	Soil Washing or Soil Washing & Amendment
Control	Unamended soil	Unamended soil
Biochar	0.8% w/w biochar	–
BZVI 5%	0.8% w/w biochar & 5% w/w ZVI	–
ZVI 0.5%	–	0.5% w/w ZVI
ZVI 5%	5% w/w ZVI	–
Washing 1%	–	1% w/w ZVI (for soil washing)
Washing +ZVI 0.5%	–	1% w/w ZVI (for soil washing) & 0.5% w/w ZVI (for soil amendment)

Note: *Biochar and BZVI modified from Ok et al., 2011

*ZVI dose developed from laboratory experiment.

4. Preparing and analysis of soil and rice plants

For rice cultivation in the treated soil, 187 rice plantlets (Oryza sativa L.; cv. Khao Dawk Mali 105) seeded in uncontaminated areas for 4 weeks were transplanted in each treated soil sample. The initial Cd concentrations in the plantlets transferred to the field studies were 0.0484–0.1248 mg kg^{-1} in the root, 0.0486–0.1244 mg kg^{-1} in the stem, and 0.0484–0.1245 mg kg^{-1} in the leaf. Surface soil samples (0–15 cm) were collected every 14 days until the harvest period. Similarly, rice plant samples were collected during the seedling stage (first 4 weeks), 60 days after the seedling stage (heading state), and during the harvesting stage (mature state). All samples were stored at 4°C and brought to the laboratory for preparation and analysis.

A five- step sequential extraction for Cd fraction in initial and harvest soils were determined according to the procedure described in **Table A1** and **Section 2 Physicochemical Soil Properties**. The soil samples were oven- dried at 105 ̊C for 24 h prior to being ground by mortar and sieved through a 2 - mm sieve to remove gravel. The equipment for soil preparation are show in **Figure 22**. The rice samples were separated into root, stem, leaf, husk, and grain fractions. Rice stem and roots were washed thoroughly in tap water to remove soil and then rinsed with deionized water. All rice parts were dried at 70 ºC for 72 h and ground to a fine powder for future analysis (Qiao et al., 2018). The total concentration of Cd, Zn and Fe in soil and rice samples were estimated by microwave-assisted acid digestion as described previously except that 2 mL of 30% H_2O_2 was additionally used for rice samples following the EPA method 3051a. Finally, all digested samples were measured using atomic absorption spectrophotometry (**Figure 23)**. Quality control was performed via the digestion and analysis of certified reference materials, MESS-3 (National Research Council of Canada), with measured values closely matching certified values (e.g., Cd = 0.236±0.005 mg kg^{-1} (n=3) vs. certified Cd value 0.24±0.01 mg kg^{-1} and Zn = 152.413±1.254 mg kg^{-1} (n=3) vs. certified value 159±8 mg kg^{-1}).

5. Physicochemical Analysis of Soil and Rice Plants from Field-scale Experiments

Concentrations of Cd and Fe and five chemical fractions of Cd were measured from soil samples collected during the field experiments using a five-step sequential extraction. Moreover, the rice samples were separated into root, stem, leaf, husk, and grain for chemical analysis. In parts of the rice plant, Cd accumulation at different stages was reported as the enrichment factor (*EF*) using the initial Cd concentration in the rice plant at the transplant stage for standardization (Eq. 12):

$$EF^{i,j} = \frac{Cd\ in\ i\ at\ j\ stage}{Cd\ in\ i\ at\ transplant\ stage}, \qquad (12)$$

where *i* represents the part of rice and *j* represents the rice stage.

On the other hand, the translocation factor was also considered to determine relative translocation of Cd from soil to parts of the rice plant such as, root, stem, leaf, husk, and grain (Satpathy et al., 2014; Bu-Olayan, & Thomas, 2009) Cd Translocation factor (TF) in rice plants from soil to parts of rice was defined as:

$$TF = \frac{C\ tissue}{Csoil} \qquad (13)$$

where C_{tissue} is the Cd and Fe concentration in rice plant tissue (grain, stem or root) and C_{soil} is the Cd and Fe concentration in the corresponding soil.

Moreover, we examined the effect of soil amendment and washing on rice growth and stress via the rice height at each stage.

a) prepared the area as 2x4 m^2

b) ridge preparing

c) adding amendments as sow

d) mixing amendment and soil

e) prepared rice seedlings

f) transplanted rice seedlings

Figure 20 Preparing and cultivation of soil amendment experiment (picture taken in 2015)

a) installed magnetic-assisted soil washing prototype and mixing tank on field

b) excavated soil (0-15 cm) to machine

c) released mixing solution to magnetic-assisted soil washing and transplanted rice seedlings.

Figure 21 Preparing and cultivation of soil washing experiment (picture taken in 2015)

a) mortar **b)** 2-mm sieve **c)** oven

Figure 22 The equipment for sample preparing

a) MW digestion **b)** Atomic Absorption Spectrophotometry

Figure 23 The equipment for sample analysis

Batch experiment for solar-powered electrokinetic separation

1. NZVI, MZVI and Iron-Rod

NANOFER STAR (Nanoiron, Czech Republic) and H200 (Hepure, Claymond, DE) were the NZVI and the MZVI used in this study, respectively. MZVI was used as received while NZVI was prepared according to the manual provided by the manufacturer (Nano Iron s.r.o., 2018). Both particles were characterized for their size and morphology, mineralogical composition, and magnetic properties using a scanning electron microscope (SEM) equipped with EDS (PHILIPS LEO 1455 VP), X-ray diffraction (XRD) (PW 3040/60, X'Pert Pro MPD), and a vibrational sample magnetometer (VSM) (VSM, Lakeshore 7303), respectively. Also, their surface areas were measured N2 adsorption on Brunauer-Emmett-Teller (BET) surface area analyser (Micromeritics TriStar II). In addition, iron-rod is a commercial material (5 mm in Length x 2 mm in diameter). All reagents used in the experiments were of laboratory grade.

2. Electrokinetic experimental setup

The EK experiments was conducted in the laboratory using Cd contaminated soil from this area. The apparatus in these EK tests are illustrated in **Figure 24**. The reactor for EK batch experiment is designed with an inner size of length 280mm x width 108mm x height 100 mm which consists of two main parts as the soil region and the electrode areas. Titanium coated iridium oxide sheet (length 100mm x width 100mm x thickness 1 mm) and stainless-steel plate (length 100mm x width 100mm x thickness 5 mm) were placed at anode and cathode areas, respectively. Solar Cell (SC) (13 volts: V) was connected to reactor as voltage gradient 0.65 V/cm. Sodium sulphate (Na_2SO_4) 0.1 mol/L was added to water components as electrolyte. A 1.7 kg contaminated soil (50% moisture content) with 5% ZVI or nZVI or iron rod or without material were placed in the soil region. All experiments were connected to the SC while the experiment without SC was conducted for comparation as show in **Table 11** and **Figure 25**. The soil region was evenly divided into three parts: S1 is near the cathode component, S2 is middle area, and S3 is near the anode component. Each experiment was done in duplicate in the batch experiments. All investigations were carried out over 15 days (0, 1, 3, 5, 7, 10, and 15 day).

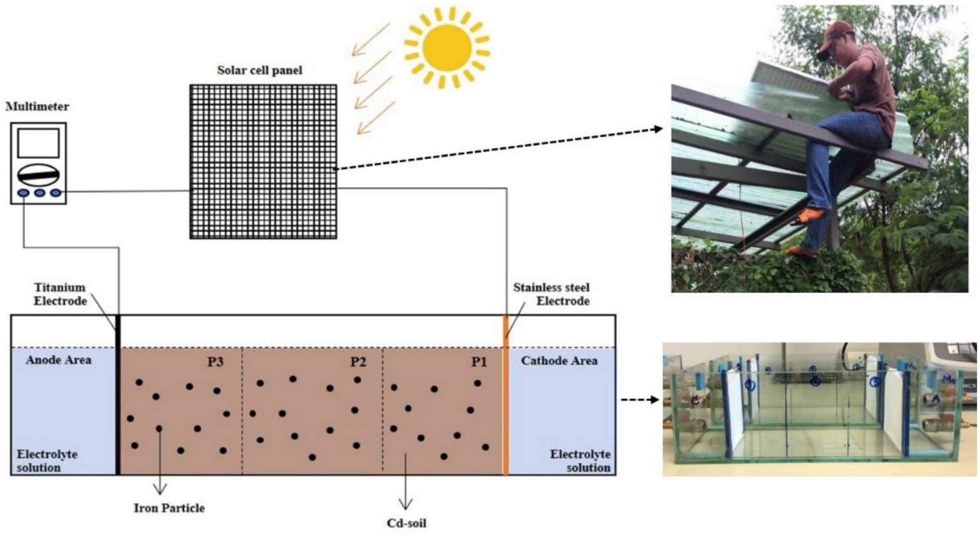


Figure 24 Illustration of EK experimental set up

Table 11 Summary of EK experimental condition designed in this study

Experiment number		E1	E2	E3	E4	E5	E6	E7
Cd-spiked sample		387.06±36.10 mg Cd kg^{-1}						
Media (5%)		without	ZVI	nZVI	Iron rod	ZVI	nZVI	Iron rod
Power supply (13V)		SC	SC	SC	SC	without	without	without
Electrode	**Cathode**	Stainless-steel plate (100mm x 100mm x 5 mm)						
	Anode	Titanium coated iridium oxide sheet (100mm x 100mm x 1 mm)						
Electrolyte		Sodium sulfate (Na_2SO_4) 0.1 mol/L						
Duration time (day)		15 day						

a) Prepared Cd contaminated paddy soil by sieve 2 mm and spiked Cd

b) Prepared MZVI/NZVI/IRON-ROD for experiments

c) Mixing Cd-spiked soil and iron by ultrasonic sonicator

d) Adding soil sample and Sodium sulfate (Na_2SO_4) 0.1 mol/L as electrolyte in reactor

e) Connected with Solar cell

f) Measured , collected and prepared sample

g) Analyzed the total concentration of Cd and Fe in samples

Figure 25 Processes of EK experiments (picture taken in 2017)

3. Analytical method

The soil electrical conductivity (EC), pH, and oxidation-reduction potential (ORP) were measured by an EC meter, a pH meter and an ORP meter, respectively. A five- step sequential extraction for Cd in initial and last soils (without iron) was determined according to the procedure described in **Table A1** and **Section 2 Physicochemical Soil Properties**. The total concentration of Cd and Fe in samples from investigations (soil and separated-iron from soil) were determined using AAS after microwave-assisted acid digestion with 10 mL of 65% nitric acid following EPA method 3051a for solid samples.

4. Rice Seed Germination Test

After the test, the treated soils of the soil region in this investigation were collected for a phytotoxicity test to gauge the effect of the remediation technique on rice seed germination. Eight different conditions of the rice seed germination test were conducted including soil of control experiment (untreated soil), soil of the electrokinetic with SC without media, soil of the electrokinetic with SC using ZVI (with ZVI and without ZVI), soil of the electrokinetic with SC using nZVI (with nZVI and without nZVI) and soil of the electrokinetic with SC using iron rod (with iron and without iron). In the case of soil with media (ZVI, nZVI, iron rod), each sample was separated according to the media type (ZVI, nZVI, iron rod) by magnetic-assisted soil washing with DI water. Four replicates were performed in each condition. For each condition, the total of 180 g of soil was used. Rice seed (Oryza sativa L) for the experiment was prepared by soaking in water overnight. Then, after pouring the water out, the seed was wrapped in a wet cloth for two days until the germination of root was observed. Ten seeds were planted in each plastic cup with treated soil. The germination tests were done in an opaque room at 25 ˚C for 3 days. Then, the germinated seeds were counted and their shoot lengths (elongated representative) were measured by means of a ruler to the closest millimetre (**see Figure 26**). The germination index (GI) was evaluated using Eqs. 14-16 (Komilis, Karatzas, & Halvadakis, 2005; Zucconi, Pera, Forte, & de Bertoldi, 1981).

$$Relative\ seed\ germination\ (\%) = \frac{Number\ of\ seed\ germinated\ in\ sample}{Number\ of\ seed\ germinated\ in\ control}\ x\ 100 \quad (14)$$

$$Relative\ root\ elongation\ (\%) = \frac{Mean\ root\ elongation\ in\ sample}{Mean\ root\ elongation\ in\ control}\ x\ 100 \quad (15)$$

$$GI = \frac{(\%\ Seed\ germination) x\ (\%Root\ elongation)}{100\%} \quad (16)$$

a) Gemination test after experiments

b) counted a germinated seeds and their shoot lengths

Figure 26 Gemination test for EK experiments (picture taken in 2017)

Economic Decision Analysis

This research examines the cost-benefit of risk management and restoration from Cd contaminated paddy soil in the Mae Sot district of the Tak province, Thailand. In order to evaluate the procedure, we follow these steps:

1. Policy and Cost/Benefit Assumptions

A literature review was performed of the Cd contaminated background data including Cd contaminated rice grain, the burden of diseases associated with Cd exposure, investigating and resolving information by governmental management in this study area (see **Figure 6**) (Padungtod et al., 2006; PCD, 2010; Phenrat, & Otwong, 2015; Simmons et al., 2005). That database is from 2004 for risk assessment, and risk management. We assumed the policy and cost/benefit of attempts under this history (see in **Figure 27**). We set up the 7 policies (cases) for this area including i) no action, ii) the risk assessment by only the Thai government, iii) risk management (sugarcane cultivation) by the Thai government, iv) restoration by soil washing, v) soil amendment, vi) phytoremediation and vii) electrokinetic. Costs and benefits of the policy were calculated under the historical situation and previous research, which consisted of health costs, the value of life, loss opportunity, management costs, material costs, monitoring costs, machine costs and the benefits of sugarcane and rice. The relation between policy and cost / benefit are presented in **Figure 27**.

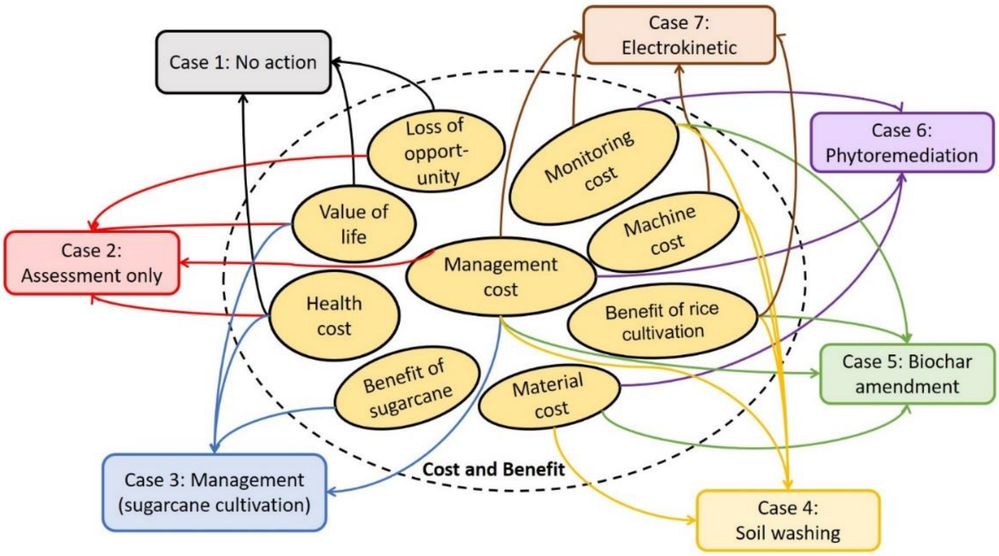


Figure 27 The relation of the policy and cost/benefit for Cd contamination area

2. Cost and Benefit

2.1 Monte Carlo Simulation for Health Cost

We simulated the health outcome (random cost) with the MCS based on information on the contamination area. MCS has become increasingly common in risk assessment of environmental pollution (Poulter, 1998; Qu et al., 2012; Zupunski et al., 2010). Because of risk assessment is a complex procedure that is inherently linked with uncertainty and variability, which arises from a lack of precise knowledge, data scarcity, and the variability inherent in the environmental systems (Qu et al., 2012). In addition, The EPA and the National Academy of Sciences have recognized Monte Carlo methods as a mean of quantifying variability and uncertainty in risk assessments (Poulter, 1998; USEPA, 1997). Monte Carlo analysis is a computer-based method of analysis that uses statistical sampling techniques in obtaining a probabilistic approximation to the solution of a mathematical model (USEPA, 1997; Zupunski et al.,2010). Therefore, the processing of MCS in risk assessment is a major step forward because of introducing an uncertainty analysis in the process of risk assessment. It is used a large number of input data (distribution of pollutants in soil, plant or distribution in the body after intake) in order to decrease uncertainties in the resulting risk assessment (Zupunski et al., 2010).

For this study, Monte Carlo analysis was simulated to predict the expense of health outcome associated with Cd exposure. The disease associated with chronic Cd exposure in the Cd contaminated area has been reported to be associated with the nephrosis/nephritis, osteoporosis, cardiovascular disease, cerebrovascular disease and cancer (Chunhabundit, 2016; Satarug et al., 2010; Songprasert et al., 2015). The correlative parameter impact to Cd health outcome was showed in **Figure 28**. The correlative parameters were set through an assumed that 1) the health risk of the villager occurred together with Cd contamination in this area, 2) all of villager risk to consume Cd rice, and 3) the occurred health expense was the treatment cost for survival and value of life when death. The random parameter is Cd in rice, number of villagers (male, female or age base on contaminated area) to consume. We predicted Cd in urine (Eq 17) and Cd daily intake (Eq 18) (Zhao et al., 2017) from random parameters for the probable risk definition of Cd exposure disease (see in **Figure 28**). We used the risk of disease (OR, RR or HR) for the health outcome of each disease (see in **Table A2**). If risk of Cd disease of the villager showed more than 1, they can be presumed to have the disease. After the diseases have been identified, the approximate health costs are determined along with an approximate value of life which is calculated according to the costs of the illness after treatment. The health cost and value of life were calculated from the survival and death percent of each disease, respectively (**see Figure 28**). The 1,000, 5,000, and 10,000 simulations were applied for random parameter in health cost and the value of life. The reference expense, survival and death percentages of each disease showed in **TableA3 and A4.** The value of the loss of opportunity and the benefits of rice cultivation are calculated from the quantity of rice (Oryza sativa L.; cv. Khao Dawk Mali 105) produced multiplied by the market price of rice per cultivation. This area can produce in 416 kg rai^{-1} which is distributed at a price of 11.72-baht kg-kg^{-1} (Ricethailand, 2017).

$$Cd_{urine}(age) = \frac{f_u \times f_k}{\log(2)} \times d \times t_{1/2} \frac{\left[1-exp\left(-\frac{\log(2)\times age}{t_{1/2}}\right)\right]}{\left[1-\exp(-\frac{\log(2)}{t_{1/2}})\right]} \qquad (17)$$

where, $t_{1/2}$ is the Cd half-life, f_k is a factor aggregating several physiological and Cd-related constants, and f_u is the ratio between Cd in urine and in kidney cortex. We used $t_{1/2}$ at 11.6 years and $f_u \times f_k$ at 0.005

$$d = \frac{C \times IR}{BW} \qquad (18)$$

where, d is Cd intake from rice consumption, C is Cd concentration (μg g^{-1}) in rice sample, IR is rice ingestion rate ($g\ d^{-1}$), and BW is the body weight of corresponding participant.

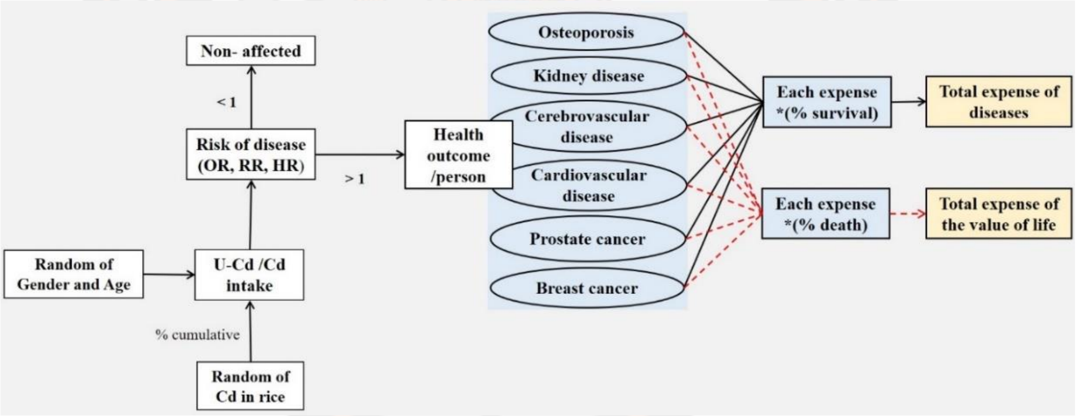


Figure 28 Monte Carlo simulation for health cost and the value of life

2.2 The Assessment and Management cost by the Thai government

The assessment and management of costs were conducted using data from previous reports and previous research such as reports by the Pollution Control Department (PCD) (PCD, 2010), International Water Management Institute (IWMI) and Land Development Department (LDD) (Simmons et al.,2005), annual report 2008 of Padaeng Industry (PDI) (PDI, 2008), research of Padungtod et al. 2015, Centre of information and research for Mae Tao Creek (Panyathep, 2017).

The area in Mae Sot district, Tak province in Thailand was found to be contaminated by Cd in the soil in 2001 by IWMI (Simmons et al.,2005). This finding gained the attention of the Thai government and lead to an investigation, solution processes and a health risk plan for the Cd contaminated area in 2003-2009 (**Figure 6**), such as the environmental sampling of the Department of Agriculture (DOA), LDD, DPC or Department of Primary Industries and Mines (DPIM), the individual sampling of Mae Sot hospital for surveillance. In addition, the government purchased and burned all the rice produced from contaminated paddy fields. The cultivated prohibition on contaminated lands and the promotion of non-food cultivation such as sugar cane, decorative palms and rubber plantations to replace rice cultivation were conducted (Padungtod et al., 2006; Phenrat, & Otwong, 2015). However, the previous restoration cannot succeed in this area because villagers returned to rice cultivation for local consumption after finding that sugarcane did not suit their arable land or their lifestyle. The consumption of contaminated rice affected the cadmium level in their urine leading to the risk of kidney disease (Phenrat, & Otwong, 2015). This assessment and management were calculated for the economic decision analysis together with other restoration. The cost of assessment and management (baht rai^{-1}) with the Cd contaminated area under the Thai government as shown in **Table 12**.

However, the Cd contaminated paddy area led to lose income from rice cultivation. We set up the loss of opportunity and benefit of rice cultivation for economic decision analysis while the benefit of sugarcane cultivation was calculated in policy. For the benefit of sugarcane cultivation calculated by product of sugarcane in 9.5-ton rai^{-1} and distribution with 700-baht ton^{-1} (OCSB, 2019). In addition, the management and monitoring cost of sugarcane alternative cultivation was 1750-baht rai^{-1} (PCD, 2010).

2.3 Other costs and benefit

For this study, we proposed the alternative technique, which consists of soil washing, biochar amendment, phytoremediation and electrokinetic, for economic decision analysis. In each technique will has the cost and benefit of restoration in the contaminated areas. The relation between technique and cost and benefit of this study presented in **Figure 27**. The detail of the cost and benefit was calculated in **Table A5**

Table 12 The assessment and management cost in the Cd contaminated area in Thailand

Year	**Risk management**	**Expenses (baht/rai)**
	A risk assessment by the Thai government	
2004	Short plan for dealing with contaminated paddy soils such as stopping cultivation, management of the rice produced in contaminated paddy soils, determined according to the cultivated area, and the career, and assessment of human health in this area	6,856
2005	The compensated farmers plan (part 1)	4,220
2006	The compensated farmers plan (part 2) and supporting Mae Tao centre for Mae Tao Creek development	4,296
2006	The master plan for Mae Tao Creek development over 3 years	10,265
2009	Population survey and estimation by Contracting the Unit for Primary Care (CUP) and the Hospital of Mae Sot district)	694
2013	Examination and follow up by PCD	1,031
	Risk management by the Thai government	
2006	The cultivation of sugarcane for ethanol was promoted by the Department of Agriculture Extension (DOAE)	857
2006	Promoting sugarcane cultivation for ethanol production by Tak Provincial Agricultural Extension Office	4,289
2006	The Mae Sot Clean Energy company was established for supporting sugarcane cultivated in this area (PDI)	148,820
2009	The reservoir and substructure development were conducted by the Ministry of Agriculture and Cooperatives (MOAC)	51,305
2009	The sugarcane farmers receive compensation by Tak Province	24,168
2009	The promotion and training associated with sugarcane cultivation (by The Ministry of Education; MOE)	1,665
2009	The Mae Sot Clean Energy company set up a loan fund for supporting farmers, purchased sugarcane and devised sugarcane cultivation	51,385

Source: Panyathep E, 2017; PCD, 2010

3. The Net Present Value (NPV)

The cost and benefits of each policy are compared using the net present value (NPV). The NPV is the sum of discounted costs and benefits, using a social discount rate in order to account for time preferences and productivity of capital (Bergion et al., 2018). The net present value (NPV) of all costs and benefits for this area used a core consumer price index (CPI) of Thailand in 2004 - 2019 as calculated using Eqs 19 and Eqs 20 (below) with 240 years based on the time of phytoremediation (started in 2004).

$$NPV = \sum_{i=1}^{n} \frac{Net\ cashflow_{\ i}}{(1+dicount\ rate)^{i}} \tag{19}$$

$$PV = \frac{FV}{(1+dicount\ rate)^{n}} \tag{20}$$

CHAPTER IV

RESULTS AND DISCUSSION

This study was an investigation into the evaluation of using ZVI particles for Cd contaminated paddy soils. The investigations were further separated into soil amendment, soil washing and solar-powered electrokinetic separation. ZVI was used as a pilot-scale project for soil amendment and soil washing while solar-powered electrokinetic separation was tested as a batch experiment. In addition, the cost-benefit analysis was estimated as a gauge of approximate costs. The results are presented as follow:

Field Experiments

1. Physical and chemical properties of paddy fields

The soil texture in studied area was clayey soil (clay 63%, silt 26.7% and sand 10.2%) according to the USDA textural triangle (**See Table B1**) (Ditzler, Scheffe, & Monger, 2017) with the pH of 7.67 and total organic carbon of 4.52%. The CEC and other ionic components of the soil samples were summarized in **Table 13**. The total Cd concentration was 41.02±5.47 mg kg^{-1}, which is 273 times greater than the 95% upper investigation level of the Cd concentrate ion of Thai soil (0.15 mg kg^{-1}) (Zarcinas et al., 2004). The Cd contamination in untreated paddy soil exceeds the acceptable level for EU's agricultural soil (3.0 mg kg^{-1}) (Simmons et al., 2005) and for Thai's agricultural soil (37 mg kg^{-1})(Pollution Control Department, 2004). Fe concentration in untreated soil in study field was as 38,223.92±7240.11 mg kg^{-1}.

Nevertheless, based on the five-step sequential extraction, the bioavailable Cd fractions (sum of exchangeable and carbonate fractions) of the initial soil was 25.11-29.1% (7.667±4.15-13.10 ± 0.25mg Cd kg^{-1}) while the Fe-Mn oxide, the organic, and the residual fractions were 62.20 - 65.52, 7.30 - 8.47, and 1.34-1.39% (20.00±6.25-27.94±2.18, 2.45±0.62-3.28±0.20, and 0.40±0.15-0.62±0.06 mg Cd kg^{-1}), respectively (**Figure 29**). This reveals that only small portion of the Cd in paddy soil was the residual and organic-bound. Therefore, there is high potential for the leaching of Cd from soil to plant and to run-off (John & Leventhal). This result agrees with previous studies which reported that the portions of Cd from the area of the Padaeng Zinc mine in Mae Sot, Tak Province, Thailand were exchangeable fraction (~30-77%) and Fe/Mn oxide fraction (~19-46%) (see **Table 14**) (Akkajit, & Tongcumpou, 2010; Kosolsaksakul, Farmer, Oliver, & Graham, 2014; Phenrat et al., 2019). Nevertheless, the different Cd proportion in soil may be from the different chemical properties (i.e., soil texture, OM) and distance from Cd source.

Table 13 Chemical properties of paddy soil before treatment

Properties	**Value**
pH $_{(1:5)}$	7.67 (±0.132)
OM (%)	4.52 (±0.149)
CEC ($cmol_c kg^{-1}$)	34.30 (±0.726)
Na^+ ($cmol_c kg^{-1}$)	0.33 (±2.548)
K^+ ($cmol_c kg^{-1}$)	0.59 (±0.011)
Ca^{2+} ($cmol_c kg^{-1}$)	19.88 (±0.115)
Mg^{2+} ($cmol_c kg^{-1}$)	5.49 (±0.002)
Cd (mg kg^{-1})	41.02 (±5.47)
Fe (mg kg^{-1})	38,223.92 (±7240.11)

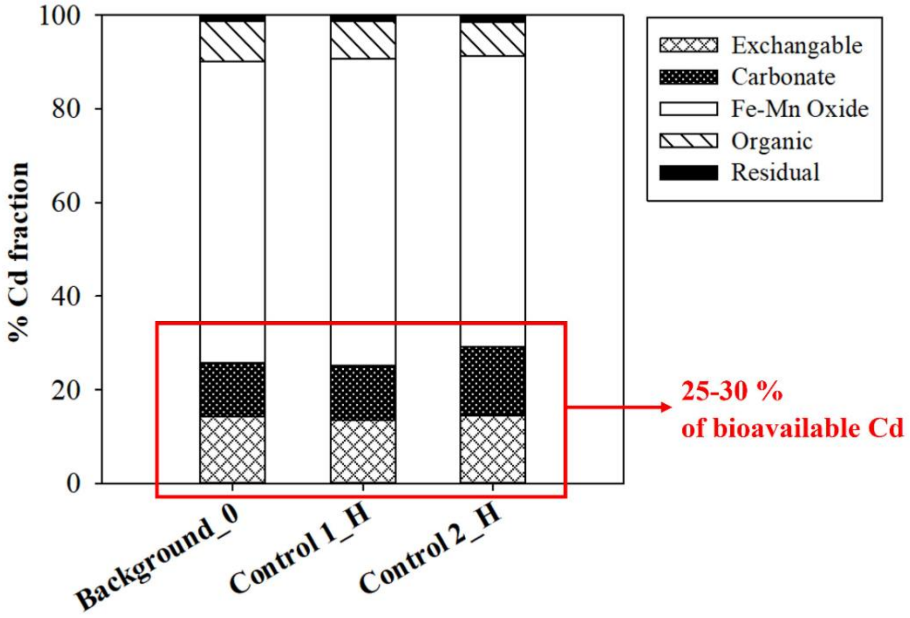


Figure 29 The Cd fraction of initial soil as background_0 and harvest soil as control 1, 2_H

Table 14 the fraction of Cd in this study and previous of this area

Total Cd (mg kg^{-1})	Exchangeable Cd	Carbonate Cd	Fe-Mn Oxide Cd	Organic Cd	Residual Cd	Reference
41.02	25-30%		62.2-65.5%	7.3-8.5%	1.34-1.4 %	This study
114.8	~50%		~1%	33.98%	33.61%	Phenrat et al., 2019
3.7-4.7	~44-45%		~45-46%	~10%	-	Kosolsaksakul et al.,2014
16.8-35.4	~65-71%		~29-30%	~15%	-	
83.7-81.9	~75-77%		~19-21%	~4%	-	
0.73-173	~30%		~40%	~30%		Akkajit, & Tongcumpou, 2010

2. ZVI and Biochar

ZVI and biochar were determined according to the physiochemical characteristics including morphology, mineralogy, surface areas were examined by sieve analysis, SEM or microscope, X-ray diffraction, the Brunauer Emmett Teller (BET), respectively

According to XRD results (**Figure 30**), the ZVI mainly comprised of Fe^0 as evident by the diffraction at 44.6˚ (2Ɵ). Small peaks at 65˚ (2Ɵ) and 82.3˚ (2Ɵ) were also observed on both samples and this peak assigned to zero valent iron which agrees with previous studies (Chen et al., 2008; Frost et al., 2010; Singhal et al., 2012). On the other hand, XRD patterns of biochar are presented in **Figure 31**. The sharp peaks of the biochar indicate the presence of inorganic components such as SiO_2 (peaks at 26.56˚(2Ɵ)), KCl (peaks at 28.35˚and 39.4˚(2Ɵ)), $CaCO_3$ (peaks at 36˚, 39.4˚, 46.9˚ and 48.5˚(2Ɵ)) (Wu et al., 2012; Yuan et al., 2011). The FT-IR spectra of biochar (**Figure 32** and **Table B2**) indicated that the main peak at 1062 cm^{-1} which can be assigned to stretching from varieties of C-O bonds in carbonates (Chia et al., 2012). In addition, it displayed silicon-containing group vibration absorptions at 464 cm^{-1} (Liu et al., 2012). The morphology as well as surface characteristics of both ZVI and biochar were shown in a SEM micrograph (**Figure 33**). In addition, surface area and pore size of the ZVI and biochar are summarized in **Table B3**.

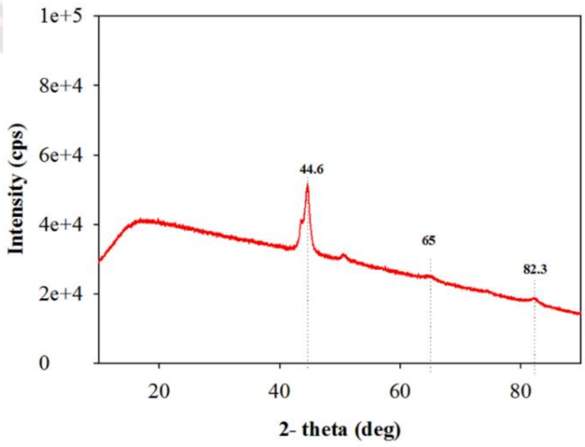


Figure 30 X-ray diffractogram of the ZVI particles

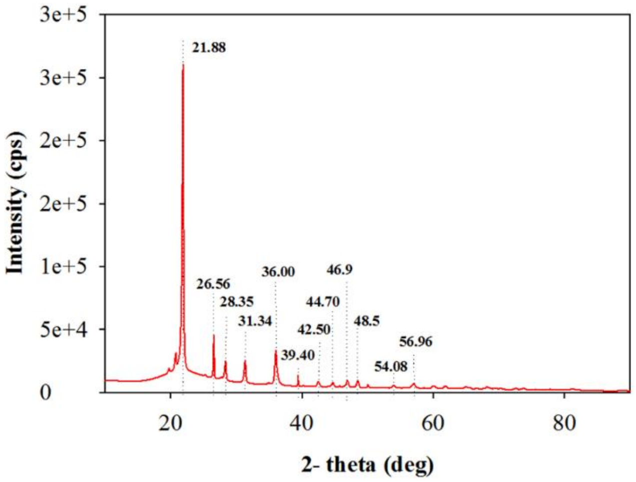


Figure 31 X-ray diffractogram of the biochar

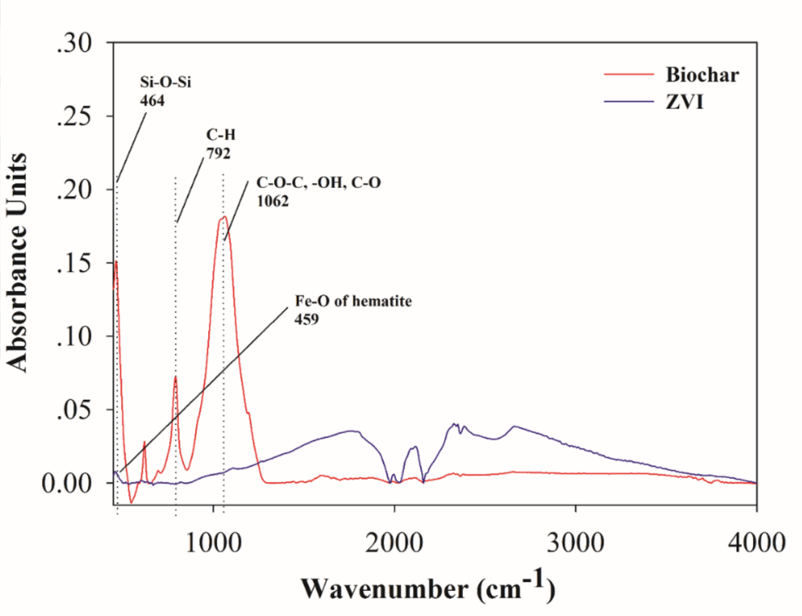


Figure 32 FT-IR analysis of biochar and ZVI materials

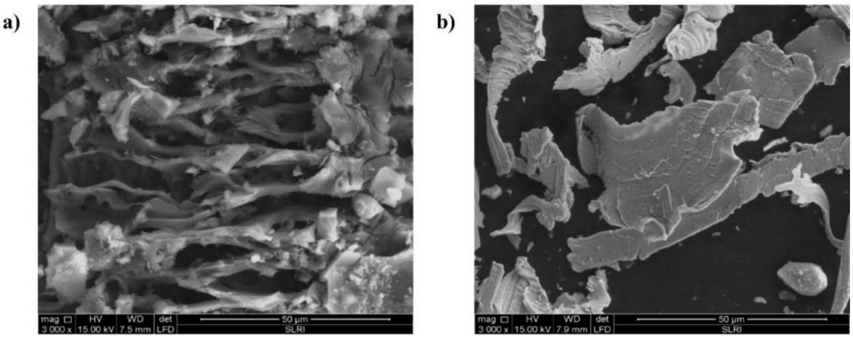


Figure 33 SEM micrographs of (a) biochar and (b) ZVI

3. Cd and Fe in the Control Experiments

The Cd concentrations in the soil samples from the CEs were relatively stable with slight changes over the experimental periods (see **Figure 34**). The average Cd concentration in control experiment increased from 31.63 ± 4.39 mg kg^{-1} to 36.8 ± 7.43 mg kg^{-1} in 28 days and declined to 32.76 ± 6.10 mg kg^{-1} in 84 days (**Figure 34a**). The similar pattern was also observed for Fe (**Figure 34b**). During the harvest time, the Cd concentration in the soil of the two control experiments were 30.12 ± 11.86 mg kg^{-1} (CE1) and 50.62 ± 3.67 mg kg^{-1} (CE2) while the Fe concentration in soil of the two control experiments were 29,977.70 ± 1025.66 mg kg^{-1} (CE 1) and 32,886.47 ± 1725.99 mg kg-1 (control 2). During harvest time, Cd concentrations in the soil were 30.12±11.86 mg kg^{-1} (CE 1) and 35.39±0.32 mg kg^{-1} (CE 2).

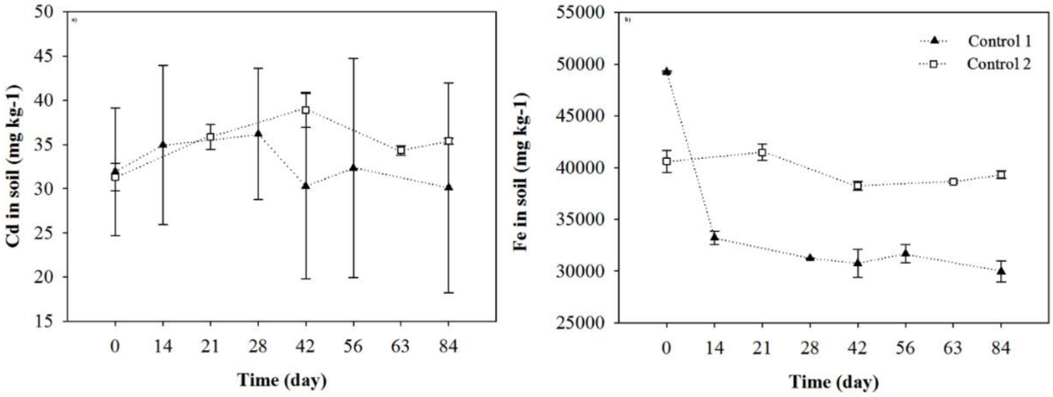


Figure 34 a) Cd concentration and b) Fe concentration in soil of control experiments

The Cd accumulation in rice plants in the CEs during the three stages (*EF*) for each part of the plant are shown in **Figure 35a and 35b**. Notably, the *EF* values of Cd in each rice part at the transplant state were set as unity. Thus, any increase of *EF* was caused by Cd uptake in the rice from the soil. The results showed that, for CE 1 in the heading and mature states, respectively, the Cd accumulation in the CE was in the order of root (EF^{r}=314.88±199.26 and 435.12±221.74)>stem (EF^{s}=62.58±40.76 and 137.17±50.62)>leaf (EF^{l}=9.15±1.12 and 52.04±21.26). Similarly, for CE 2, in the heading and mature states, respectively, the Cd accumulation was in the order of root (EF^{r}=94.92±2.71 and 91.17±1.48)>stem (EF^{s}=21.65±0.39 and 21.34±0.90)>leaf (EF^{l}=14.15±0.02 and 14.67±0.03). Notably, the EF values of the same rice parts at the same stages of CE 1 were always greater than those of CE 2. Presumably, this could be because CE 1 was conducted during the rainy season, when Cd may be more readily leached from the soil to rice plants than in winter when CE 2 was conducted. The water conditions when the experiments were conducted is shown in **Figure 36**.

Nevertheless, the Cd concentrations in the rice grain were 0.84±0.20 mg kg^{-1} and 0.86±0.01 mg kg^{-1} for CEs 1 and 2, respectively (**Figure 37**), which are greater than the acceptable amount (Codex Alimentarius Commission, 2018). For CE 1, the Cd translation factors were 0.70, 0.32, 0.38, 0.12, and 0.13 for soil to root, root to stem, stem to leaf, stem to husk, and stem to grain, respectively (**Figure 38**). For CE 2, the Cd translation factors were 0.47, 0.13, 0.50, 0.32, and 0.28 for soil to root, root to stem, stem to leaf, stem to husk, and stem to grain, respectively (**Figure 38**). Notably, the translocation factors from soil to root and root to stem of CE 2 were smaller than those of CE 1, which is presumably explainable by the greater leachability of Cd in the rainy season. The other translocation factors (stem to leaf, stem to husk, and stem to grain) for CE 2 were greater than those for CE 1. This explains why the Cd concentration patterns in the rice grain of the two experiments are similar, though the amounts of rice plants reflected differ.

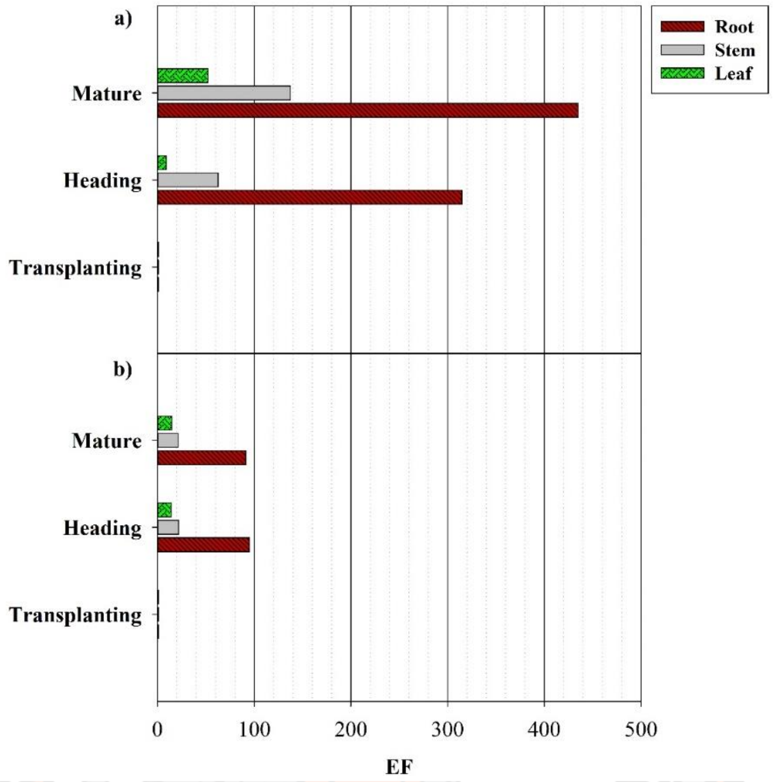


Figure 35 Cadmium change in rice plants during cultivation in a) CE 1 and b) CE 2

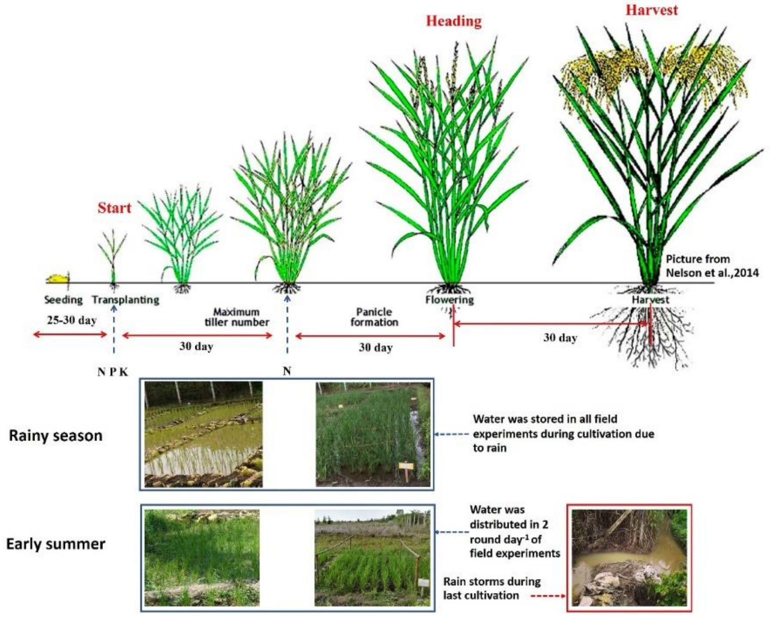


Figure 36 Water condition during cultivation in rainy and early summer seasons

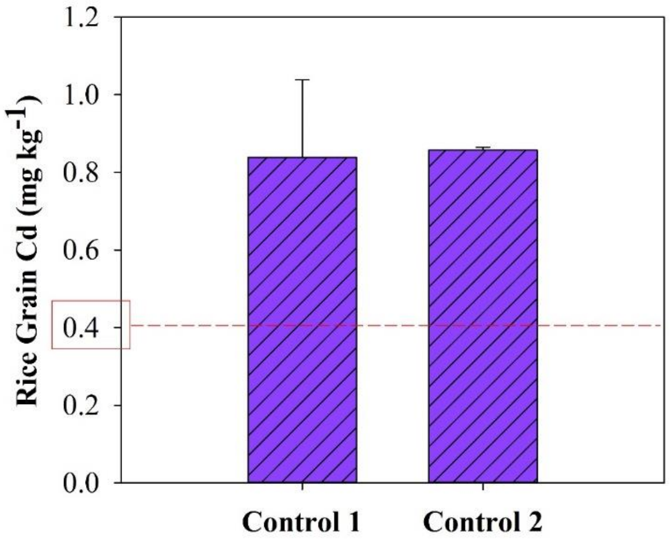


Figure 37 Cadmium level in rice grain during harvest in soil amendment and washing

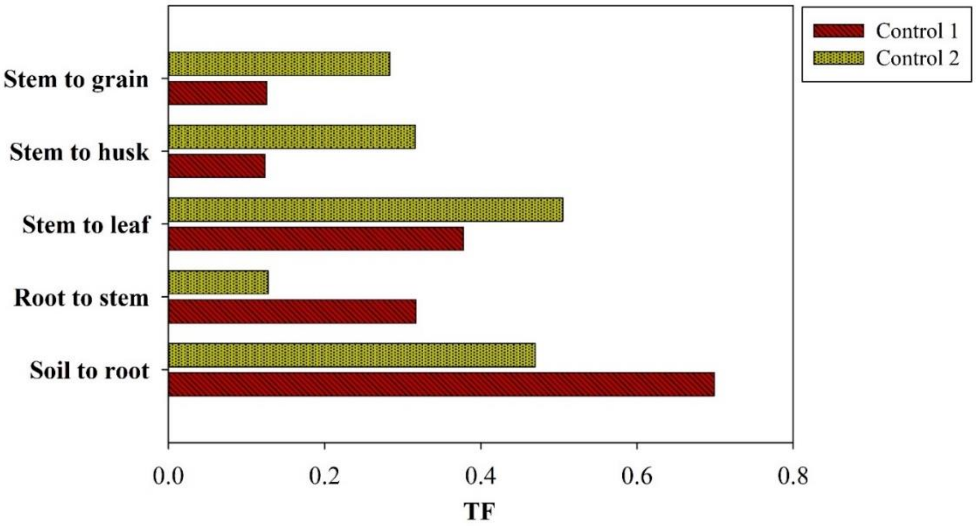


Figure 38 TF of Cd from soil to rice plants during harvest in CEs

4. Cd and Fe in Soil and Rice in Soil Amendment

Slight changes in Cd were observed in the soil treated using the three soil amendments (**Figure 39a**). Adding ZVI 5% and BZVI 5% increased the Fe soil concentration (from 30 g kg^{-1} to 55 g kg^{-1}). During harvest time, the Cd concentrations in the soil in the three soil amendments were 41.20±5.99 mg kg^{-1} (biochar), 34.82±6.27 mg kg^{-1} (ZVI 5%), and 39.60±2.90 mg kg^{-1} (BZVI5%). The Fe concentrations were 30,506.95±60.04 mg kg^{-1} (biochar), 54,712.58 ± 1751.25 mg kg^{-1} (ZVI 5%), and 57,086.83 ± 602.52 mg kg^{-1} (BZVI 5%; **Figure 40**).

The Cd accumulations in rice plants during the three stages (*EF*) and Cd concentration in rice plant were shown in **Figure 41a** and **Table 15** for all three soil amendments. As expected, at the heading stage, the *EF* values of Cd in the root treated by soil amendment techniques (biochar (EF^r=619.31±70.16), ZVI 5% (EF^r=357.09±237.88), and BZVI5% (EF^r=472.79±17.14)) were greater than those of the CE1 experiment (EF^r=314.88±119.26), suggesting that the soil amendments immobilized the Cd in the root. This trend was also valid in the mature state, except for BZVI 5%, which has a slightly lower *EF* value (EF^r=342.54±89.30) than the CE (EF^r=435.12±221.74). Moreover, the presence of all three soil amendments kinetically reduced the Cd translocation to the stem and leaf in the mature state **(Figure 41a)** in comparison to the CE 1. Whereas the *EF* values of CE1 at the stem and leaf were 137.17±50.62 and 52.04±21.26, respectively, the *EF* values of the biochar treatment were 86.42±10.10 for the stem and 24.36±9.33 for the leaf. The *EF* values of the ZVI 5% and BZVI 5%, treatments substantially declined (EF^s=88.30±31.43 and 73.32±30.10 for ZVI 5% and BZVI 5% and EF^l=32.07±3.02 and 32.70±2.46 for ZVI5% and BZVI5%, respectively). The Cd uptake to the rice grain harvested from soil amended fields decreased to 0.19±0.11 mg kg^{-1} for BZVI 5%, 0.29 ± 0.15 mg kg^{-1} for biochar, and 0.58±0.06 mg kg^{-1} for ZVI 5% in comparison to CE1 (0.84±0.20 mg kg^{-1}; **Figure 39b**). Successfully, BZVI 5% and biochar decreased Cd in the rice grain to lower than the safety guideline (0.4 mg kg ^{1}). The uptake of Cd to rice grain decreased in the order of BZVI 5% (16.85%) <biochar (25.50%) <ZVI 5% (60.34%) <control (100%; **Table 16**).

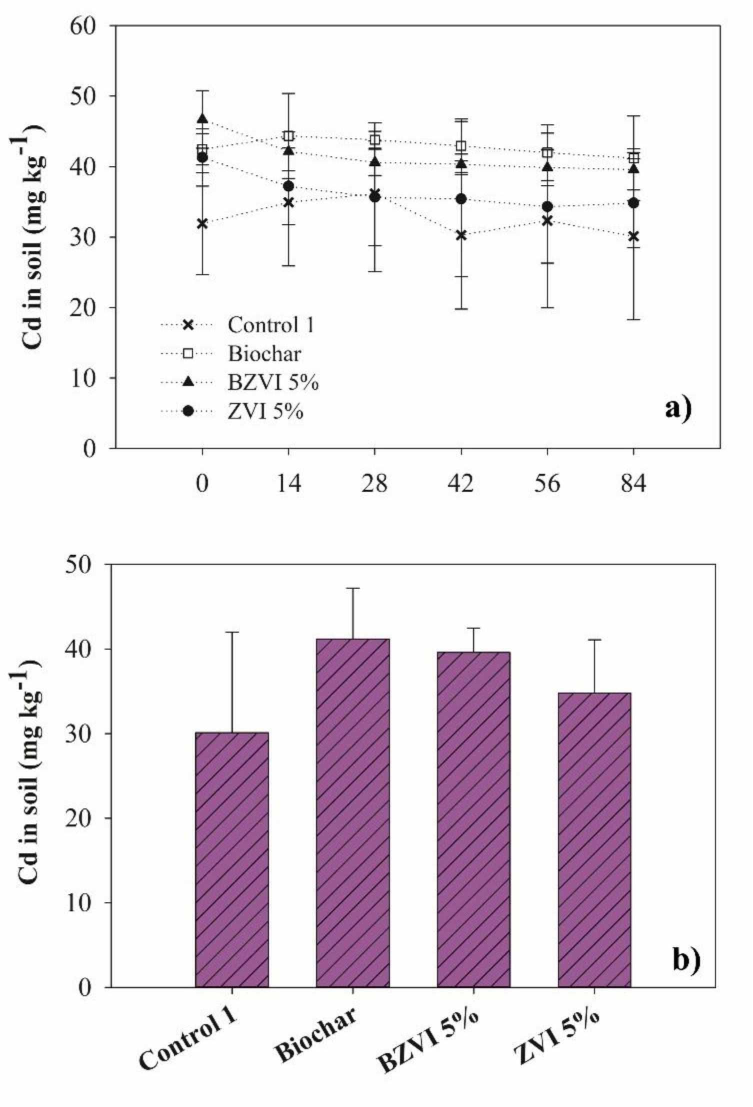


Figure 39 a) the changes Cd in soil treated under flood conditions and b) Cd content in soil during the rice harvest

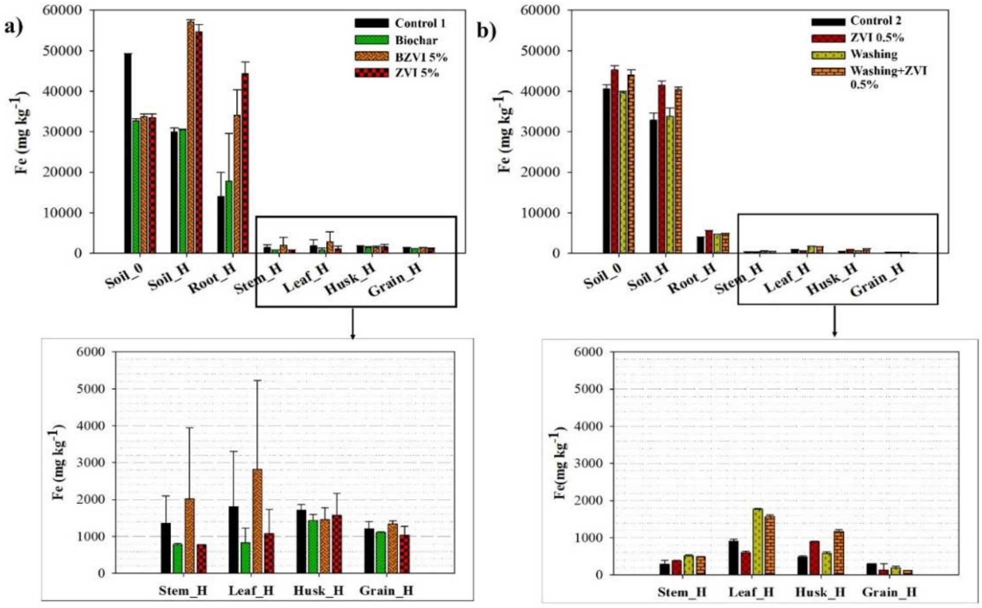


Figure 40 Fe contents in soil and plant tissue under untreated soil and treated soils in harvest a) flooded and b) non-flooded conditions

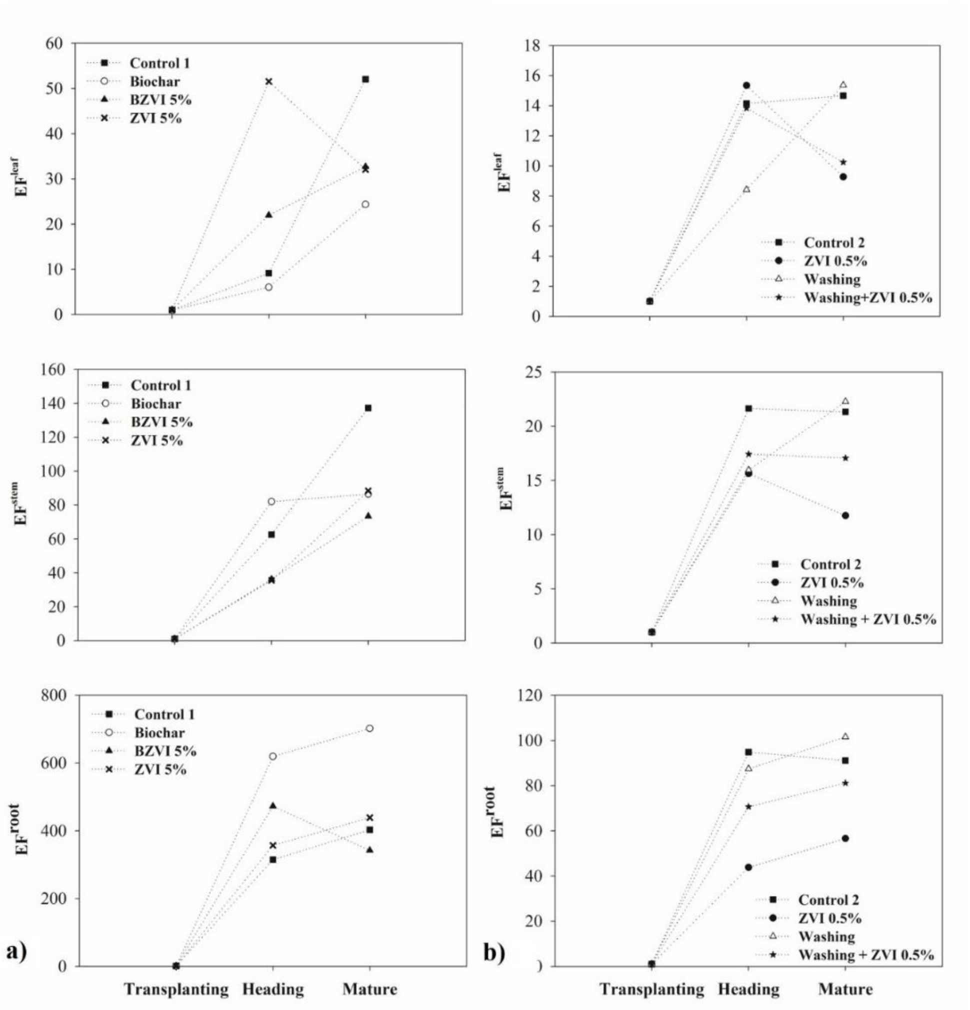


Figure 41 Cadmium change in rice plants during cultivation under a) flooded and b) non-flooded conditions

Table 15 Concentration of Cd in rice plants during cultivation

Treatment	Heading (mg kg^{-1})			Mature (mg kg^{-1})		
	Root	Stem	Leaf	Root	Stem	Leaf
Control 1	15.24±5.78	3.04±1.98	0.44±0.05	19.51±14.68	6.67±2.46	2.52±1.03
Biochar	29.98± 3.40	3.99± 2.70	0.29± 0.05	33.98± 3.20	4.20± 0.49	1.18± 0.45

Treatment	Heading (mg kg^{-1})			Mature (mg kg^{-1})		
	Root	Stem	Leaf	Root	Stem	Leaf
BZVI (5%)	22.89± 0.83	1.76± 0.10	1.06± 0.22	16.58± 4.32	3.57± 1.46	1.59±0.12
ZVI (5%)	17.29±11.51	1.7248±0.00	2.4963±0.00	21.25±12.18	4.29±1.53	1.55±0.15
Control 2	11.84± 0.34	2.69± 0.05	1.76± 0.002	11.37± 0.18	2.65± 0.11	1.83± 0.003
ZVI (0.5%)	5.47± 0.46	1.94± 0.05	1.91± 0.64	7.06± 0.37	1.46± 0.51	1.15± 0.003
Washing (1%)	10.92± 0.28	1.99± 0.10	1.05± 0.05	12.67± 0.65	2.77± 0.05	1.91± 0.001
Washing + ZVI (0.5%)	8.82± 0.19	2.17± 0.05	1.72± 0.15	10.13± 0.14	2.12± 0.038	1.28± 0.05

Note: ***Transplanting stages were 0.048±0.0, 0.049±0.0 and 0.048±0.0 mg kg^{-1} of root, stem and leaf, respectively in soil amendment experiment (Control1,Biochar, Biochar & ZVI (5%) and ZVI (5%)), while soil washing were 0.125±0.0, 0.124±0.0 and 0.124±0.0 mg kg^{-1} of root, stem and leaf, respectively (Control2, ZVI (0.5%), washing (1%) and washing + ZVI (0.5%))

Table 16 Concentrations of Cd in soil and rice grain in paddy soils with various treatments

Treatment	Soil $_{\text{initial}}$ (mg kg^{-1})	Soil $_{\text{harvest}}$ (mg kg^{-1})	Rice (mg kg^{-1})	Uptake index*	Uptake rate** (%)
Control 1	31.93	30.12	0.84	0.0210	100
Biochar	42.46	41.20	0.29	0.0070	25.50
BZVI (5%)	46.69	39.60	0.18	0.0047	16.85
ZVI (5%)	41.31	34.82	0.58	0.0170	60.34
Control 2	31.33	50.62	0.86	0.0169	100

Treatment	Soil $_{initial}$ (mg kg^{-1})	Soil $_{harvest}$ (mg kg^{-1})	Rice (mg kg^{-1})	Uptake index*	Uptake rate** (%)
ZVI (0.5%)	18.90	49.43	0.59	0.0121	71.39
Washing (1%)	34.33	50.36	1.20	0.0240	141.69
Washing + ZVI (0.5%)	32.40	49.41	0.33	0.0067	39.82

Note: * Cd concentration in rice/ Cd concentration in soil

** (Treatment uptake index/ Control uptake index) x 100

This Cd accumulation and translocation was also analyzed for *TF* values at the harvesting state (**Figure 42**). Interestingly, the addition of ZVI 5% and BZVI 5% reduced the *TF* from the soil to the root by 79.22% and 59.93% in comparison to the CE1. This suggests that the ZVI-based amendment immobilized the Cd in the soil and decreased the uptake via the root. This agrees well with the increased EF^r in the ZVI-based treatments discussed previously. This suggests that ZVI-based amendment mechanistically immobilized the Cd in the root matrix more than in the CE1. This is also supported by the chemical fraction of Cd in the soil of CE1 and the ZVI treatment, as evident in the five-step sequential extraction of Cd in the soil treated with ZVI-based amendments after the harvesting state. Exchangeable Cd was transformed to Fe-Mn oxide fraction and residual fraction (**Figure 43**). Moreover, ZVI may be corroded in the soil, forming nanoscale iron oxyhydroxide/oxide structures in the soil and rhizosphere, which binds metals in the soil or root matrix. In the rhizosphere, the amorphous Fe oxide/hydroxide may be in the form of Fe plaque (Qiao et al., 2018) on the root, which acts as a barrier to Cd uptake and translocation to rice grain (Liu et al., 2007), supporting the study findings. As suggested in a recent study (Phenrat et al., 2019) ,the further oxidation of ZVI materials promotes the growth of the oxide shell and shrinkage of the core, resulting in embedding adsorbed Cd into the particle matrix (oxide and zerovalent). This potentially explains the increase of the residual fraction of Cd in soil treated by ZVI or BZVI (**Figure 43**) because the embedded Cd in the ZVI particle matrix should be very stable and difficult to extract via sequential extraction.

While biochar experiment increased the *TF* from the soil to the root (~120%) in comparison to the CE1. Biochar presumably attached at the root and reduced Cd transfer from the root to the upper parts of the rice plant by ionic exchange, surface complexation, and physical adsorption. the Fe-Mn oxide fraction of the biochar-amended soil samples was transformed to the carbonate fraction, while the other fractions remained unchanged (**Figure 43**). This indicates that the XRD and FTIR results for biochar show the presence of C-O bonds in the carbonates and the silicon-containing group (**Figure 31 and 32**) (Chia et al., 2012; Liu et al., 2012). This suggests that the biochar stabilized Cd in the soil by co-precipitation to carbonates and/or silicate by surface complexation with C-O and Si-O-Si functional groups.

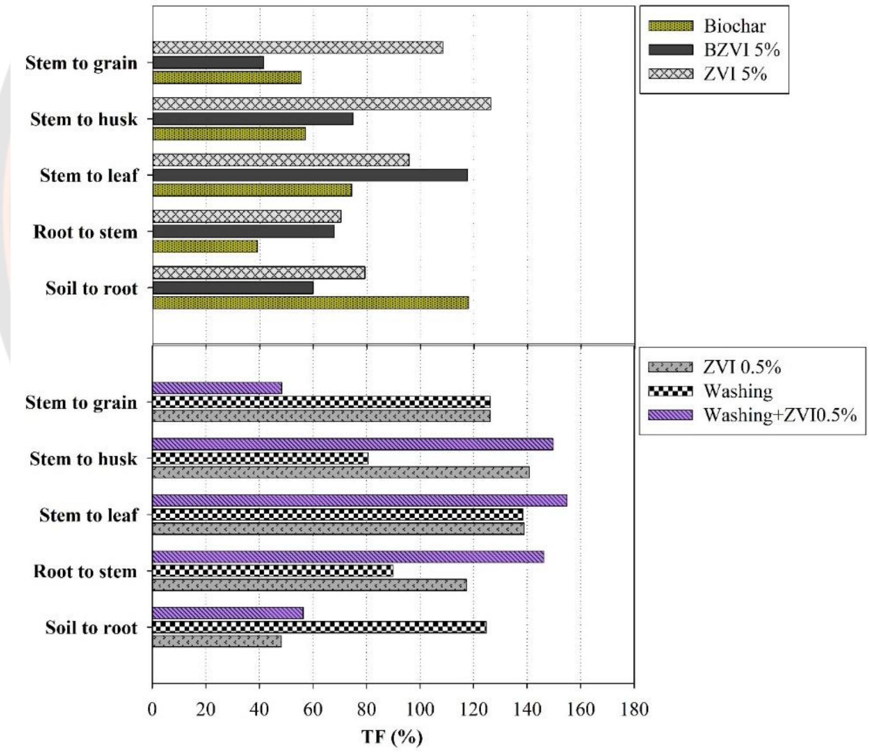


Figure 42 TF of Cd from soil to rice plants during harvest in soil amendment and washing

The combined amendments of biochar and ZVI substantially reduced Cd uptake by rice in comparison to the single application of either biochar or ZVI (Pan, Liu, Yu, & Li, 2019; Qiao et al.,2018). This agrees well with a recent study reporting that the presence of carbon in biochar can accelerate ZVI corrosion and rapidly and extensively form iron oxide/hydroxide structures, the adsorption site for Cd immobilization (Dou et al., 2010; Qiao et al., 2018). The possible of rapid ZVI corrosion may be from biochar's electrically conductivity (this study was 189.43±13.70 µs cm^{-1}) to electron acceleration between ZVI and biochar. In addition, biochar of this study presented the aromatic structures of biochar (i.e., C-O, C-H (**Table B2**)) which can facilitate electron transfer (Klüpfel et al., 2014; Qiao et al., 2018). This supported by Cd fraction result (see **Figure 43**) that Fe-Mn oxide species in the combined amendments of biochar and ZVI presented more than the single biochar and single ZVI amendments.

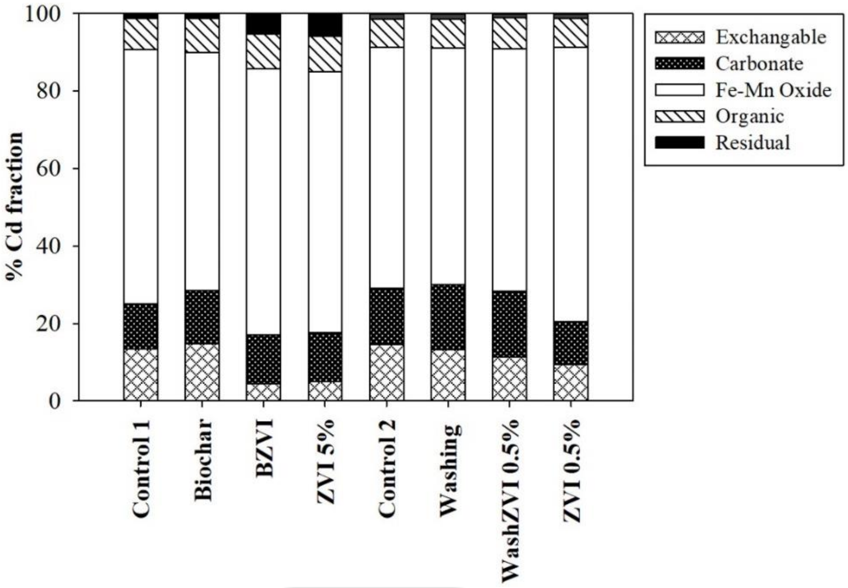


Figure 43 Cd fraction of soil treatments after harvesting state

5. Cd and Fe in Soil and Rice of Magnet-assisted Soil Washing

Figure 44 represents the dynamics of the Cd concentration in soil for washing experiments with and without ZVI (0.5%) amendment (washing and washing + ZVI 0.5%, respectively). These experiments are compared with the experiment using ZVI (0.5%) amendment without soil washing. Magnet-assisted soil washing decreased the Cd concentration from 42.97±0.44 to 34.33±1.78 mg kg^{-1} (i.e., the process removed

21% of the Cd). Notably, while a recent laboratory experiment removed 78% of the Cd from the soil (Phenrat et al., 2019) , this pilot-scale experiment could remove only around 21% of the Cd from the soil presumably because of different chemical fractions of the soil in the studies. In the recent laboratory experiment, the sum of exchangeable and carbonate fractions of the untreated soil was 50.15% (Phenrat et al., 2019) , whereas the sum of the two fractions of the untreated soil was 25.69% for this pilot-scale study. Thus, the Cd fraction removed by magnet-assisted soil washing using ZVI in this experiment is 1.36 times the two mobile fractions, which is similar to the Cd fraction removed by magnetic-assisted soil washing in laboratory experiments in the previous study (1.55 times the two mobile fractions of Cd in the soil) (Phenrat et al., 2019).

During the cultivation period, Cd concentration changed as a result of the flooding event. Initially, for the soil-washing experiment, Cd concentrations increased from 34.33±1.78 mg kg^{-1} to 37.45±0.94 mg kg^{-1} in 21 days and decreased to 35.71±0.74 mg kg^{-1} in 84 days. Similarly, for the soil washing and amendment, Cd soil concentrations were relatively stable (i.e., from 32.40±2.18 to 35.52±5.92 mg kg^{-1} in 21 days, decreasing to 33.63±0.57 mg kg^{-1} in 84 days). Nevertheless, in the mature stage (**Figure 36**) after heavy rain that generated run-off and caused flooding in the experimental fields from 90 days to harvest, the Cd soil concentrations from the two soil-washing experiments were increased to 50.62±3.67 mg kg^{-1} (washing) and 49.41± 0.52 mg kg^{-1} (washing + ZVI 0.5%) (**Figure 44**). This has serious consequences on the Cd accumulation in the soil and rice as the heavy rain increased the amount of Cd in accumulating in the soil and, consequently, in the rice.

The Cd accumulation in rice during the heading and mature states (*EF*) is presented in **Figure 41b** for the washing experiments. At the heading stage, the *EF* values of Cd in the root treated with soil washing (EF^r=87.53±2.28, EF^s=15.97±0.77, and EF^l=8.422±0.42) and soil washing and amendment (EF^r=70.73±1.54, EF^s=17.44±0.41, and EF^l=13.83±1.24) were lower than those of CE 2 (EF^r=94.92±2.71, EF^s=21.65±0.39, and EF^l=14.15±0.02). This finding suggests that soil washing eliminated the phytoavailable Cd fraction and reduced the Cd accumulation in the rice parts. Nevertheless, because of heavy rain on the 90th day, when *EF* values were considered at mature state, the *EF* values of the soil-washed rice plants (EF^r=101.61±5.14, EF^s=22.29±0.41, and EF^l=15.36±0.01) were higher than those of CE 2 (EF^r=91.17±1.48, EF^s=21.34±0.90, and EF^l=14.67±0.03). For soil washing and amendment, the EF values (EF^r=81.21±1.09, EF^s=17.07±0.31, and EF^l=10.25±0.40) were lower than those of CE 2 This suggests that soil amendment with ZVI was required after soil washing to provide an adsorbent to sequester Cd, which may come with contaminated run-off during heavy rain. This suggests that soil washing alone is insufficient to restore paddy soil if upgradient soil is still contaminated with a mobile Cd fraction. Using soil amendment after soil washing is the preferred solution.

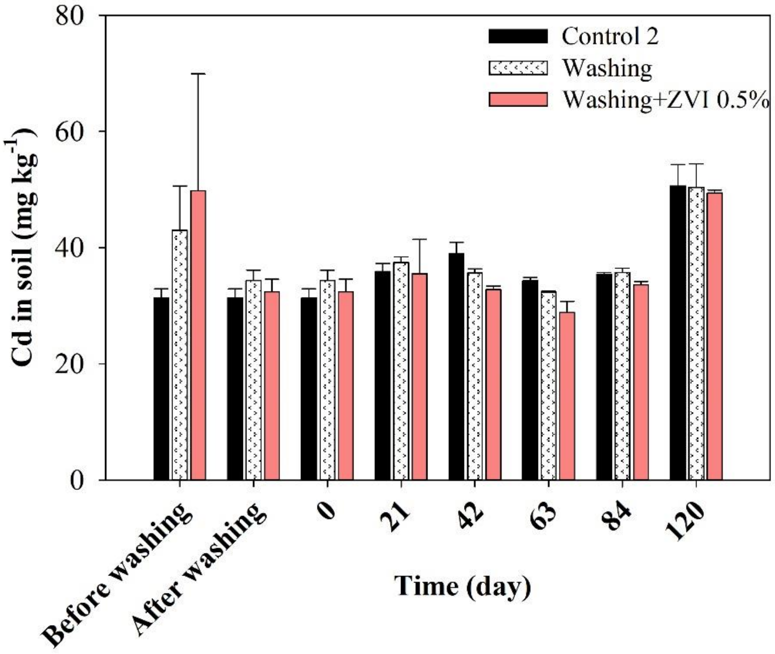


Figure 44 Change in cadmium concentration in soil-washing experiments

During the harvest stage, the Cd concentration in rice grain cultivated in the soil-washing experiment was 1.21±0.01 mg kg^{-1}, whereas that of the soil washing and amendment decreased to 0.33±0.00 mg kg^{-1} in comparison with CE 2 (0.86±0.01 mg kg^{-1}; **Figure 45**). The Cd uptake in rice grain increased in the soil-washing experiment (141.69%), whereas the soil washing and amendment decreased the Cd accumulation to around 39.82% compared with CE 2 (100%). This is presumably because of the mobile Cd delivery from contaminated run-off from the upgradient soil to the fields. Nevertheless, the Cd concentration in rice grain after soil washing and amendment is lower than the acceptable level (Codex Alimentarius Commission, 2018). Noticeably, using ZVI (0.5%) as soil amendment alone yields rice grain with a Cd concentration of 0.60±0.05 mg kg^{-1}. This implies that using magnet-assisted soil washing prior to amendment with ZVI (0.5%) decreased the Cd accumulation in rice grain by a further.

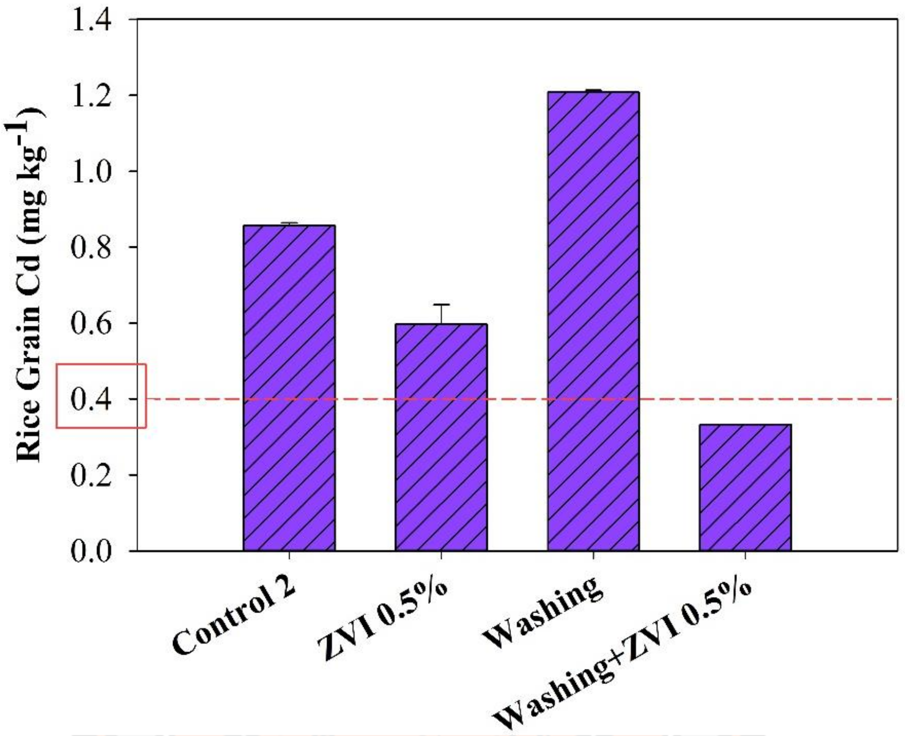


Figure 45 Cd content in soil harvest in soil washing experiment

These findings are theoretically supported when analyzing the relationship between the combination of exchangeable and carbonate fractions of Cd in the soil and the Cd concentration in rice grain from the same contaminated area (Kosolsaksakul et al., 2014). Right after soil washing, the sum of exchangeable and carbonate fractions of Cd in the soil was 8.37 mg kg^{-1}. Thus, if no additional Cd contamination from Cd-contaminated run-off causes further re-contamination of the soil with Cd, the hypothetical concentration in the grain would be 0.31 mg kg^{-1} (**Figure 46**). Nevertheless, the Cd-contaminated run-off flooded the fields, causing re-contamination in the soil. This increased the sum of exchangeable and carbonate fractions of Cd in the soil treated with soil washing to 13.66 mg kg^{-1}. This should yield a Cd contamination in the rice grain of 0.57 mg kg^{-1}, which is smaller than the observed value (1.21±0.01 mg kg^{-1}). This suggests that Cd-contaminated run-off increased the Cd contamination in the soil and the uptake by the rice. While the field treated with soil washing and amendment were also affected by Cd-contaminated run-off, the sum of exchangeable and carbonate fractions of Cd in the soil increased slightly to 11.87 mg kg^{-1} because ZVI sequestered the additional available Cd. This should yield a Cd contamination in rice grain of 0.48 mg kg^{-1}, which is greater than the observed value (0.33±0.00 mg kg^{-1}; **Figure 46**) and is similar to the mentioned hypothetical concentration in the rice grain (0.31 mg kg^{-1}). This confirms that adding a low concentration of ZVI (0.5%) as a soil amendment after magnet-assisted washing helped adsorb Cd from Cd-contaminated run-off and decreased the Cd uptake by the rice, although the amendment did not help decrease the Cd in the soil.

The results were also analyzed as *TF* values compared CE (see Figure 4.13). For the soil-washing experiment, the character of Cd translocated to the plant in soil washing tended to be in the order of grain TF^g (126.47%)>root TF^r (124.73%)>stem TF^s (89.95%)>husk TF^h (80.67%). For soil washing and amendment, the values were in the order of TF^h (149.70%)>TF^s (146.26%)>TF^r (56.32%)>TF^g (48.34%). These results can explain the Cd level and uptake in the rice grain.

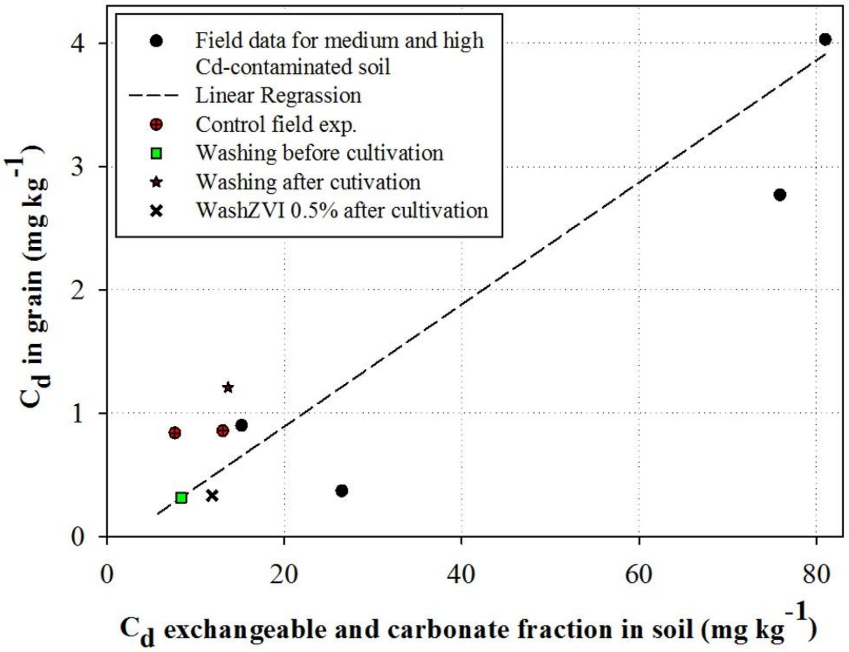


Figure 46 Hypothetical Cd content in untreated and treated rice grain with soil washing

6. Effect of Treatment on the Stress of Rice

Figure 47 illustrates effect of different treatments on Cd removal from the rice and the stress of the rice compared to the CEs. Notably, soil amendment using biochar and magnet-assisted soil washing did not affect the rice growth substantially, whereas ZVI amendment at a high concentration (5%) greatly influenced the rice growth. The daily rice growth in the CEs was 0.602 cm for CE 1 and 1.024 cm for CE 2 (**Table 17 and Figure 48**). The daily rice growth was 0.601 cm for biochar, 0.213 cm for BZVI 5%, 1.140 cm for ZVI 0.5%, and 0.203 cm for ZVI 5%. These results indicated that high ZVI concentrations affected rice growth by as much as three-fold compared with the CEs. For the soil-washing experiment, the daily growth was 1.278 cm for soil washing and 1.077 cm for soil washing and amendment (ZVI 0.5%), which is slightly higher than CE 2 (1.024 cm) and agrees well with a recent study (Phenrat et al., 2019) . For this reason, considering the stress on the rice growth and the Cd reduction efficacy, amending the soil using biochar and magnet-assisted soil washing followed by ZVI amendment (0.5%) is promising. Moreover, magnet-assisted soil washing followed by ZVI amendment (0.5%) is a better restoration alternative if systematic permanent Cd removal from soil is a remedial action goal.

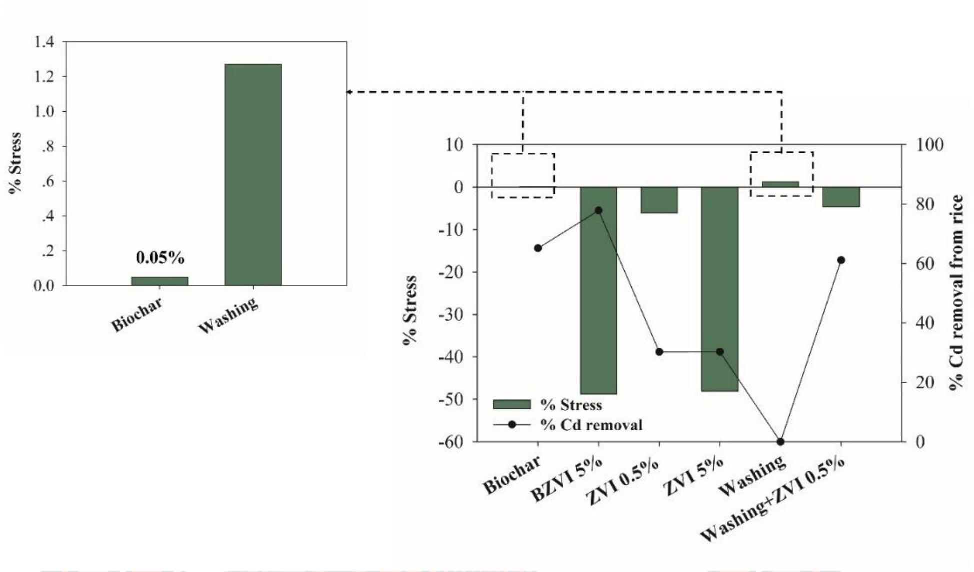


Figure 47 Soil treatments on the stress on rice growth compared to the control results

Table 17 Rice growth equation and rate in paddy soils with various treatments

Treatment	Rice growth Equation	Rate (cm.day^{-1})	R^2
control 1	y= 0.602x+13.582	0.602	0.9974
biochar	y= 0.6015x+13.639	0.601	0.9974
BZVI 5%	y= 0.2136x+15.345	0.213	0.986
ZVI 5%	y= 0.2033x+16.419	0.203	0.9955
Control 2	y=1.0238x-29.073	1.024	0.9996
ZVI 0.5%	y=1.1404x-44.524	1.140	0.991
Washing	y=1.2783x-53.927	1.278	0.9985
Wash + ZVI 0.5%	y= 1.0774x-37.333	1.077	0.9963

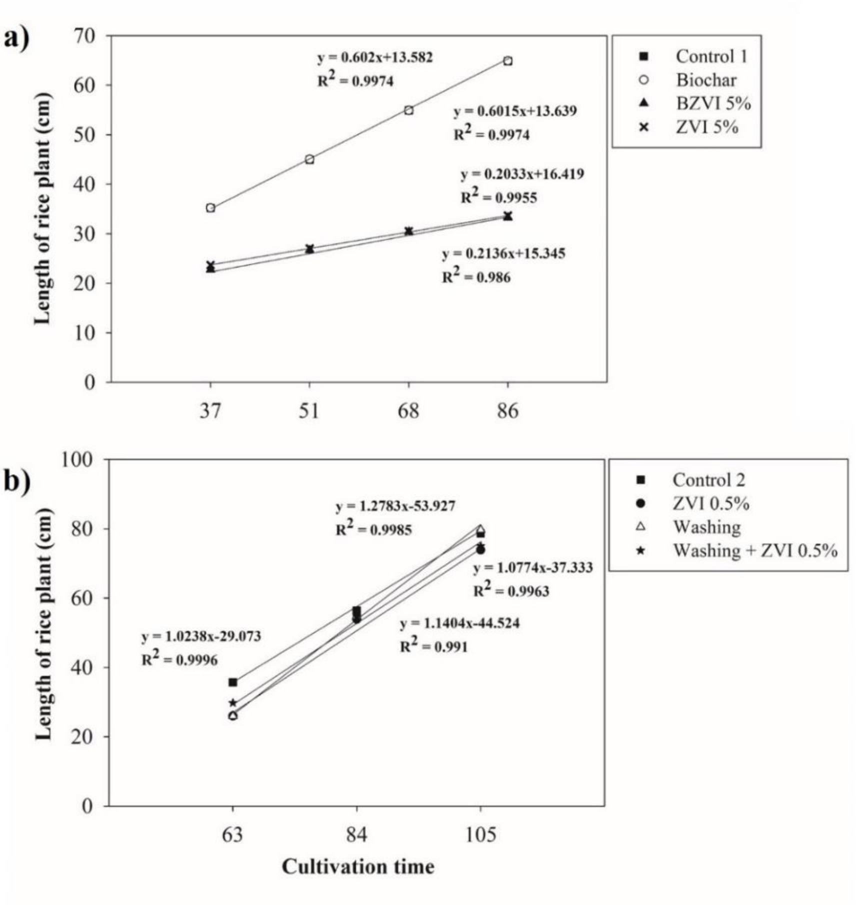


Figure 48 Relative of rice plant growth and cultivation time under a) soil amendment and b) soil washing

7. Summary of Field Experiment

This study performed the first pilot-scale experiments on Cd-contaminated paddy restoration via magnet-assisted soil washing using zerovalent iron (ZVI) particles and compared this novel technique with soil amendment using biochar, ZVI, and a combination of biochar and ZVI (BZVI). The pilot tests were conducted in a Cd-contaminated paddy (39.54±8.69 mg kg^{-1}) in Thailand. To promote citizen science, the affected villagers were trained as community researchers to perform remedial actions and post-harvest sampling. Without treatment, the Cd concentration in rice grain from the contaminated paddy ranged 0.84±0.20 - 0.86±0.01 mg kg^{-1} greater than acceptable (0.4 mg kg^{-1}). Magnet-assisted soil washing followed by ZVI amendment (0.5%) successfully reduced the Cd concentration in rice grain to 0.33 mg kg^{-1}. Similarly, as soil amendments, biochar and BZVI (5%) successfully decreased Cd concentrations in rice grain to 0.29 and 0.19 mg kg^{-1}, respectively. Nevertheless, application of high concentrations of ZVI or BZVI (5%) caused substantial stress on the rice growth. Thus, considering the stress on the rice growth and the Cd reduction efficacy, magnet-assisted soil washing followed by ZVI amendment (0.5%) is a promising alternative.

Batch experiment for solar-powered electrokinetic separation

1. Characterizations of soil and materials

The soil texture in studied area was sandy clay loam soil (clay 29.2%, silt 13.72% and sand 57.08%) according to the USDA textural triangle (Ditzler et al., 2017) with the nature pH (7.94) and total organic matter of 3.74%. The calcium ions (Ca^{2+}) was 16.62 cmol$_c$kg^{-1} as shown in **Table 18**. The total Cd concentration in soil was 55.70±12.53 mg kg^{-1}, which exceeds the acceptable level for agricultural soil (3.0 mg Cd kg^{-1} (Simmons et al., 2005).

Nevertheless, based on the five-step sequential extraction, the bioavailable Cd fractions (combination of exchangeable and carbonate fractions) of the initial soil was 51.58% (23.13±0.44 mg Cd kg^{-1}) while the Fe-Mn oxide, the organic, and the residual fractions were 43.72, 2.71, and 1.99% (19.60±1.66, 1.21±0.03, and 0.89±0.06 mg Cd kg^{-1}), respectively (**Figure 49a**). When the spike soil sample was added of Cd solution for the concentration in soil to be 387.06±36.10 mg Cd kg^{-1}, the speciation of Cd in soil presented as 74.51% (252.66±55.68 mg Cd kg^{-1}) of the bioavailable Cd fractions, 23.54% (79.81±12.16 mg Cd kg^{-1}) the Fe-Mn oxide, 1.14% (3.86±0.81 mg Cd kg^{-1}) the organic, and 0.81% (2.74±0.98 mg Cd kg^{-1}) the residual fractions (**Figure 49b**). This result exposed that adding of Cd will increase the bioavailable Cd fractions.

Table 18 Physicochemical properties of soil sample

Category	Result
Soil texture	Sandy clay loam
Sand (%)	57.08±1.41
Silt (%)	13.72±1.41

Category	Result
Clay (%)	29.2±0.00
pH $_{(1:5)}$	7.94±0.09
OM (%)	3.74±0.89
CEC ($cmol_c kg^{-1}$)	10.54±1.52
Na^+ ($cmolckg^{-1}$)	0.16±0.255
K^+ ($cmolckg^{-1}$)	0.47±0.007
Ca^{2+} ($cmolckg^{-1}$)	16.62±0.109
Mg^{2+} ($cmolckg^{-1}$)	2.90±0.005
Cd ($mg\ kg^{-1}$)	55.70±12.53

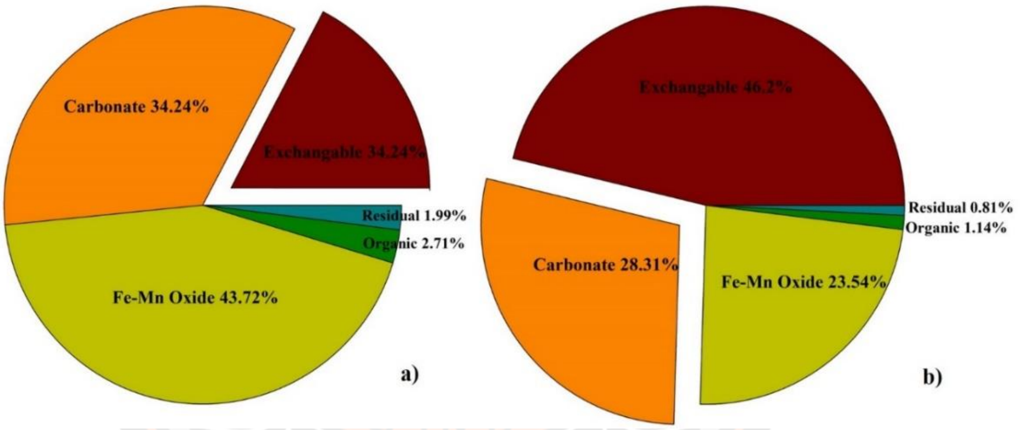


Figure 49 Cd fraction in a) initial soil and b) Cd-spiked soil sample

2. Variation of electrical potential

The solar cell (SC) power supply provided a voltage of 13 V to the system during the entire EK experiment period. The variation of input and output potential in soil in the EK process are shown in **Figure 50**. However, the solar-powered system supplied electrical input potential to the system ranging as 12.24±0.27 -12.42±0.13 V. The output potential in soil started differently as 3.93±0.68, 4.55±0.34, 4.17±1.32, 5.49±0.07 V of EK, EK&MZVI, EK&NZVI, and EK&Fe-rod respectively. After that, an output potential in all EK with SC experiment gradually raised and steady to 6.61±0.13, 6.12±0.57, 7.38±0.14, 6.1±0.33V of EK, EK&MZVI, EK&NZVI, and

EK&Fe-rod respectively. In general, the hydrogen ions (H^+) and the hydroxide ions (OH^-) are continuously generated in EK process because of the constant voltage. The continuous supply of conducting ions, including oxalate and H^+, greatly increased the current while the neutralization reaction between the H^+ and OH^- decreased the current value (Jeon, Ryu, & Baek, 2015). Moreover, increasing of voltage may affect from liquid conductivity. The increase in electrical conductivity with time may be due to an increase in the concentration of dissolved ionic species and this behaviour may be related to the electrolysis of water in the electrode regions especially the migration of acid solution leads to ion desorption (Rosales, Loch, & Dias-Ferreira, 2014). In addition, this study implied that the applied potential in soil was dependent on output potential and an inputted substance in soil. This result suggests that large particles of a substance (MZVI or Iron-rod) hindered the reaction of current and ions in the soil while NZVI generated more electricity than the initial system.

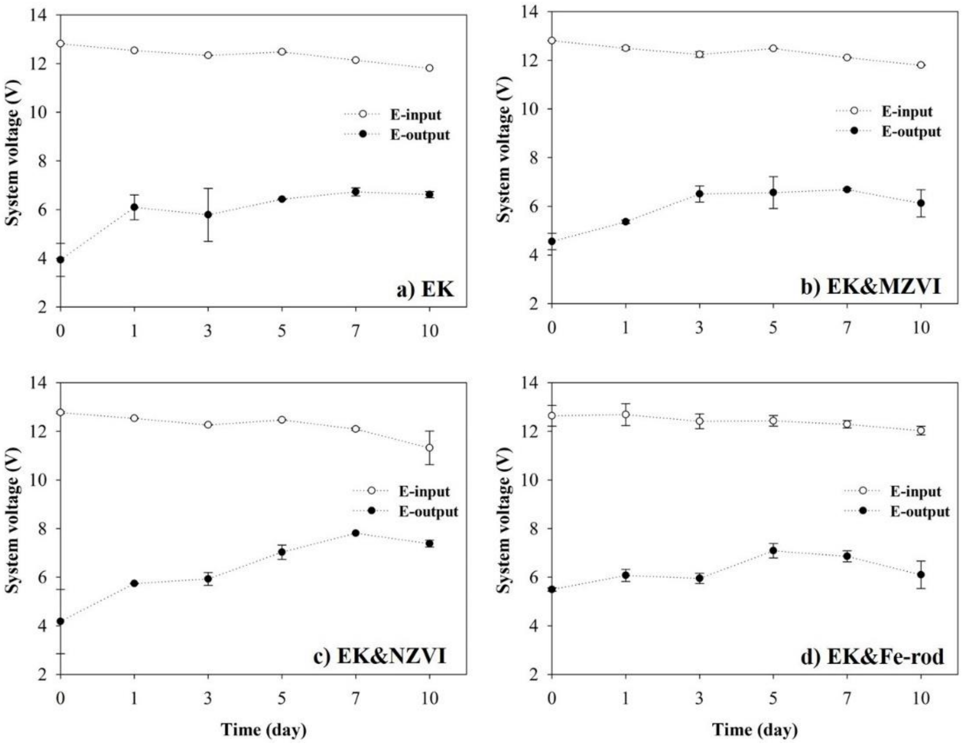


Figure 50 Change of electrical potential (input and output electrical) during the experiment period when connected with SC (13 V)

3. Effect of Cd migration and Cd accumulation on EK experiment

3.1 The EK experiment with SC without media (E1)

When the EK with SC (13 V) was conducted in reactor which contain of Cd-contaminated soil, the voltage variations with respect to time are shown in **Figure 51**. The average input voltage in system was 12.35±0.011 V. The initial output voltage stated at 3.93 ±0.68 V. After that, it immediately increased to 6.09 ±0.51 V in 1 day and lightly to change during run. Effect pH in system as presented in **Figure 51**, pH value in initial system ranged 7.32- 7.34. Next, pH value clearly tended to 3.56-3.86 after 3 day and then 10.21 and 9.57 of pH were observed in middle and near anode respectively. While the pH value in the cathode reduced to 2.43, after 5 of the fifteenth day, when the process ended, the pH was 7.44.

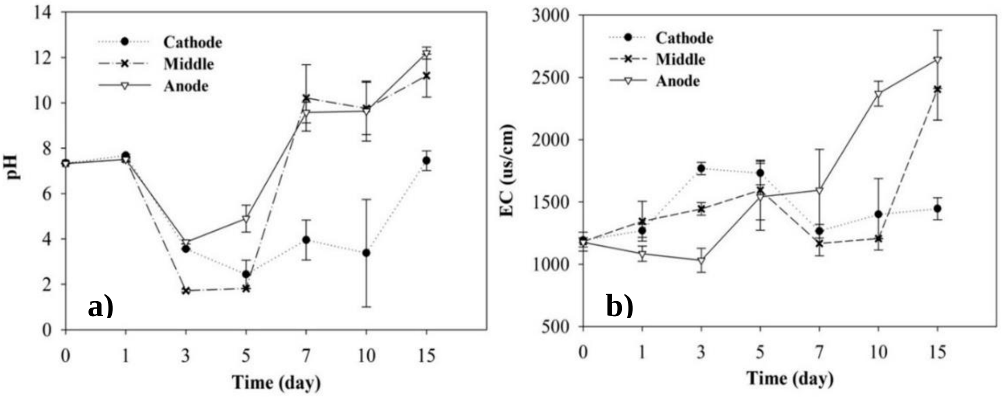


Figure 51 Change of a) soil pH and b) EC during the experiment period in E1

Generally, it has been well known that electrolysis reaction with electric field produce H_2 and OH^- at the cathode and O_2 and H^+ at the anode. The acid (H^+) and the base (OH^-) fronts travel by electromigration towards the cathode and the anode, respectively (Nasim et al., 2012; Virkutyte et al., 2002). H^+ are lighter than the OH^-. Therefore, the acid front typically travels a longer distance than the base front and the two fronts meet closer to the cathode. The variation of soil pH affects the electromigration of H+ to the cathode and OH- to the anode (Moghadam, Moayedi, Sadeghi, & Hajiannia, 2016). Soil pH in most regions was lower than the initial time, which was described to the faster electromigration rate of H+ than that of OH-similarly in results of this study. However, the soil pH value in this experiment tended to be alkaline in anode and middle while the pH near cathode was lower than the anode creating an acidic zone. These results are similar to those of previous research (Dos Santos, Medeiros, Dos Anjos, Martínez-Huitle, & Da Silva, 2014). It was assumed that the corrosion of the cathode electrode with sodium sulphate (Na_2SO_4) solution affected the pH features at the cathode. The cathode electrode (stainless-steel) corrosion assumed from the sulphate ions which can act as depolarization agents of iron reaction (Eq.21) and became to iron (II) sulphate ($FeSO_4$) (Eq.22) (Arzola, Palomar-Pardavé, & Genesca, 2003; Hasan & Sadek, 2013). In this experiment $FeSO_4$ was found to be a green solution in the cathode region (see **Figure 52**).

$$Fe_{(s)} \leftarrow\rightarrow Fe^{2+}_{(aq)} + 2e^{-} \tag{21}$$

$$SO_4^{2-}{}_{(aq)} + Fe_{(s)} \leftarrow\rightarrow FeSO_{4(aq)} + 2e^{-} \tag{22}$$

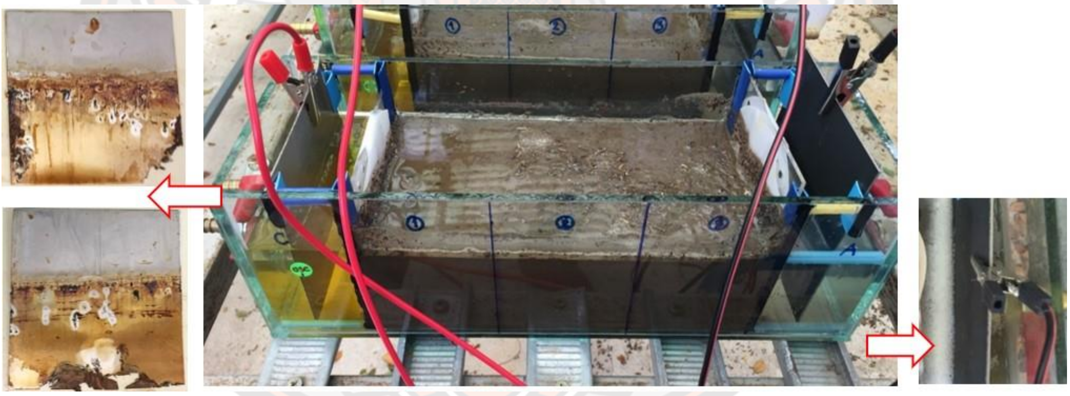


Figure 52 Behavior of electrolytes in E1 system connect with Solar cell

The movement of Cd and Fe in EK system was shown in **Figure 53**. The results presented the Cd content in the soil for each section (cathode, middle, anode) after application of EK with the solar cell. The initial mass of Cd was 5.653 ± 0.512 mg after that it moved from the anode to the cathode. The cell was connected from the outset of the experiment. After the seventh day, until the fifteenth day when the experiment concluded, it was clear that Cd moved from the anode to the cathode. The Cd accumulation in near cathode, middle and near anode section in end time (day

15) were 5.857 ± 1.947, 3.866± 0.176 and 3.892± 0. 207 mg, respectively. The percent of Cd accumulation was calculated as 100% near the cathode, 68.39% in the middle and 68.84 % of near the anode section when the mass was compared in initial time (see in **Figure 54**). In addition, Fe moved from the anode to the cathode, the same as the Cd. The initial mass of Fe was 279.87±1.056 mg. Fe started moving on the seventh day of the running of the experiment and accumulated as 214.57± 6.95 mg in near cathode, 175.99 ± 8.59 mg in middle and 174.86±2.76 mg in near anode at the end of test. In theory, the electromigration of heavy metal in contaminated soil involved the heavy metal desorption from soil and the subsequent electromigration (Yuan et al., 2008; Yuan et al., 2009). It has been demonstrated by experiments that when heavy metals enter into alkaline conditions, they adsorb to soil particles or precipitate as hydroxides, oxyhydroxides, etc. while those ions desorb solubilize and migrate in acidic conditions (Virkutyte et al., 2009). In this study, Cd electromigration under solar cell power supply can migrate from anode to cathode and was accumulated near cathode. The soil pH was highly related to the desorption of Cd from soil onto the pore solution (Yuan et al., 2008). Previously, Yuan et al. (2007) investigated the effect of pH on Cd desorption from kaolin (Yuan et al., 2007). Result exposed that the Cd desorption increased sharply and linearly with decrease of pH below 4.8. So, the decrease of pH in 3-5 day of all region in this study may encourage the Cd desorption onto pore water and migrate to the next region where there has more pH. However, the most Cd in system migrated and accumulated near cathode regions after 10-15 day.

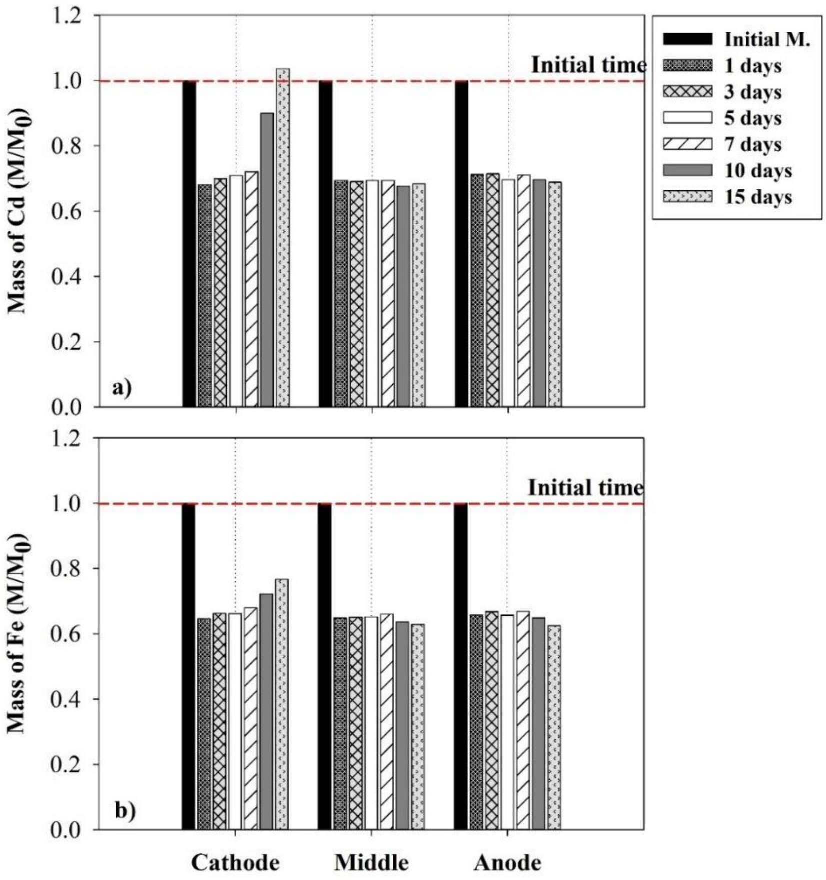


Figure 53 Mass change of a) Cd and b) Fe during the experiment period in E1

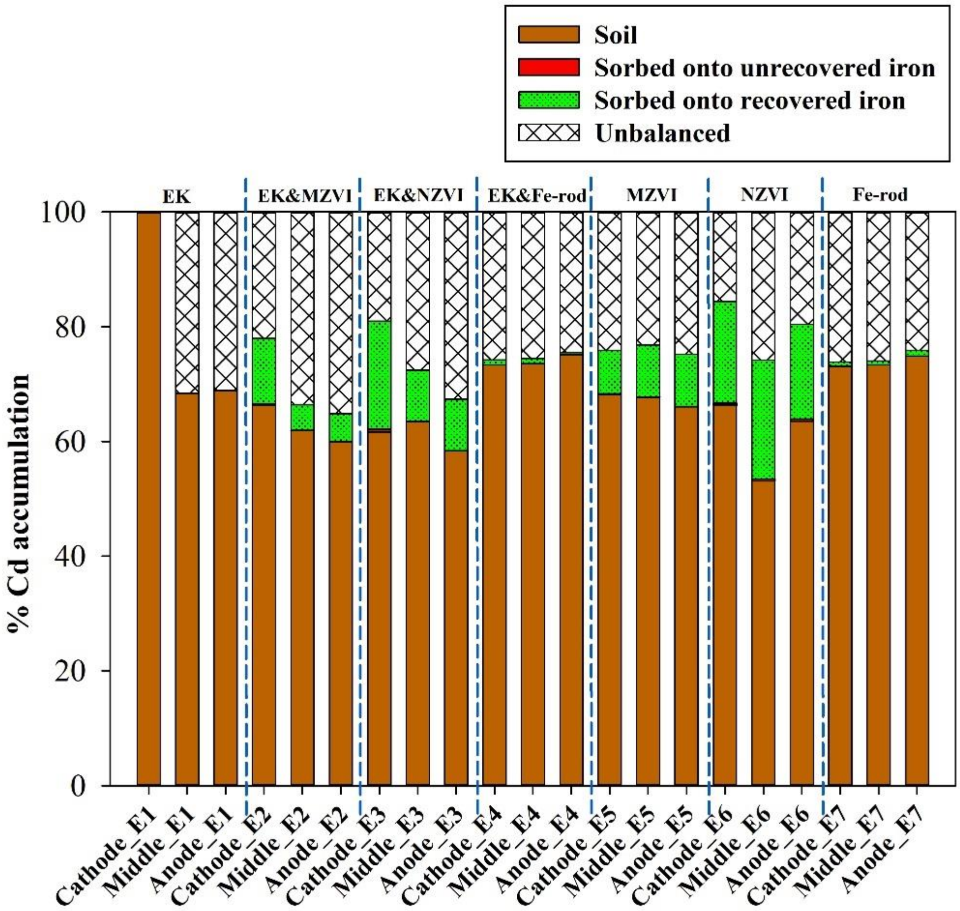


Figure 54 Accumulation of Cd in soil and iron as soil amendment during the experiment period

3.2 The EK experiment with/without SC using MZVI (E2/E5)

When the EK with SC (13 V) was conducted in reactor which contains of Cd-contaminated soil and MZVI as soil amendment (E5), the voltage variations with the conducted time are shown in **Figure 50**. The average input voltage in system was 12.32±0.043 V. The initial output voltage stated at 4.55 ±0.34 V. After that, it gradually increased to 5.36 ±0.07 V in 1 day and up to 6.12 ±0.56 – 6.68 ±0.05 V. Effect pH and electrical conductivity (EC) in system as presented in **Figure 55a and b**, pH value in initial system ranged 7.53±0.08-7.72±0.06. Next, the pH value clearly tended to acidic processes 0.58±0.00–2.24±0.5 after first day of all regions and then the pH value gradually was to 5.86±1.70 in middle and 9.22±0.25 near anode respectively. While the pH in near cathode region came back to 6.51±0.53 after the third day and gradually rising to 12.65 at the end of the system processes. Therefore, the behaviour of pH at the end of system was cathode > middle > anode. The using of MZVI as a soil amendment process in the EK system will increase the pH value even though the cathode region occurs with electrode corrosion (Rosales et al., 2014). In addition, EC was considered in EK experiments. The EC value ranged 867±38.18–914±26.87 us cm^{-1} in the initial system and clearly tended rising to 5,010±197.99, 5,305±431.33 and 6,430± 28.25 us cm^{-1} near the cathode, middle and near the anode region respectively.

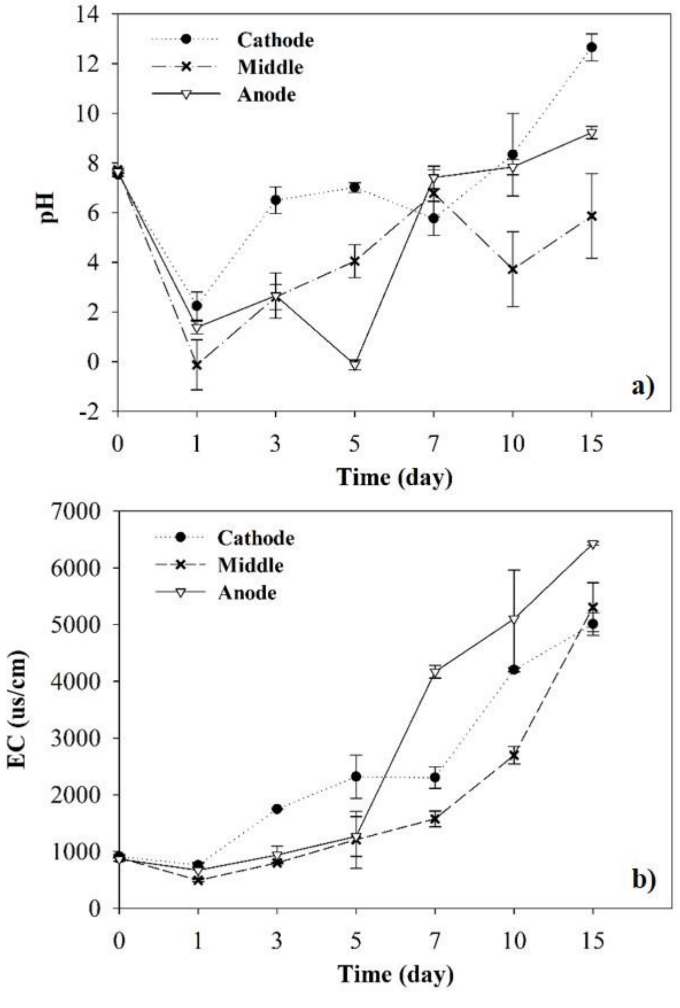


Figure 55 Change of a) soil pH and b) EC during the experiment period in E2

The movement of Cd in EK with SC and MZVI as soil amendment in each region as shown in **Figure 56**. The mass of Cd in the initial soil was 4.736±0.0084 mg. When system connected with SC power (13V), the Cd accumulation in the soil reduced as 3.144±0.016, 2.934±0.094 and 2.841±0.006 mg in cathode, middle and anode respectively. Most of Cd moved from anode to cathode region during experiment. On the other hand, this result was observed that the Cd accumulated in MZVI as 4-11% **(Figure 56 b)**. The reaction started after the first day with SC power, increasing Cd in MZVI was the order of the anode (0.398±0.026 mg), middle (0.344±0.004 mg) and the cathode (0.321±.0054 mg). However, Cd accumulation in MZVI was high in the cathode region from the seventh day to end time (averaged 0.394±0.104-0.541±0.159mg) where there was more than in the middle and the anode region. The percent accumulation was determined in the cathode, middle and anode in the end (present in **Figure 54**), Cd in soil was as 66.39%, 61.94% and 59.98% while Cd in MZVI was as 11.41%, 4.46% and 4.84% near cathode, middle and near the anode region respectively.

When the result of EK with MZVI as soil amendment experiment without SC (E5) was presented in **Figure 57 and 58**. In **Figure 57 a)** was a pH value in this experiment. It shows that pH value started at 7.48±0.028-7.50±0.011 of all regions. After that pH value tended to alkaline condition as 8.45±0.00, 8.02±0.039 and 8.56±0.102 in cathode, middle and anode regions respectively. In addition, EC (in **Figure 57 b**) gradually developed more than initial time especially in the anode region. EC value in the end were 1,683±86.27, 1,513.5±246.78 and 3 ,445± 516.19 us cm^{-1} in cathode, middle and anode regions respectively. This pH and EC value indicated that EK with MZVI as soil amendment experiments without SC reacted lower than with SC.

The movement and accumulation of Cd in soil and MZVI without SC represented in **Figure 58.** This result described that the Cd distribution of soil and MZVI were in similar of all regions as 3.793±0.063-5.084±0.803 mg from 6.365±0.081 in initial soil. The percent accumulation in the end was presented in **Figure 54**, Cd in soil was as 68.26%, 67.72% and 66.04% while Cd in MZVI was as 7.52%, 9.01% and 9.08% near cathode, middle and near anode region respectively. Therefore, EK with solar power enhanced Cd adsorption with MZVI and Cd movement to cathode region.

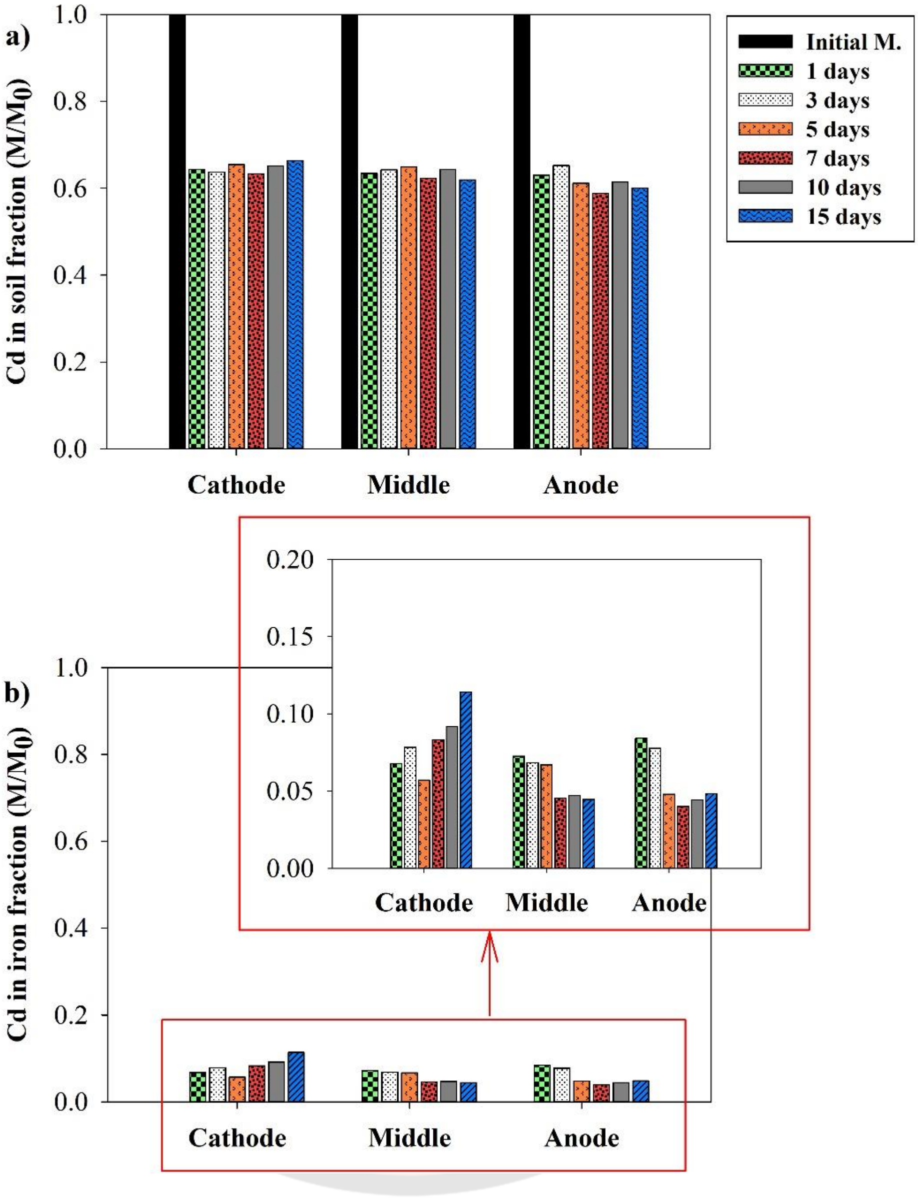


Figure 56 Change of mass a) Cd and b) Fe during the experiment period in E2

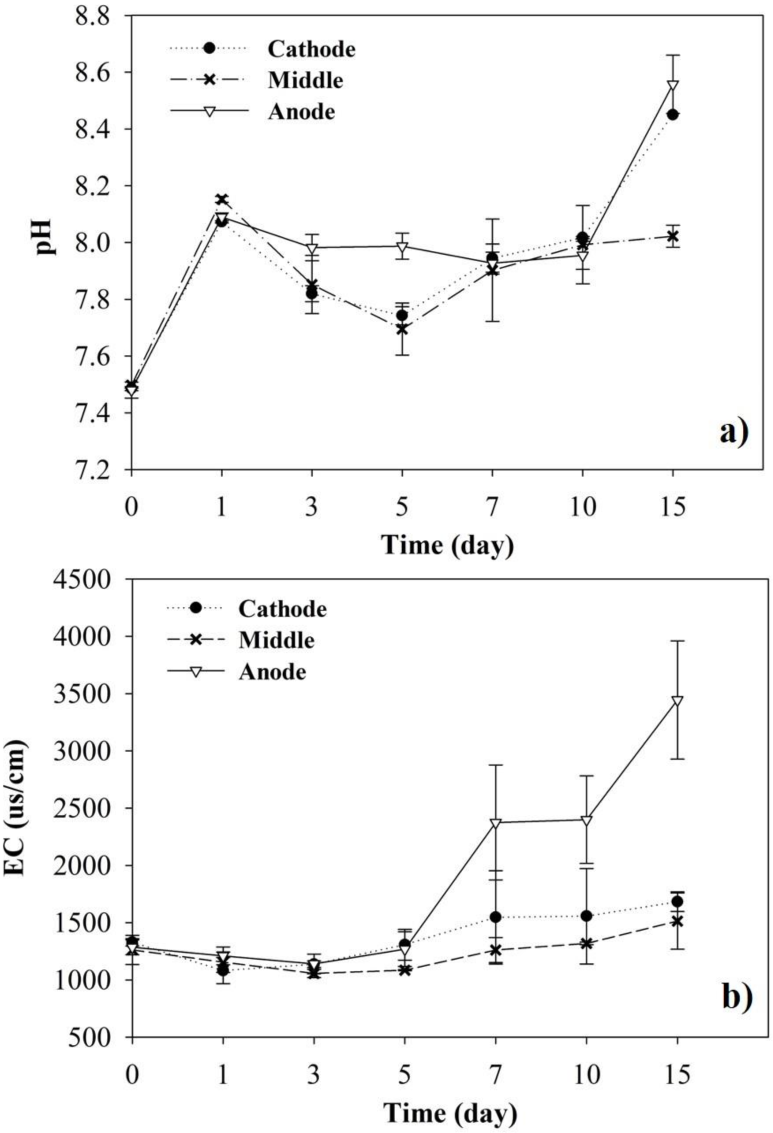


Figure 57 Change of a) soil pH and b) EC during the experiment period in E5

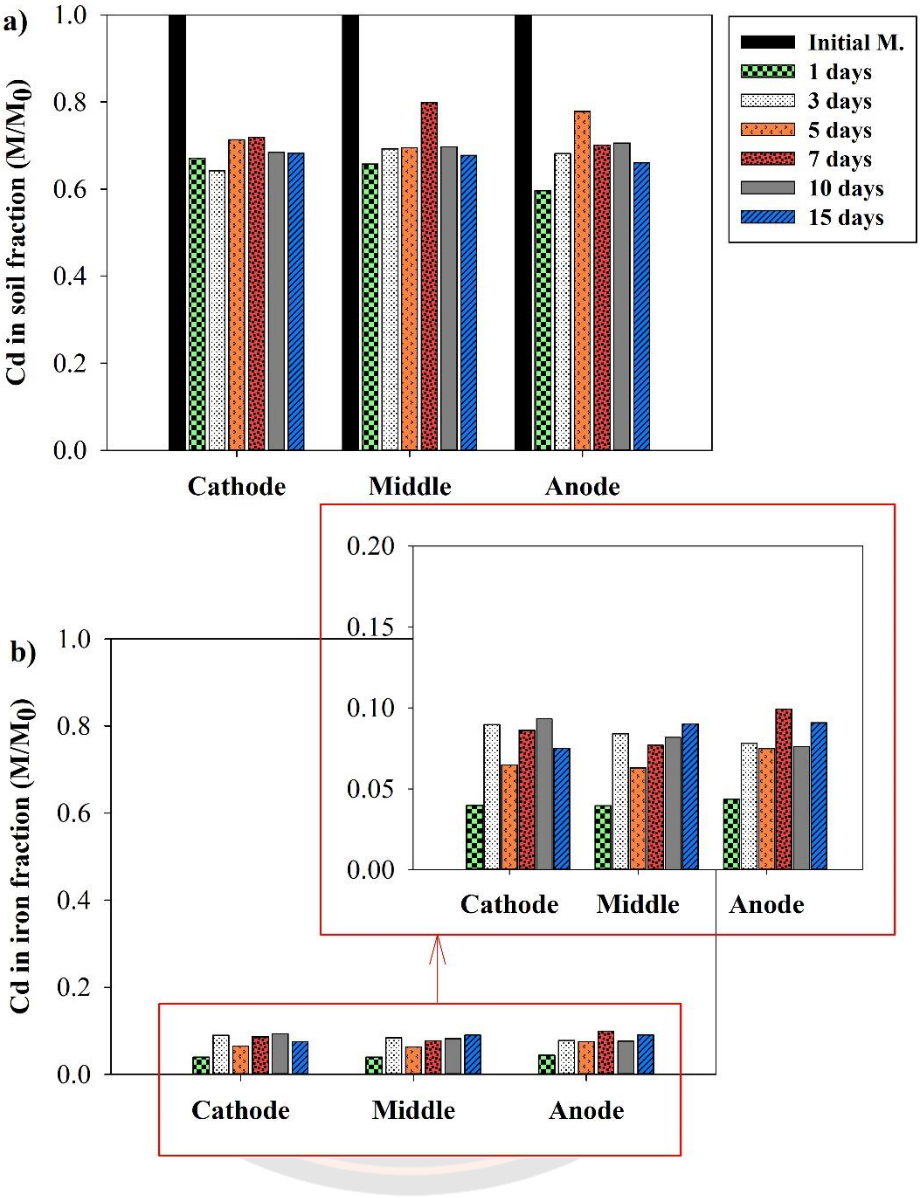


Figure 58 Change of mass a) Cd and b) Fe during the experiment period in E5

3.3 The EK experiment with/without SC using nZVI (E3/E6)

When NZVI was applied as soil amendment together EK with SC (13 V) for Cd contaminated soil treatment, the results presented that (see **Figure 50**) the average input current was 12.24 ± 0.27 V. The initial output voltage stated at 4.15 ± 1.32 V. After that, it gradually increased to 5.73 ±0.01 V in 1 day and up to 7.03 ±0.30 – 7.81 ±0.00 V in the end run. Effect pH and electrical conductivity (EC) in system as presented in **Figure 59**, pH value in initial system ranged 7.24±0.01 - 7.32±0.08. Next time, pH value clearly reduced to acidic processes 0.22±0.00–2.12±1.16 after 1 day of all regions (anode >middle > cathode) and then soil pH is gradually changed with time becoming alkaline at near cathode (10±0.11), middle (6.185±2.95) and near anode (9.37±1.07). The behaviour of pH in end system was cathode > anode > middle when NZVI was employed. It is interesting to see the effect, probably because of reaction taking place between NZVI and the soil (Rosales et al.,2014). It was similar to the MZVI experiments. In addition, EC (in **Figure 59 b**) at initial time, ranged 1,035±25.45 - 995±0.00 us cm^{-1} and tended to increase until the end of system. The EC values at the end were 4,220±735.39, 3,680±0.00 and 7,765± 0.00 us cm^{-1} in the cathode, middle and anode regions respectively

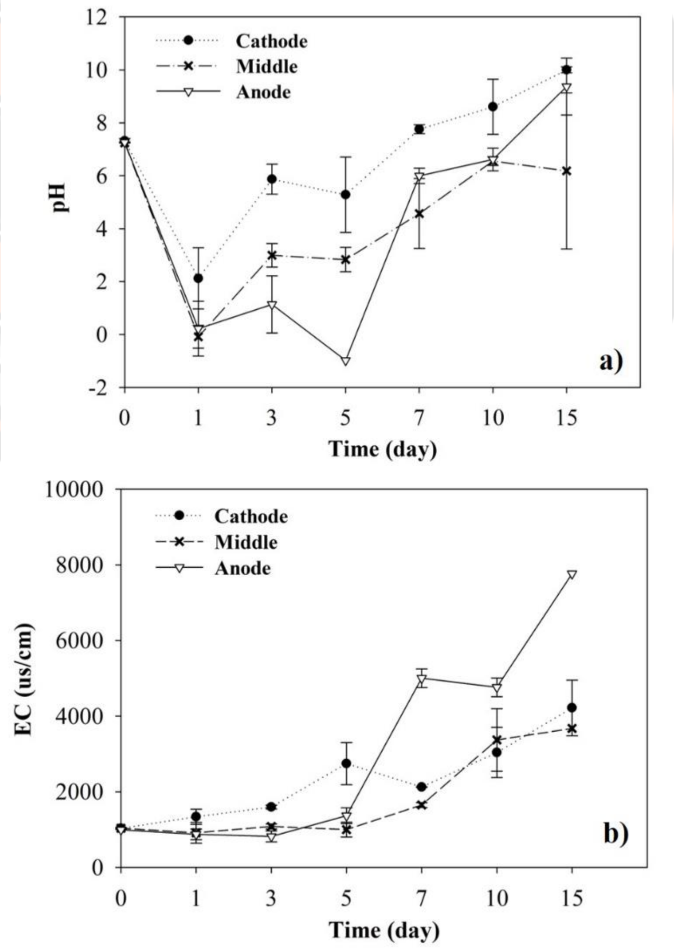


Figure 59 Change of a) soil pH and b) EC during the experiment period in E3

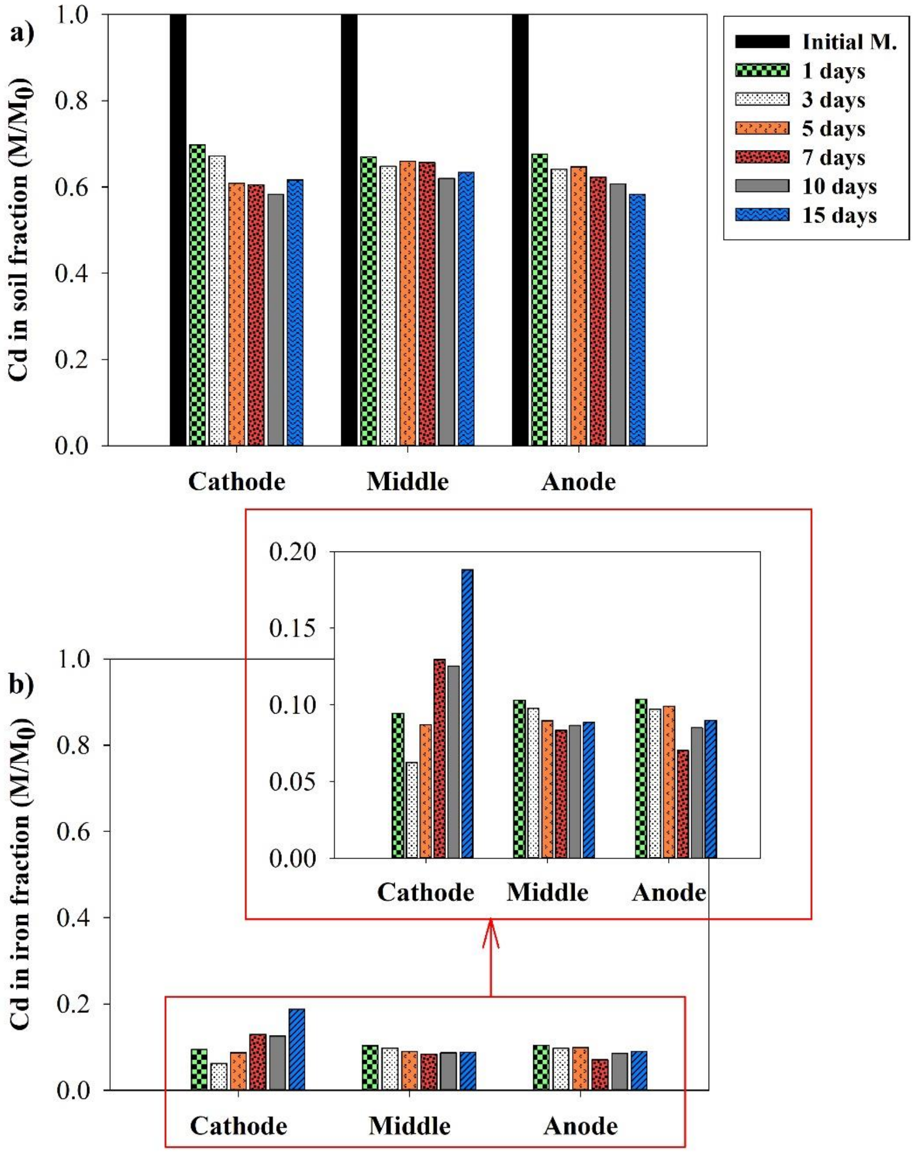


Figure 60 Change of mass a) Cd and b) Fe during the experiment period in E3

Effect to Cd transport was shown in **Figure 60**. The Cd mass initially in the soil when the experiment began was 4.411±0.133 mg. When system was connected with SC power, the Cd accumulation in soil clearly reduced. The Cd gradually accumulated in NZVI and the NZVI moved from the anode to the cathode over the seven days until the end of the experiment. Cd in soil at the end of system were as 2.718±0.095, 2.796±0.0285 and 2.573±0.053 mg (or 61.62%, 63.40% and 58.3%) at the cathode, the middle and the anode respectively. While Cd in NZVI were as

0.830±0.537, 0.391±0.0035, 0.396±0.262 mg (or 18.82%, 8.86% and 8.98%) at the cathode, the middle and the anode respectively

When compared with results of NZVI as soil amendment together EK but without SC (see in **Figure 61 and Figure 62**), the variation of the pH in all regions gradually tended from acid to base (8.15±0.113–8.95±0.240) from the initial value (7.13±0.085-7.16±0.127) of the experiment without SC. Moreover, the EC at the beginning of the experiment, ranged from 1,386.5±0.71–1,410±12.73 us cm^{-1} to 1,006.5±144.96–2,790±0.00 us cm^{-1} in the end, which was lower than in the experiment with SC (see **Figure 61**). The Cd in the system was gradually adsorbed in NZVI as ranging 8.57% - 23% (0.567±0.129-1.534±0.218 mg) and distributed all over the reactor while the Cd in the soil decreased from 6.611±0.232 mg to 4.384±0.104 in the cathode, 3.513±0.387 in the middle and 4.200±0.011 in the anode (see in **Figure 62 and Figure 54**). This result indicates that the application of NZVI only to Cd contaminated soil lead to Cd adsorption in NZVI. When NZVI is applied with EK&SC it leads to Cd desorption from the soil to pore solution or re-adsorption with NZVI and the movement to the cathode region.

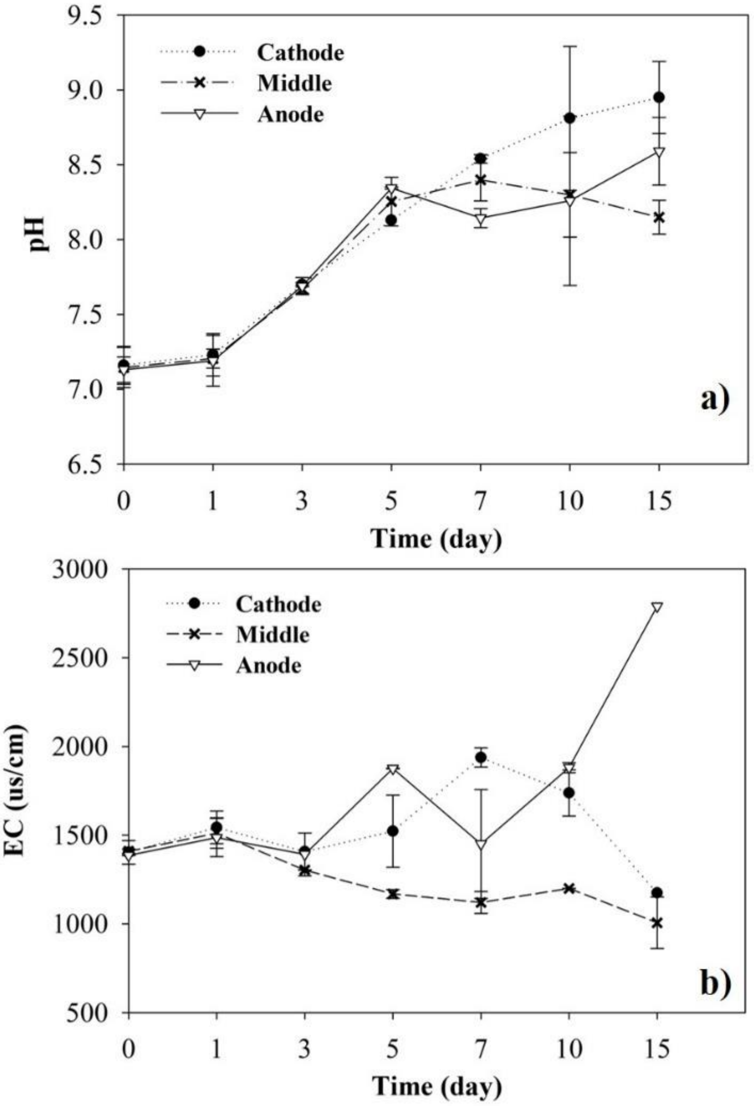


Figure 61 Change of a) soil pH and b) EC during the experiment period in E6

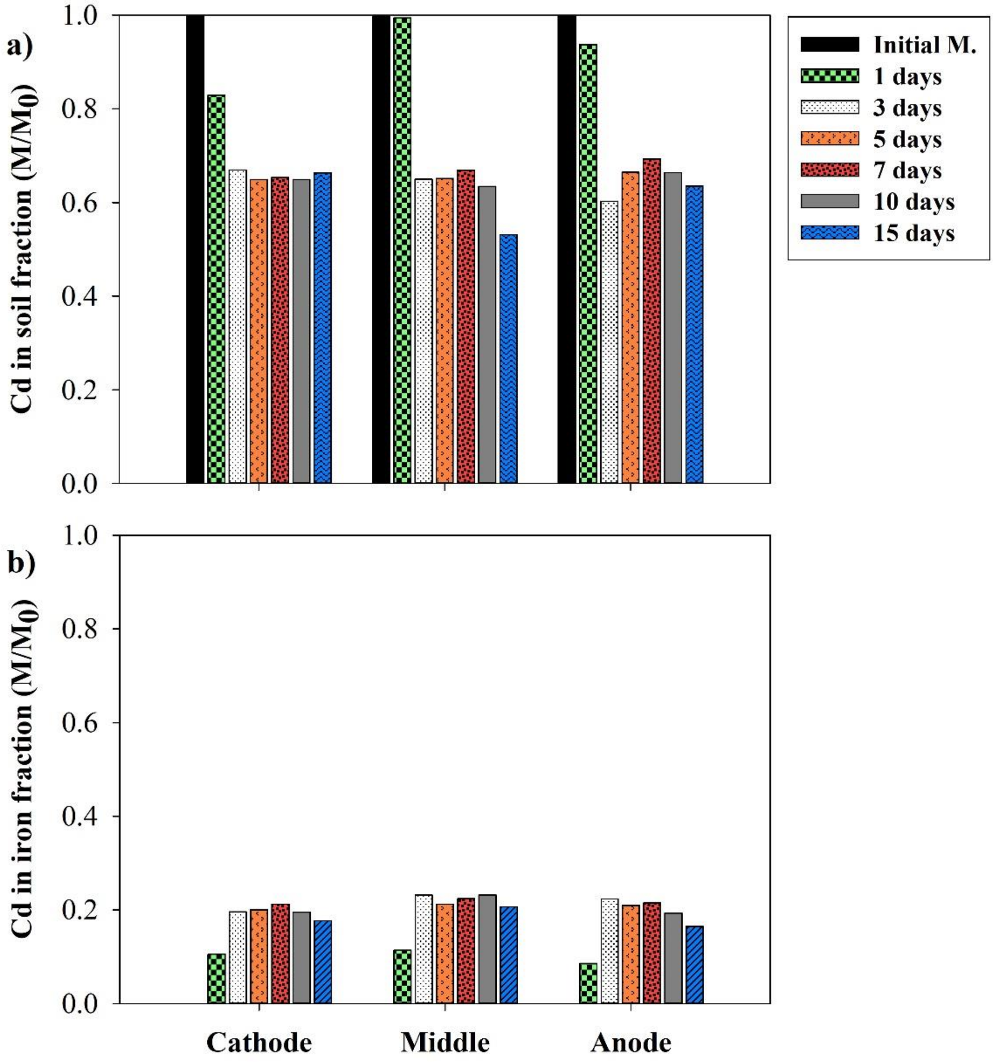


Figure 62 Change of a) Cd and b) Fe mass during the experiment period in E6

3.4 The EK experiment with/without SC using iron-rod (E4/E7)

The Fe-rod was applied as soil amendment together EK with SC (13 V). The results presented that the average input potential was 12.42 ± 0.13 V. The initial output voltage stated at 5.49 ± 0.07 V. Next, it gradually increased to 7.75 ±0.33 V in the end run (see **Figure 50**). Variations of pH and electrical conductivity (EC) in system was presented in **Figure 63**. The pH value in initial system ranged 7.45±0.00 – 7.50±0.13. In this experiment, the pH value was slightly acid to slightly alkaline in cathode and middle, while near anode the pH tended to be more alkaline. In addition, EC (in **Figure 63b**) initially ranged between 1,160±33.94 – 1,211.5±61.52 us cm^{-1} and tended to gradually increase until the end of the system especially near the anode region. The EC values were in the end were 2,850±933.38, 5,250±0.00 and 6,240± 1,046.52 us cm^{-1} in cathode, middle and anode regions respectively.

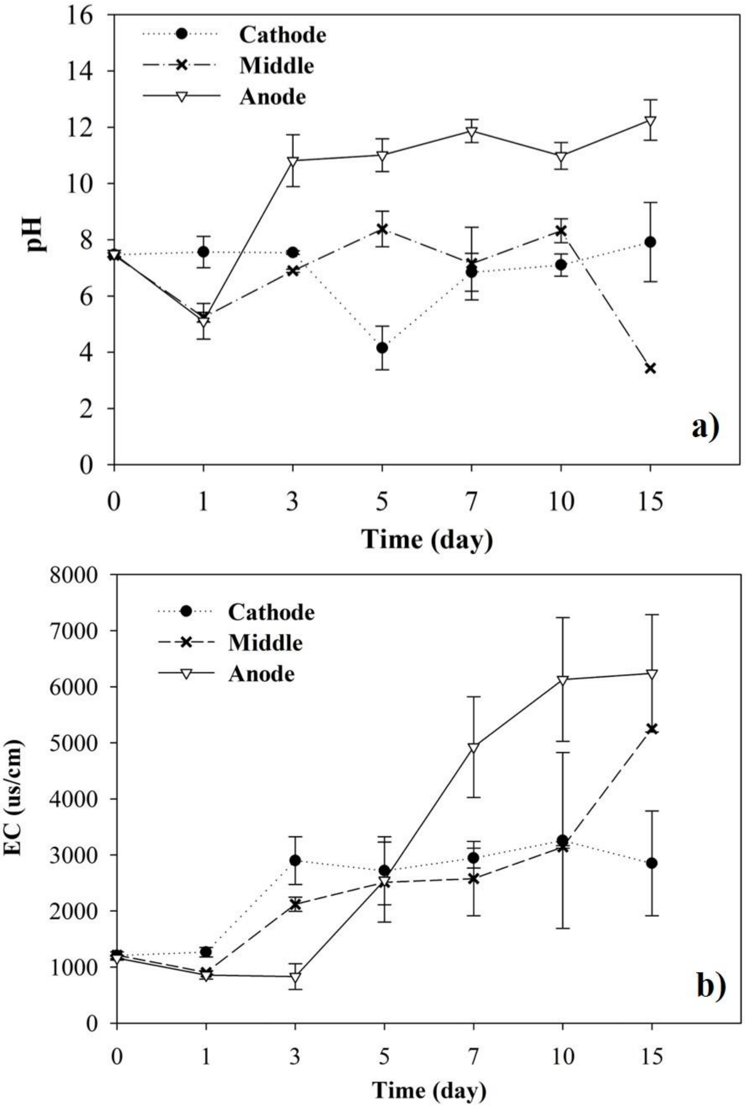


Figure 63 Change of a) soil pH and b) EC during the experiment period in E4

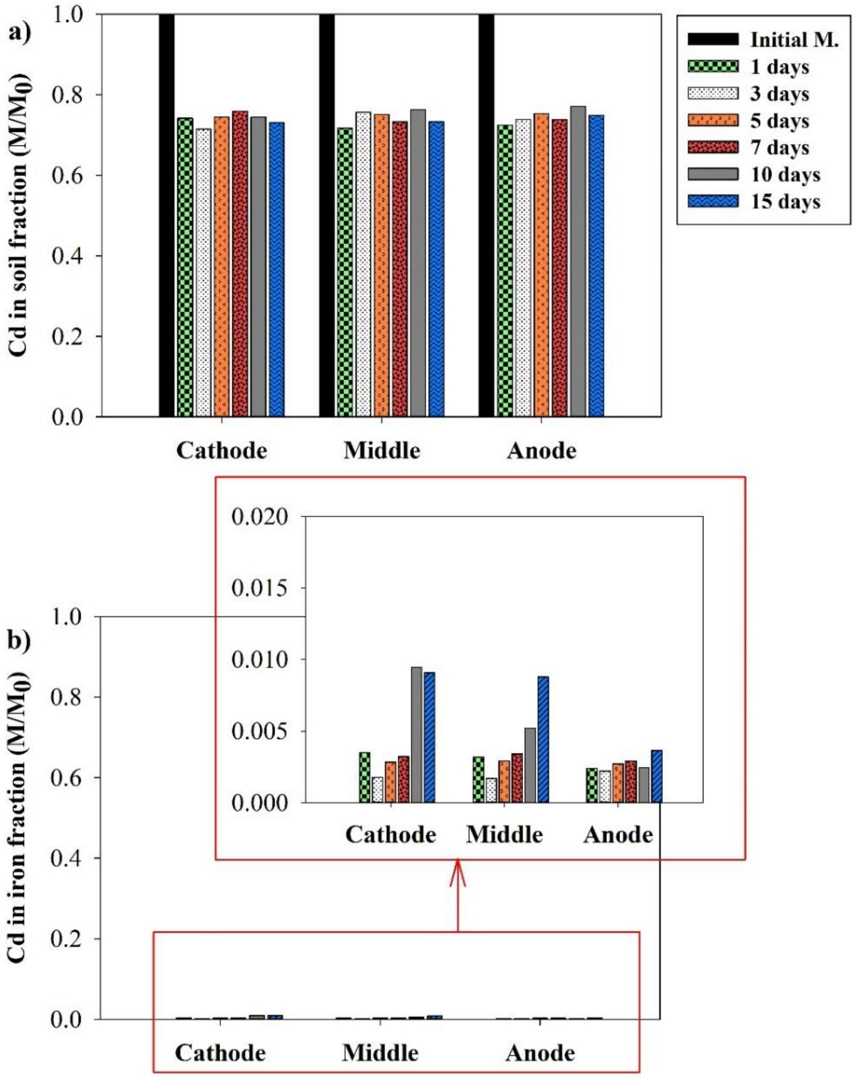


Figure 64 Change of a) Cd and b) Fe mass during the experiment period in E4

The movement and accumulation of Cd in EK with SC in the soil and the Fe-rod in each region is shown in **Figure 64**. The initial mass of Cd in the system ranged 5.768±0.044 mg. When system applied with SC power (13V), the Cd accumulation in soil gradually reduced in the anode (4.128±0.077 mg) and the middle (4.533±0.137 mg), however it increased and moved to the cathode (6.727±0.444 mg). On the other hand, Cd slightly increased in the Fe-rod (1%) especially during the 10-15 day period of the connection with solar power and most of Cd in the Fe-rod accumulated in the middle and the cathode. Looking at the result of using the Fe-rod without SC, the pH value in this experiment tended to slightly high from 7.4±0.04 (ranged at initial time) to 8.67±0.47 (ranged at the end). In addition, the EC value ranged 1,131±1.41 - 1,171± 48.08 us cm^{-1} and gradually tended to 4,390±777.8, 3,610±212.13 and 5,635±1110.2 us cm^{-1} in the cathode, the middle and the anode respectively (see **Figure 65**). While the Cd accumulation in the soil system was 5.788±0.008 mg and gradually decreased to 4.231±0.026, 4.244±0.045 and 4.334±0.131 mg in the cathode, the middle and the anode respectively (see in **Figure 66**). This result suggests that 1% of Cd was adsorbed in the Fe-rod similar in E4 (Fe-rod with SC) but using SC led to Cd-Fe-rod movement to the cathode region. Therefore, the Fe-rod as soil amendment is not efficient in Cd adsorption. The connection with SC enhanced Cd movement to the cathode.

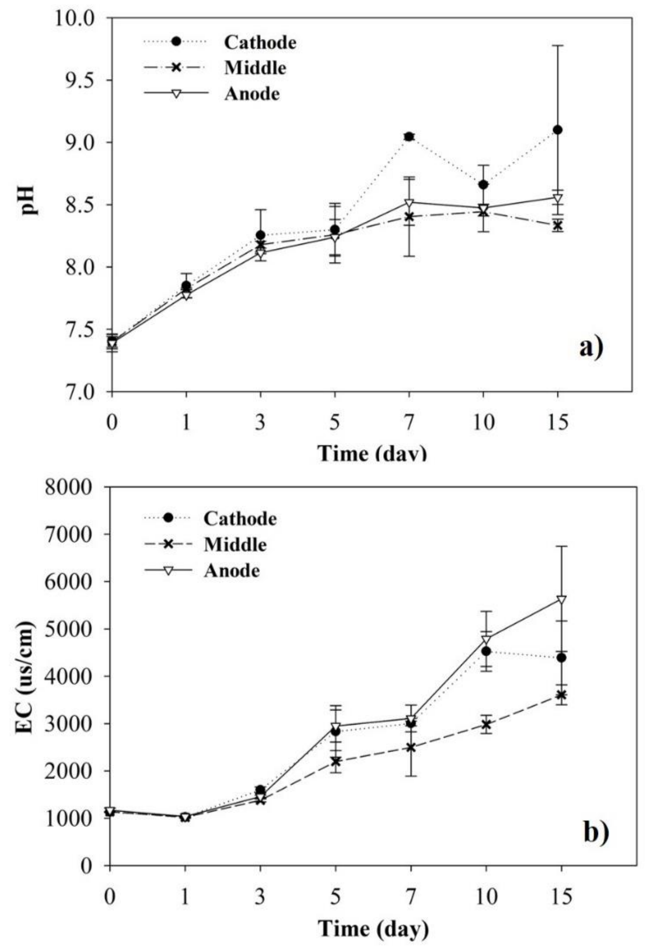


Figure 65 Change of a) soil pH and b) EC during the experiment period in E7

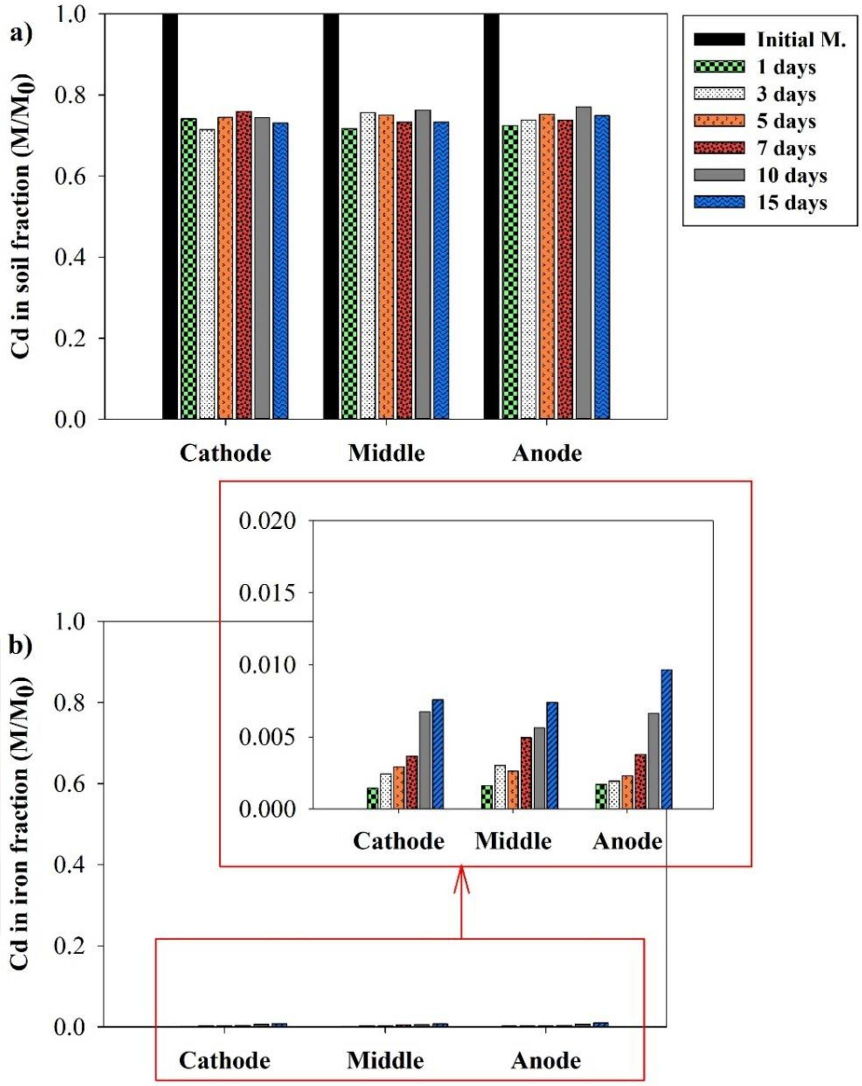


Figure 66 Change of a) Cd and b) Fe mass during the experiment period in E7

4. Changes in Cd Speciation

Initially, the Cd concentration in soil was 387.06±36.10 mg Cd kg^{-1} and 46.2% (156.67±41.39 mg Cd kg^{-1}) as the exchangeable form, 28.31% (95.99±21.68 mg Cd kg^{-1}) as the carbonate fraction, 23.54% (79.81±12.16 mg Cd kg^{-1}) as the Fe-Mn oxide, 1.14% (3.86±0.81 mg Cd kg^{-1}) as the organic, and 0.81% (2.74±0.98 mg Cd kg^{-1}) as the residual form. The EK with SC treatment led to the moving of the exchangeable form as 35.62%, 19.28% and 26.29% near the cathode, the middle and near the anode respectively (see in **Figure 67**). The application of iron (MZVI, NZVI and Fe-rod) with

EK and SC can not only move the bioavailable Cd form but also reduce the bioavailable fraction especially exchangeable form. The exchangeable Cd form in MZVI with EK and SC was 14.06%, 3.06% and 4.39% near the cathode, the middle and near the anode respectively. The exchangeable Cd form in NZVI with EK and SC was 17.59%, 6.34% and 3.71% near the cathode, the middle and near the anode respectively. The final type of iron (Fe-rod), the exchangeable Cd form was 32.25%, 27.30% and 14.85% near the cathode, the middle and near the anode respectively. The results exposed the application of iron especially MZVI and NZVI with EK and SC can be enhanced to reduce the exchangeable Cd. In addition, using MZVI and NZVI with EK and SC increased a Fe-Mn oxide and residual forms especially a Fe-Mn oxide. The Fe-Mn oxide form existed as 41.27%, 56.41% and 57.30% near the cathode, the middle and near the anode respectively when MZVI was applied. While application of NZVI increased to 44.40%, 56.20% and 57.61% near the cathode, the middle and near the anode respectively.

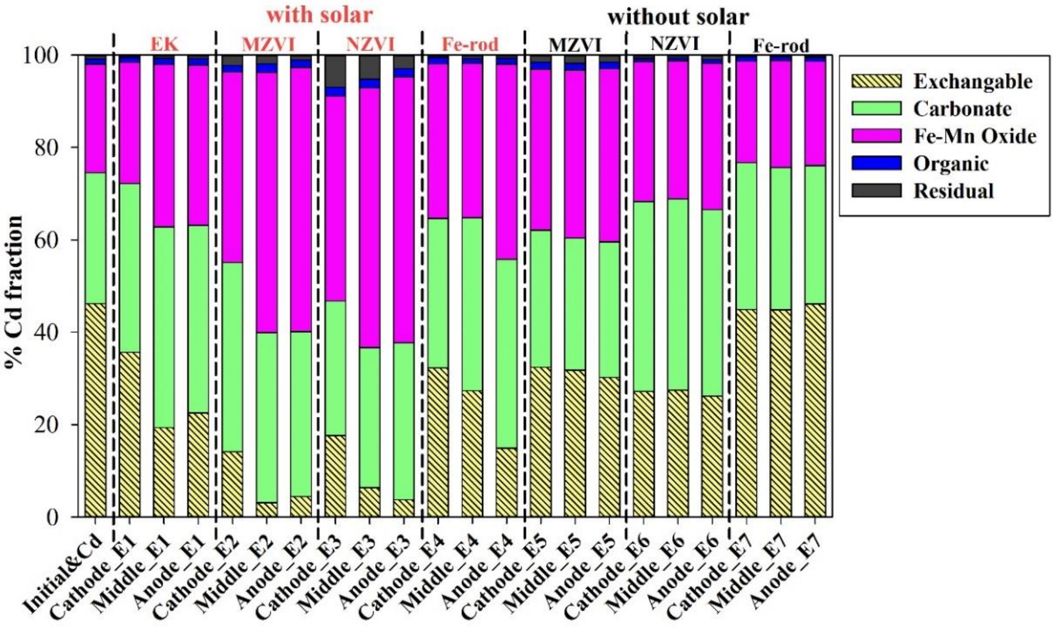


Figure 67 Fraction change of Cd during the experiment period

The results of Cd accumulation, movement, and Cd speciation suggested the using MZVI and NZVI & EK with SC enhanced Cd adsorption in M&NZVI

movement to the cathode by electrophoresis which was the movement of iron oxide form (Chowdhury, O’Carroll, Xu, & Sleep, 2012; Jones, Reynolds, Wood, & Thomas, 2011; Pamukcu, Hannum, & Wittle, 2008).

When using exchangeable Cd values of the anode part, which exchangeable Cd remained at the lowest level. This experiment predicted the Cd in rice by isotopically exchangeable Cd (rice grain Cd = (- 0.312) + 0.166 x (E-value (mg/kg)) from previous study of the similar area (Kosolsaksakul, Oliver, & Graham, 2018). E value was the best predictor of rice grain Cd for several of the soils and correlated well with Tessier 1 extracts or exchangeable Cd of this study. Rice grain Cd was predicted in **Table 19**. Rice grain Cd (in **Table 19**) exposed the application EK with solar cells can reduce Cd in rice as (13.68 mg kg^{-1}). While using iron especially, MZVI and NZVI & EK with SC promoted Cd immobilization in irons which lead to the reduction of Cd in rice as 1.24 mg kg^{-1} of MZVI & EK with SC and 0.85 mg kg^{-1} of MZVI & EK with SC.

Table 19 Rice grain Cd predicted from regression equations of previous study

EK exp.	Exchangeable Cd (mg kg^{-1})	Grain Cd (mg kg^{-1})	Cd to rice grain (%)
Initial	7.77	0.98	-
Initial & Cd	156.67	25.70	100
E1(EK)	84.26	13.68	98.95
E2(EK&MZVI)	9.33	1.24	80.83
E3(EK&NZVI)	6.98	0.85	73.96
E4(EK&Fe-rod)	57.66	9.26	97.91
E5(MZVI)	130.26	21.31	99.75
E6(NZVI)	59.09	9.50	97.99
E7(Fe-rod)	185.06	30.41	100.20

5. Relative of germination and EK experiments

After the EK test, the treated soil of cell was determined the gemination index (GI). The GI of EK experiments (E2-E4) were compared with untreated soil (E0) (see **Table 20** and **Figure 68**). EK with SC and combination of EK and amendments

(MZVI, NZVI and Fe-rod) with SC has no effect on the number of germinated rice seeds and shoot growth except Fe-rod. Obviously, application of EK treatment cause to positive relation of seed gemination and shoot elongation more than untreated soil. Thus, GI values were 243% for EK with SC, 162% for EK and NZVI with SC, 149% for EK and MZVI with SC and 93% for EK and Fe-rod with SC.

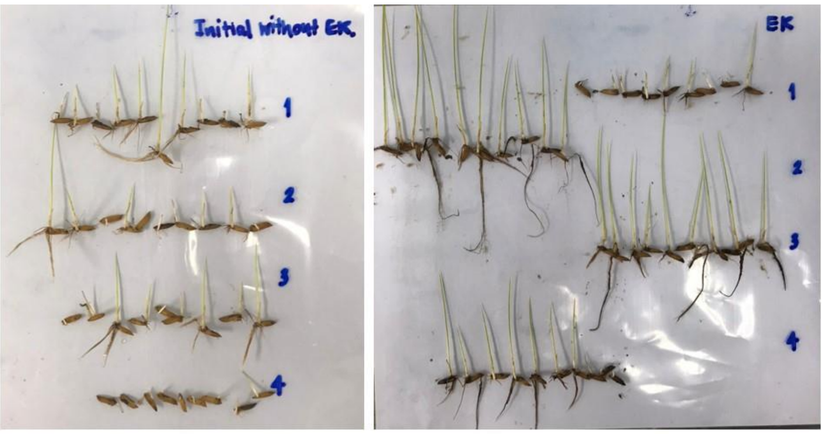
Table 20 Germination index determination for evaluation after conducted EK

EK exp.	Number of Germinated Seeds	Shoot Length (cm)	Relative Seed Gemination	Relative Shoot Elongation	Gemination Index (GI)
E0	9.00±1.41	1.78±1.41	100	100	100
E1	9.75±0.50	4.00±2.33	108	225	243
E2	10.00±0.00	2.40±1.01	111	134	149
E3	9.75±0.50	2.66±1.06	108	149	162
E4	9.25±0.96	1.61±0.96	102	90	93
E2 (Sep.)	9.00±0.82	1.81±1.20	100	102	102
E3 (Sep.)	8.75±0.50	1.92±0.84	97	108	105
E4 (Sep.)	7.25±0.50	1.10±0.68	81	61	49

Note: *E0 = untreated soil or initial soil

Generally, the electric field can affect plant growth in two ways. Firstly, it increases the ions in the soil. Secondly, it can have an impact on the overall activities of plants related to the metabolism of electrons and ions (Celestino, Picazo, & Toribio, 2000; Rezaei-Zarchi, Imani, Mehrjerdi, & Mohebbifar, 2012) such as the effect to the electron transport chain which is one of the respiratory pathways in plant tissues, leading to changes in the cellular respiration (Allen et al.,1985; Rezaei-Zarchi et al., 2012). In addition, electric polarization of the membrane system causes abnormal accumulation of water in the plant. These factors lead to inflation which is excessive storage macro molecule and lead to break the membrane systems and tissues of irregular shape and thus may increase germination rate (Isobe, Ishida, Koizumi, Kano, &

Hazlewood, 1999; Rezaei-Zarchi et al., 2012). Previously study can describe that electric field treatment improves germination of this study.



Initial soil

Control with EK

EK&MZVI

EK&NZVI

EK&Fe-Rod

EK&MZVI-retrieved

EK&NZVI-retrieved

EK&Fe-Rod-retrieved

Figure 68 the seed gemination shoot elongation after experiment with EK

6. Summary of batch experiment for solar-powered electrokinetic separation

6.1 The application of EK, EK&MZVI, EK&NZVI and EK&Fe-rod may be an increase in the ion concentration effect to behaviour of electrolysis in the electrode regions and migration of ion. In addition, large particles of the substance (MZVI or Fe-rod) hindered the reaction of the current and ions in the soil while NZVI generated the voltage.

6.2 When the system connected to SC, reduction of soil pH in the system led to Cd desorption and Cd migration to accumulate in the cathode region. On the other hand, using MZVI and NZVI as a soil amendment in the EK system will accelerate to decrease pH, leading quickly to Cd desorption and the turning of the system to alkaline.

6.3 EK with SC treatment can decrease and move the bioavailable Cd to the cathode. While using iron (MZVI, NZVI, and Fe-rod) with EK and SC cannot only move the bioavailable Cd form but also reduce the bioavailable fraction especially exchangeable form. However, using MZVI and NZVI with EK and SC increase a Fe-Mn oxide and residual forms especially a Fe-Mn oxide. Therefore, the use of MZVI and NZVI as a soil amendment in the EK system, can promote Cd adsorption as Fe-Cd leading to move of Fe-Cd to the cathode by electrophoresis which was the movement of iron oxide form.

Cost-Benefit Analysis

1. Health Cost with Monte Carlo Simulation

Based on the MCS results, we separated the Cd diseases in two groups including chronic kidney diseases (CKD) (nephrosis/nephritis, osteoporosis, cardiovascular and cerebrovascular diseases) and cancer diseases (prostate and breast cancers) for health cost analysis. The average of Cd level in urine from MCS simulation was 14.61±18.47 μg g^{-1} creatinine over the standard limit of 0.2 μg g^{-1} creatinine (Songprasert et al., 2015; WHO, 1992) while the average of dietary Cd was 3.34±3.96 μg day^{-1} higher than the Joint FAO/WHO Expert Committee on Food Additives (JECFA) Provisional Tolerable Weekly Intake (PTWI) of 7 μg Cd kg^{-1} body weight (BW) per week (1 μg day^{-1}) (Satarug S, & Moore MR, 2004; Satarug et al., 2010). When the risk value of Cd diseases (see in Table S1) was inputted in the 1,000, 5,000 and 10,000 MCS simulations for the health outcomes and health expanses, the result showed in Figure 4. The trend of health expanses from **Figure 69** indicated that most of the villagers are at risk of contracting CKD diseases rather than cancer, which is significantly different. The confidence interval (±95%CI) of average health cost in 10,000 simulation was 7,022,191 (±82,665.66)-baht patient^{-1} of CKD diseases while the cancer disease presented 9,576 (±840.72)-baht patient^{-1}. In addition, the confidence interval (±95%CI) of death value of CKD and cancer disease was 1,501,155(±11,633.53)-baht patient^{-1} and 8,413(±715.66)-baht patient^{-1}, respectively on 10,000 MCS simulation. However, the usual simulation model not only generates the inclination but also making 10,000 simulations leading to confidence in the average data.

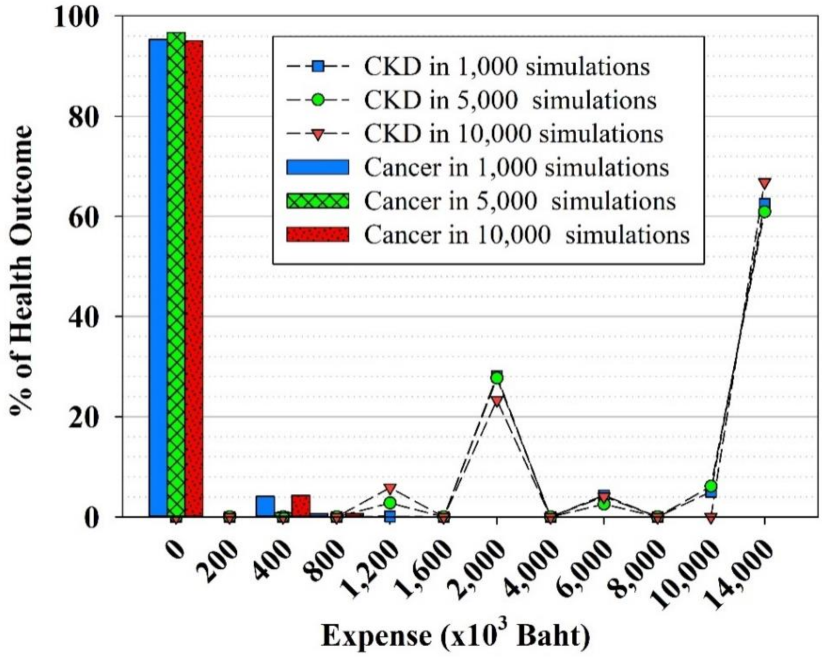


Figure 69 Health cost of Cd exposure from Monte Carlo Simulation

2. The costs and benefits of policy

7 policies (cases) for this area including i) no action, ii) the only risk assessment by Thai government, iii) risk management (sugarcane cultivation) by Thai government, iv) the restoration by soil washing, v) soil amendment, vi)

phytoremediation and vii) electrokinetic had the net benefit present value presented in Table 2. In non-remediation cases, villagers in Cd contamination areas suffered the expense from health outcome, the value of life and loss of opportunity of rice cultivation in 3,603,234-baht rai^{-1}year^{-1}. In the only risk assessment by Thai government case led to the expense of management and villagers still suffered the expense from health outcomes, the value of life and loss of opportunity. The expense of this case was 3,604,115 -baht rai^{-1}year^{-1}. When management by sugarcane cultivation, the expense reduced in 2,184,884-baht rai^{-1}year^{-1} because villagers received benefits from sugarcane.

In alternative techniques of soil restoration such as, soil washing, soil amendment, electrokinetic and phytoremediation, had an expense from machines, materials and management costs while they had benefits from rice cultivation. The expenses were in order of biochar amendment > soil washing> electrokinetic> phytoremediation (see in **Table 21**)

Table 21 Summary of NBPV in each policy

Policy	**NBPV (baht rai^{-1}year^{-1})**	**NBPV (*US dollar rai^{-1}year^{-1})**
1. No action	-3,603,234	-117,649
2. Biochar amendment	84	2.73
3. Soil washing	-1,404	-46
4. Electrokinetic	-87,373	-2,854
5. Phytoremediation	-100,626	-3,286
6. Management (sugarcane cultivation)	-2,184,884	-71,338
7. Assessment only	-3,604,115	-117,678

Note: NBPV is net benefit present value
* Exchange rate is 30.627 baht/US dollar at 1st October 2019 from https://www.bot.or.th

The cumulative costs, benefits and year of policy were applied for the comparation of different policies. It showed in **Figure 70**. The highest of cost and benefit is for the policy of no action and the only risk assessment by Thai government. Most of the costs and benefits are from the health and value of life costs. Next, the remediation costs with sugarcane cultivation (government management) started low cost in 2005-2015 after that the villagers returned to rice cultivation because they found that the sugarcane did not suit their land or their way of life. This fact increased health cost from diet Cd-rice. In addition, the alternative restoration costs and benefits including soil washing, biochar amendment, phyto- and electrokinetic remediation presented lower costs. Therefore, this area should restore the Cd contaminated soil with alternative technique for the reduction of health outcomes among the villagers. However, using biochar amendment and soil washing presented the lowest value costs (see in **Table 21 and Figure 70**). Compared with the year for restorations; soil washing and electrokinetic take approximately 2 years, while phytoremediation takes approximately 204 years while using biochar amendments may be applied while that land is under cultivation. Therefore, soil washing is recommended for this area because of the lower costs as 1,404-baht rai^{-1} in 2 years.

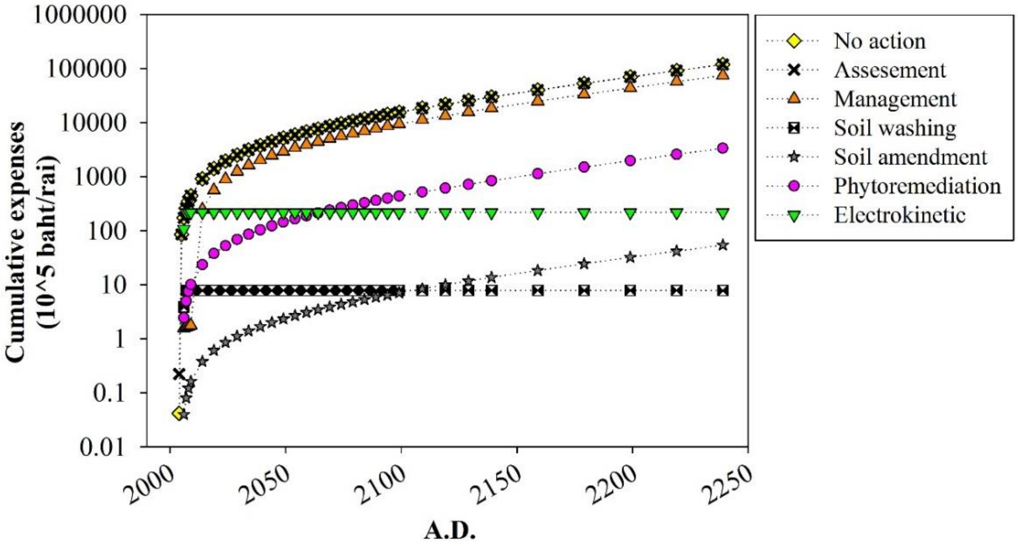


Figure 70 Cumulative cost and benefit of management actions

3. Discussion of CBA for the restoration of Cd contamination in Mae Sot district, Tak province in Thailand

This study demonstrated the health costs from cumulative Cd in rice in 2004 using Monte Carlo Simulation. The main results indicated that health costs depend on the Cd disease that the patient presents the type and severity may vary according to their exposure level. Most of the Mae Sot villages could risk CKD diseases including nephrosis/nephritis, osteoporosis, cardiovascular and cerebrovascular diseases lead to high health costs and value of life. This risk was estimated according to the presence of Cd in urine levels from MCS. While 5% of the villages risked cancer based on their daily intake of contaminated rice. A previous study of this area clearly indicated that villagers with prolonged excessive Cd exposure can be CKD due to positive relationships between urinary cadmium, renal dysfunction, and bone toxic effects (Limpatanachote et al., 2009; Limpatanachote et al., 2010; Swaddiwudhipong et al., 2007; Swaddiwudhipong et al., 2012; Swaddiwudhipong et al., 2010). In addition, the Jinzu river basin area in Toyama, Japan was found to be contamination with Cd lead to Cd related musculoskeletal and bone outcomes following Cd nephropathy through the continued and excessive renal excretion of calcium and phosphate (Li et al., 2011; Sasaki et al., 2019). However, Cd exposure by foodstuff ingestion is positively associated with cancer (Chunhabundit R., 2016). Therefore, the villagers will suffer from health outcomes and health expenses if the Cd contaminated area is not restored. The Thai government failed to manage by sugarcane cultivation because some villagers returned to rice cultivation for local consumption. In addition, they also consumed various vegetables grown in contaminated soil (Phenrat, & Otwong, 2015). However, the villagers believed that their lifestyle and culture are closely associated with rice leading to them returning to the cultivation of rice. Their diet traditionally consisted mainly of rice and vegetables. This area is still heavily contaminated with Cd. Thus, soil restoration is vital for their future well-being. This study estimated the alternative remediation for Cd contaminated in this area and showed a reduction of health costs if alternative remediation is carried out. Consequently, the results from this study can be useful information for the decision to restore the Mae Sot district, Tak province in Thailand and other land contamination problems.

CHAPTER V

CONCLUSION

Conclusion

This study was conducted to evaluate the remediation techniques for Cd contaminated paddy soil in Mae Sot District, Tak Province, and Northwestern Thailand. The remediation techniques included using ZVI for Cd immobilization as soil amendment, separation of contaminated ZVI from soil by the machine as soil washing and solar-powered electrokinetic separation for Cd contaminated soil remediation. The pilot-scale experiments on Cd-contaminated paddy restoration performed via magnet-assisted soil washing using zerovalent iron (ZVI) particles and compared soil amendment using biochar, ZVI, and a combination of biochar and ZVI (BZVI). This pilot tests were conducted with the community researchers. Magnet-assisted soil washing followed by ZVI amendment (0.5%) successfully reduced the Cd level in rice grain to 0.33 mg kg^{-1}. Similarly, as soil amendments, biochar and BZVI (5%) successfully decreased Cd concentrations in rice grain to 0.29 and 0.19 mg kg^{-1}, respectively. However, the application of high dose of ZVI or BZVI (5%) caused substantial stress on the rice growth. Therefore, considering the stress on the rice growth and the Cd immobilization, magnet-assisted soil washing followed by ZVI amendment (0.5%) is a promising alternative.

Nevertheless, using ZVI with the solar-powered electrokinetic separation was evaluated for this Cd contaminated area in batch experiments. The iron particle size (MZVI, NZVI, and Fe-rod) was assessed to effect of voltage and Cd movement in EK systems. The results the EK system by SC lead to Cd desorption and 30% of Cd migrated from the soil to accumulate in the cathode region. When using iron as a soil amendment, the large particle of a substance (MZVI or Fe-rod) hindered the reaction of current and ions in soil while NZVI generated the voltage (from 6.61V to 7.38V). The application EK&NZVI with SC can decrease the Cd in soil (53.14%-66.31%) and increase the Cd adsorption in NZVI (16.5%-20.66%) more than other iron (MZVI and Fe-iron). Nevertheless, EK&NZVI with SC reacted to Cd movement to the cathode region more than without SC. Moreover, the EK with SC treatment led to decrease (from 46.20% to 19.29%) and movement of the bioavailable Cd form to cathode while the application of EK and iron especially MZVI and NZVI with SC can not only move and reduce the exchangeable Cd form but also increase a Fe-Mn oxide and residual forms especially Fe-Mn oxide form. However, using EK&NZVI with SC is the best for Cd reduction and Cd movement to cathode region.

Finally, this research studied a methodology for an integrated economic decision analysis to make an appropriate decision on a remedial selection with maximum social benefit in Cd contamination of agricultural soil in Mae Sot district as a case study. To the best of our knowledge, this is the first study using Monte Carlo Simulation to predicts the health costs of villager living in an area with a contamination problem together with alternative remediation cost through other risk management activities in the past and in the future. Alternative remediation includes biochar amendment, soil washing, electrokinetic, phytoremediation and sugarcane cultivation by the Thai government. This result indicates that the highest cost is in non-remediation, the only risk assessment and management by the Thai government, which received from health costs. While the alternative restoration cost presents a lower cost due to the reduction of the health costs of villagers and implies that the area contamination should apply the alternative restoration for reducing health effects. However, this study recommends that applying soil washing for Cd contamination of the agricultural soil in the Mae Sot District, is the best because the cost is projected as 1,404-baht rai^{-1} in 2 years.

Recommendations

This study uses the Cd contaminated paddy fields in agricultural soil in the Mae Sot district, as a case study. The study is successful in pilot-scale for using ZVI as a soil amendment and magnetic-assisted soil washing in contaminated paddy fields. Moreover, this project trained a villager who was affected by Cd contamination in order to increase a skill and knowledge about the restoration of Cd contaminated areas by the researcher.

We should publish the results of this project to villagers in this area and third parties such as the local government or implicated administration for planning and management.

We should promote citizen science to perform remedial actions and post-harvest sampling to support researchers and establish funding for remediation.

We should treat the Cd at its source as otherwise farmers use contaminated water for irrigation.

The result in the batch experiment indicated that NZVI and EK are efficient in reducing the bioavailable Cd and moving to the cathode region. However, we should assess and develop the suitability and cost-effectiveness of this technique in the pilot-scale study.

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APPENDIXES

APPENDIX A THE DETAIL OF INFORMATION FOR RESEARCH METHODOLOGY

Table A1 Sequential extraction procedures used in this study. Dried soil (1.0 g) was extracted using the steps below

Step	Fraction	Reagent
1	Exchangeable (F1)	8 mL of 1M $MgCl_2$ (pH 7), 1h with continuous agitation
2	Bound to Carbonates (F2)	8 mL of 1M NaOAc (pH 5; HOAc), 5 h with continuous agitation
3	Bound to Fe and Mn Oxides (F3)	20 mL of 0.04 M NH_20H-HCl in 25% (v/v) HOAc, 6 h at 96˚C with occasional agitation
4	Bound to Organic Matter (F4)	5 mL of 0.02M HNO_3, 2 h at 85˚C with occasional agitation and 3 mL of 30% H_2O_2 (pH 2 with HNO_3) at 85˚C with occasional agitation again in 3 h After cooling, 3.2 M CH_3COONH_2 in 20% (v/v) HNO_3 was added and diluted by deionized water to 20 mL
5	Residual (F5)	digested with 10 mL of 65% nitric acid

Source: Tessier, Campbell, & Bisson, 1979

Table A2 Selected studies with risk of health outcomes

Diseases	U-Cd (µg g^{-1} Cr) / Cd Exposure Level (µg day^{-1})	Risk (OR, RR or HR)		
		Total	Male	Female
Osteoporosis	0.99	1		
	1-1.99	1.27		
	≥2	2.59		
Femoral neck	0.5			1
	0.5-0.75			2.09
	≥0.75			3.47
Hip or spine	0.5			1
	0.5-0.75			1.27
	≥0.75			4.24
Nephrosis/nephritis	<3		1	1
	3-4.9		2.7	1
	5-9.9		4.4	1.4
	>=10		3.4	3.1
Cerebrovascular	<3			1
	3-4.9			3
	5-9.9			4.3
	>=10			3.6
Cardiovascular	<3			1
	3-4.9			2.1
	5-9.9			2.3
	>=10			2.4
Prostate Cancer	<17		1	
	17-20		1.18	
	>=20		1.29	
Breast Cancer	<13			1
	13-16			1.12
	>=16			1.27

Source: Songprasert et al., 2015

Table A3 Expenses of Cd-exposure diseases

Diseases	Expense (baht)	Reference
Osteoporosis/Hip/ Femoral neck	1,769,115	(Woratanarat P et al., 2005)
Kidney	3,576,901	(Anutrakulchai S et al., 2017; Brouwer E. D. et al., 2015)
Cerebrovascular	42,400	(Sribundit N et al., 2017)
Cardiovascular	5,320,040	(Brouwer E. D. et al., 2015; Reyes EB et al., 2016; Sribundit N et al., 2017)
Breast Cancer	274,223	(Medical Tourism Association, 2019; Medical Tourism Guide, 2019; Supakul S et al., 2006)
Prostate Cancer	229,493	(Ratchanon S et al., 2015)

Table A4 The survival and death percentages of Cd-exposure diseases in this study

Diseases	Mortality (%)	survival (%)	Reference
Osteoporosis	33.00	67.00	(Songpatanasilp T et al., 2016)
Femoral neck	33.00	67.00	
Hip or spine	33.00	67.00	
Nephrosis/nephritis	10.70	89.30	(Anutrakulchai S et al., 2017)
Cerebrovascular	0.17	99.83	(Suwanwela, 2014; Tangcharoen et al., 2011)
Cardiovascular	16.50	83.50	
Prostate Cancer	37.00	63.00	(Hu et al., 2014)
Breast Cancer	46.50	53.50	(Aphinives et al., 2010)

Table A5 The details of soil washing, biochar amendment, phytoremediation and electrokinetic remediation (EKR)

Techniques	Details	Unit.rai^{-1}*	Baht unit^{-1}.rai^{-1}	References
Soil washing	Machine	2 set	22,830	(Khum-in et al., 2019b (in preparation))
	Material	3840 kg	76,800	
	Management	1	249,700	
	Allowance	30%	104,800	
	Total		454,130	
Biochar amendment	Material	3,200 kg	3,200	(Khum-in et al., 2019a (in preparation))
	Allowance	30%	960	
	Total		4,160	
Phytoremediation**	Material	6,400	192,000	(Khaokaew & Landrot, 2015)
	Management	1	3,000	
	Allowance	30%	58,500	
	Total		253,500	
Electrokinetic	Installations and management on full-scale	1	11,003,530	(Christopher, 2009)

Note: * 13,439 rai of the Cd contamination area

** estimated from the Gynura pseudochina (L.) DC. for Cd removal based on 41 mg kg^{-1} of total Cd, 25% Cd bioavailable in soil from this area by laboratory conducted in 2017 and calculated Cd removal to 0.4 mg kg^{-1}. Therefore, the Gynura pseudochina (L.) DC. can remove Cd in 240 years.

APPENDIX B THE DATA FOR SUPPORTING RESULTS

Table B1 Soil properties in area study

Location	Clay %	Sand %	Silt %	Soil texture
Upland	29.2±0.00	57.08±1.42	13.72±1.42	Sandy clay loam
Lowland	63.0±0.00	10.2±0.00	26.8±0.00	Clay

Table B2 FT-IR assignments for biochar and ZVI

Band Position (cm^{-1})	Functional groups	Reference
	Biochar	
464	Si–O–Si flexural vibration	(P. Liu et al., 2012b; Xiao, Chen, & Zhu, 2014)
792	C-H out of plane deformations (aromatic C – H, alkene)	(Wu et al., 2015Mukome, Zhan, Silva, Six, & Parikh, 2013)
1062	aliphatic ethers (C–O–C) and alcohols –OH, C – O bonds in ethers, esters and carbonates	(Chen et al., 2011; Chia et al., 2012)
	ZVI	
459	Hematite (α-Fe_2O_3)	

Table B3 Results of the surface area, pore volume, and average pore size based on BET analysis

Materials	Biochar	ZVI
Surface area (m2/g)	18.39	1.35
Pore volume (cm3/g)	0.034	0.003
Average pore size (nm)	7.445	8.299

Table B4 Cd and Fe data in soil during cultivation for soil amendment field

Treatments	Soil$_{initial}$	Soil$_{14}$	Soil$_{28}$	Soil$_{42}$	Soil$_{56}$	Soil$_{84}$
			Cd (mg kg^{-1})			
Control 1	31.93±7.22	34.94±9.03	36.18±7.43	30.28±10.51	32.34±12.39	30.12±11.86
Biochar	42.46±2.22	44.35±6.02	43.80±1.21	42.96±3.79	41.99±3.96	41.20±5.99
Biochar & ZVI (5%)	46.69±4.08	42.16±2.75	40.59±1.87	40.33±4.16	39.84±2.56	39.60±2.90
ZVI (5%)	41.31±4.07	37.20±5.44	35.66±10.56	35.41±10.99	34.33±8.03	34.82±6.27
			Fe (mg kg^{-1})			
Control 1	49,255±75	33,228±665	31,240±22	30,761±1,370	31,687±81	29,978±1,026
Biochar	32,670±568	33,069±94	30,875±620	30,956±5.06	33,365±300	30,507±60
Biochar & ZVI (5%)	33,701±690	55,727±2,060	56,327±614	51,039±311	57,240±223	57,087±603
ZVI (5%)	33,491±853	55,972±1,878	51,294±2,198	51,066±1,153	54,130±4,588	54,712±1,751

Table B5 Cd and Fe data in soil during cultivation for soil washing field

Treatments	Soil$_{initial}$	Soil$_{21}$	Soil$_{42}$	Soil$_{63}$	Soil$_{84}$	Soil$_{120}$
			Cd (mg kg^{-1})			
Control 2	31.33±1.56	35.87±1.39	38.92±1.99	34.32±0.55	35.39±0.32	50.62±3.67
ZVI (0.5%)	18.90±0.17	27.39±0.22	25.16±1.01	27.16±1.20	32.21±3.02	49.43±1.00
Washing (1%)	34.33±1.78	37.45±0.95	35.64±0.72	32.37±0.24	35.71±0.74	50.36±4.05
Washing + ZVI (0.5%)	32.40±2.17	35.52±5.91	32.78±0.62	28.89±1.85	33.63±0.57	49.41±0.52
			Fe (mg kg^{-1})			
Control 2	40,608±1,061	41,494±803	38,255±417	38,648±165	39,335±381	32,886±1,726
ZVI (0.5%)	39,632±351	44,693±1,517	38,962±618	39,534±152	42,638±3,267	41,518±1,030
Washing (1%)	44,017±1,294	45,295±904	40,651±1,833	40,786±436	42,214±172	33,860±2,060
Washing + ZVI (0.5%)	45,240±11,12	47,162±1,570	43,221±423	44,749±116	43,871±369	40,428±603

Table B6 Cd and Fe data in rice plant during cultivation for soil amendment field

Treatments	**Initial (mg kg^{-1})**		**60 day (mg kg^{-1})**		**84 day (mg kg^{-1})**	
	Cd	**Fe**	**Cd**	**Fe**	**Cd**	**Fe**
			Root			
Control 1	0.048±0.00	25,819±0.00	15.24±5.77	25,420±980	19.51±14.68	13,941±5,987
Biochar	0.048±0.00	25,819±0.00	29.98±3.40	27,592±598	33.98±3.20	17,750±11,848
Biochar & ZVI (5%)	0.048±0.00	25,819±0.00	22.89±0.83	26,746±770	16.58±4.32	34,050±6,286
ZVI (5%)	0.048±0.00	25,819±0.00	17.29±11.51	29,476±3,625	21.25±12.18	44,313±2,888
Control 2	0.125±0.00	11,352±0.00	11.84±0.34	11,582±26.99	11.37±0.18	5,961±240
ZVI (0.5%)	0.125±0.00	11,352±0.00	5.47±0.46	3,132±184.58	7.06±0.38	6,274±595
Washing (1%)	0.125±0.00	11,352±0.00	10.92±0.28	3,610±117.00	12.67±0.65	8,717±2,719
Washing & ZVI (0.5%)	0.125±0.00	11,352±0.00	8.82±0.19	9,564±0.00	10.13±0.14	12,864±286
			Stem			
Control 1	0.049±0.00	15,467±0.00	3.04±1.98	5,780±204	6.67±2.46	1350±752
Biochar	0.049±0.00	15,467±0.00	3.99±2.70	4,975.6±2080	4.20±0.50	781.1±41.45
Biochar & ZVI (5%)	0.049±0.00	15,467±0.00	1.76±0.10	5,288±151	3.57±1.46	2,016±1,928
ZVI (5%)	0.049±0.00	15,467±0.00	1.72±0.00	9,944±0.00	4.29±1.53	766.54±17.56
Control 2	0.124±0.00	2,346±0.00	2.69±0.05	493.29±4.44	2.65±0.11	411.90±27.97
ZVI (0.5%)	0.124±0.00	2,346±0.00	1.94±0.05	653.75±8.00	1.46±0.51	514.91±53.04
Washing (1%)	0.124±0.00	2,346±0.00	1.99±0.10	832.74±41.66	2.77±0.05	518.42±15.07
Washing & ZVI (0.5%)	0.124±0.00	2,346±0.00	2.17±0.05	928.77±29.35	2.12±0.04	773.05±28.76
			Leaf			
Control 1	0.048±0.00	9,282±0.00	0.44±0.05	1,530±289.30	2.52±1.03	1,805±1497
Biochar	0.048±0.00	9,282±0.00	0.29±0.05	1,058.8±204.5	1.18±0.45	830.15±400.7
Biochar & ZVI (5%)	0.048±0.00	9,282±0.00	1.06±0.22	3,359±433.4	1.58±0.12	2,828±2402
ZVI (5%)	0.048±0.00	9,282±0.00	2.49±0.00	2,631±0.00	1.55±0.15	1,081±654.16
Control 2	0.124±0.00	2,036±0.00	1.76±0.002	767.58±1.88	1.83±0.003	713.97±16.11
ZVI (0.5%)	0.124±0.00	2,036±0.00	1.91±0.64	1240.70±5.96	1.15±0.002	652.36±15.08
Washing (1%)	0.124±0.00	2,036±0.00	1.05±0.05	756.42±11.61	1.91±0.001	1,003±33.06

Washing & ZVI (0.5%)	0.124±0.00	2,036±0.00	1.72±0.16	1,435. ±32.45	1.28±0.05	2,494±7.03

Table B7 Cd and Fe data in harvesting for field experiments

Treatments	**Soil**	**Root**	**Stem**	**Leaf**	**Husk**	**Grain**
			Cd (mg kg^{-1})			
Control 1	30.12±11.87	21.05±10.72	6.67±2.46	2.52±1.03	0.82±0.05	0.84±0.20
Biochar	41.20±6.00	33.98±3.20	4.20±0.49	1.18±0.45	0.29±0.16	0.29±0.15
Biochar & ZVI (5%)	39.60±2.90	16.58±4.32	3.57±1.46	1.58±0.12	0.33±0.31	0.19±0.11
ZVI (5%)	34.82±6.27	19.28±9.40	4.29±1.53	1.55±0.15	0.67±0.04	0.58±0.05
Control 2	50.62±3.67	23.78±1.00	3.03±0.10	1.53±0.01	0.96±0.03	0.86±0.01
ZVI (0.5%)	49.43±0.99	11.18±0.10	1.67±0.01	1.17±0.01	0.74±0.06	0.60±0.05
Washing (1%)	50.36±4.05	29.51±0.25	3.38±0.18	2.36±0.12	0.86±0.00	1.21±0.01
Washing + ZVI (0.5%)	49.41±0.52	13.07±0.00	2.43±0.01	1.90±0.01	1.15±0.02	0.33±0.00
			Fe (mg kg^{-1})			
Control 1	29,978±1,026	13,941±5,987	1,350.35±752	1,804±1,497	1,710±156	1,209.71±195
Biochar	30,507±60.64	17,750±11,848	781 ±41.45	830 ±400	1,432±167.6	1,115.44±7.0
Biochar & ZVI (5%)	57,087±603	34,051±6,256	2,017±1,928	2,828 ±2,402	1,452 ±325	1,342.8±86.8
ZVI (5%)	54,712±1,751	44,314±2,889	766 ±17.6	1,081±654	1,574±596	1,038.7±231
Control 2	32,886±1,726	3,741±224	287.87±104	911±50.65	483.2±28.73	294.05±5.76
ZVI (0.5%)	41,518±1,030	5,514±59.34	373.87±20.2	601±40.33	899.7±9.28	131.90±167
Washing (1%)	33,860±2,060	4,742±16.91	509.45±32.6	1,768±19.39	577.5±43.96	184.4±46.46
Washing + ZVI (0.5%)	40,428±603	4,840±99.	478.53±13.5	1,571±50.16	1,166±48.74	120.42±0.00

Table B8 Mass of Cd (mg) in soil and medium (iron) in electrokinetic with solar cell experiments

Time	**Cathode**		**Middle**		**Anode**	
(day)	medium	soil	medium	soil	medium	soil
E1(EK)						
0	-	5.65±0.51	-	5.65±0.51	-	5.65±0.51
1	-	3.85±0.22	-	3.92±0.34	-	4.02±0.28
3	-	3.96±0.23	-	3.91±0.27	-	4.04±0.33
5	-	4.01±0.40	-	3.92±0.34	-	3.94±0.45
7	-	4.08±0.78	-	3.92±0.20	-	4.02±0.38
10	-	5.09±1.01	-	3.83±0.21	-	3.94±0.40
15	-	5.86±1.95	-	3.87±0.18	-	3.89±0.21
E2(EK&MZVI)						
0	0	4.74±0.01	0	4.74±0.01	0	4.74±0.01
1	0.32±0.01	3.05±0.02	0.34±0.004	3.00±0.04	0.40±0.03	2.98±0.05
3	0.37±0.01	3.01±0.11	0.32±0.02	3.04±0.13	0.37±0.004	3.09±0.08
5	0.27±0.06	3.10±0.08	0.32±0.03	3.07±0.15	0.23±0.04	2.90±0.26
7	0.39±0.10	3.00±0.03	0.22±0.01	2.95±0.04	0.19±0.002	2.78±0.01
10	0.44±0.16	3.08±0.07	0.22±0.06	3.05±0.07	0.21±0.01	2.91±0.06
15	0.54±0.16	3.14±0.02	0.21±0.02	2.93±0.09	0.23±0.003	2.84±0.01
E3(EK&NZVI)						
0	0	4.41±0.13	0	4.41±0.13	0	4.41±0.13
1	0.42±0.06	3.08±0.06	0.45±0.02	2.96±0.06	0.46±0.02	2.98±0.16
3	0.27±0.01	2.96±0.12	0.43±0.02	2.86±0.03	0.43±0.04	2.83±0.10
5	0.38±0.11	2.68±0.23	0.39±0.01	2.91±0.10	0.44±0.01	2.85±0.02
7	0.57±0.01	2.67±0.06	0.37±0.02	2.90±0.18	0.31±0.02	2.75±0.10
10	0.55±0.06	2.57±0.13	0.38±0.02	2.73±0.06	0.38±0.07	2.68±0.15
15	0.83±0.54	2.72±0.10	0.39±0.003	2.80±0.03	0.40±0.03	2.57±0.05
E4(EK&Fe-rod)						
0	0	5.79±0.02	0	5.79±0.02	0	5.79±0.02
1	0.02±0.00	4.29±0.08	0.02±0.005	4.15±0.11	0.014±0.00	4.20±0.09
3	0.01±0.002	4.14±0.11	0.01±0.004	4.38±0.24	0.013±0.002	4.27±0.15
5	0.02±0.005	4.31±0.04	0.02±0.01	4.35±0.10	0.016±0.004	4.36±0.06
7	0.02±0.007	4.40±0.06	0.02±0.005	4.24±0.13	0.017±0.002	4.27±0.04
10	0.05±0.04	4.31±0.15	0.03±0.01	4.41±0.18	0.014±0.001	4.46±0.078
15	0.05±0.01	4.23±0.03	0.05±0.02	4.24±0.04	0.021±0.003	4.33±0.13

Table B9 Mass of Cd (mg) in soil and medium (iron) in electrokinetic without solar cell experiments ass of Cd

Time (day)	Cathode		Middle		Anode	
	NZVI	soil	NZVI	soil	NZVI	soil
E5 (MZVI)						
0	0	6.37±0.10	0	6.36±0.10	0	6.37±0.10
1	0.25±0.04	4.27±0.01	0.25±0.04	4.18±0.30	0.28±0.001	3.79±0.06
3	0.57±0.18	4.09±0.47	0.53±0.14	4.41±0.30	0.50±0.11	4.34±0.20
5	0.41±0.03	4.54±0.07	0.40±0.03	4.42±0.40	0.48±0.07	4.96±0.65
7	0.55±0.08	4.58±0.32	0.49±0.06	5.08±0.80	0.63±0.07	4.46±0.14
10	0.59±0.03	4.37±0.10	0.52±0.10	4.44±0.15	0.48±0.13	4.49±0.25
15	0.48±0.11	4.35±0.07	0.57±0.08	4.31±0.29	0.58±0.01	4.20±0.015
E6 (NZVI)						
0	0	6.61±0.23	0	6.61±0.23	0	6.61±0.23
1	0.70±0.02	5.48±1.85	0.75±0.001	6.57±0.67	0.57±0.13	6.20±1.80
3	1.30±0.30	4.43±0.45	1.53±0.02	4.30±0.14	1.48±0.03	3.98±0.26
5	1.32±0.20	4.29±0.11	1.40±0.03	4.31±0.07	1.39±0.06	4.39±0.50
7	1.40±0.33	4.32±0.26	1.48±0.03	4.42±0.32	1.42±0.03	4.58±0.41
10	1.29±0.10	4.29±0.20	1.53±0.22	4.19±0.32	1.28±0.03	4.39±0.17
15	1.17±0.04	4.38±0.10	1.36±0.10	3.51±0.39	1.09±0.30	4.20±0.01
E7 (Fe-rod)						
0	0	5.79±0.01	0	5.79±0.01	0	5.79±0.01
1	0.008±0.01	4.29±0.08	0.009±0.01	4.15±0.11	0.01±0.01	4.19±0.10
3	0.014±0.01	4.14±0.11	0.018±0.01	4.38±0.24	0.01±0.02	4.26±0.15
5	0.017±0.004	4.31±0.04	0.015±0.004	4.35±0.10	0.013±0.02	4.36±0.06
7	0.021±0.01	4.39±0.06	0.029±0.01	4.24±0.13	0.022±0.01	4.27±0.04
10	0.04±0.02	4.31±0.15	0.032±0.001	4.42±0.18	0.038±0.01	4.46±0.08
15	0.044±0.01	4.23±0.03	0.043±0.01	4.24±0.04	0.056±0.01	4.33±0.13

Table B10 Cd accumulation (%) in soil, iron remining, iron recovered and unbalance in all batch experiments in the end

Treatments	% Accumulation			
	Soil	Iron remaining	Iron recovered	Unbalance
	Cathode			
E1(EK)	100	0	0	0
E2(EK&MZVI)	66.39	0.167	11.41	22.03
E3(EK&NZVI)	61.61	0.531	18.82	19.04
E4(EK&Fe-rod)	73.09	0.0015	0.76	26.16
E5(MZVI)	68.26	0.0805	7.52	24.14
E6(NZVI)	66.31	0.385	17.71	15.59
E7(Fe-rod)	73.34	0	0.91	25.75
	Middle			
E1(EK)	68.39	0	0	31.61
E2(EK&MZVI)	61.94	0.019	4.46	33.58
E3(EK&NZVI)	63.40	0.125	8.86	27.61
E4(EK&Fe-rod)	73.32	0.003	0.74	25.94
E5(MZVI)	67.72	0.0889	9.01	23.19
E6(NZVI)	53.14	0.345	20.66	25.86
E7(Fe-rod)	73.57	0	0.88	25.55
	Anode			
E1(EK)	68.85	0	0	31.15
E2(EK&MZVI)	59.98	0.006	4.84	35.17
E3(EK&NZVI)	58.34	0.028	8.98	32.65
E4(EK&Fe-rod)	74.88	0.001	0.96	24.15
E5(MZVI)	66.04	0.083	9.08	24.800
E6(NZVI)	63.52	0.374	16.50	19.60
E7(Fe-rod)	75.14	0	0.37	24.49

Table B11 Cd speciation in all batch experiments in the end

Experiment	F1	F2	F3	F4	F5
Initial	7.78±0.13	15.35±0.33	19.60±1.66	1.21±0.03	0.89±0.06
Initial&Cd	156.67±41.38	95.99±21.68	79.81±12.16	3.86±0.81	2.74±0.98
Cathode_E1	182.90±55.85	187.64±21.80	134.89±13.71	5.51±0.80	2.53±0.32
Middle_E1	71.67±11.77	161.71±7.25	130.69±12.16	4.93±0.09	2.56±0.19
Anode_E1	84.26±17.76	152.32±17.68	130.11±0.00	5.23±1.10	2.90±0.49
Cathode_E2	35.23±19.30	102.82±7.37	103.41±7.22	3.57±0.40	5.56±0.27
Middle_E2	6.90±1.35	82.94±13.99	127.13±1.10	4.13±0.19	4.28±0.55
Anode_E2	9.33±0.75	75.85±1.03	121.83±3.84	3.27±0.18	2.33±0.56
Cathode_E3	37.23±26.0	61.72±7.45	93.97±13.99	4.00±0.15	14.76±2.50
Middle_E3	14.07±11.81	67.25±2.02	124.68±4.75	4.25±0.59	11.63±4.34
Anode_E3	6.98±0.59	63.97±1.19	108.45±8.86	3.26±0.09	5.59±1.46
Cathode_E4	165.52±16.85	166.22±5.87	171.74±18.65	6.69±1.65	2.98±1.12
Middle_E4	121.06±1.70	166.11±11.10	148.47±19.93	4.40±0.97	3.43±0.29
Anode_E4	57.66±8.52	158.96±3.37	163.85±3.10	4.89±0.13	2.80±0.16
Cathode_E5	144.86±1.19	132.98±3.17	156.42±7.77	6.66±1.204	6.93±1.99
Middle_E5	138.78±10.42	125.46±11.42	158.81±15.54	6.17±1.15	8.11±0.48
Anode_E5	130.26±3.69	126.39±4.00	161.72±8.32	5.86±0.70	6.73±2.13
Cathode_E6	53.12±2.73	80.42±5.27	59.26±5.11	1.36±0.37	1.37±0.412
Middle_E6	50.34±4.91	75.82±8.52	54.73±6.03	1.16±0.04	1.12±0.12
Anode_E6	59.09±46.73	90.99±20.85	71.41±19.75	1.89±0.83	2.11±1.15
Cathode_E7	184.33±3.01	130.23±6.90	90.16±0.36	3.61±0.04	1.79±0.13
Middle_E7	183.57±4.56	125.97±4.60	94.68±0.55	3.42±0.59	1.52±0.11
Anode_E7	185.06±0.08	119.94±0.99	90.67±4.57	3.39±0.22	1.95±0.25