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Review of Taiwan's Soil and Groundwater Remediation Technologies: Phytoremediation and In situ chemical Oxidation

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ABSTRACT

The purpose of this review is the analysis of the soil and groundwater remediation technologies referred as in situ chemical oxidation and phytoremediation, and to dis-cuss the successes that have been made. The technolo-gy of phytoremediation has yet to be commercially ac-cepted, but shows emerging capabilities. In situ chemi-cal oxidation (ISCO) is a frequently used technology in Taiwan for the remediation of organic compounds. Sev-eral studies have been conducted in Taiwan so show their feasibility and potential. This article reviews studies concerning these two remediation technologies. Other processes such as monitored natural attenuation, flush-ing, thermal treatment, or soil washing are not covered within this article.

Keywords Phytoremediation, In situ chemical Oxidation

INTRODUCTION

Decades ago, Taiwan began to develop its in-dustry rapidly, inevitably leading to the produc-tion of an increased amount of waste matter. This waste matter poses several hazards to the environment and to society. Since the discovery of soil and groundwater contamination in Tai-wan, more than 5,500 [1] sites have been found. Investigations show unambiguous proof that the contamination is linked to four main areas. These areas are industry, gas stations, sites con-taining storage tanks, illegal dumping sites, and farmland. Upon discovery of these polluted sites, monitoring and remediation are actions that are immediately executed by the govern-ment to minimize imminent danger to the public. Executive Taiwanese agencies such as the Tai-wan Environmental Protection Administration (TEPA), are working for the protection and conservation of the environment, and are there-fore investigating, managing, and remediating contaminated locations. Taiwan is ranked num-ber 14 in the World Economic Forum (WEF) Global Competitiveness Report [2] and gives residence to more than 62 industrial parks [3]. Hence environmental issues arise that might negatively influence the health of citizens. The industrial processes and humans are responsible for the pollution of the environment.

2. MAIN SOURCES OF POLLUTION AND CONTAMINATED SITES IN TAIWAN

2.1 Factories and Industry

Smoke exhaust, petrochemical processes, scrap metal combustion, and waste treatment are only a few of the industrial activities responsible for heavy metal pollution. Heavy metals are usually immutable or not degradable, which aggravates the remediation process. When exposed to cer-tain quantities, heavy metals such as arsenic, cadmium, chromium, copper, gallium, indium, lead, mercury, molybdenum, nickel, and zinc are linked to several adverse health effects for humans [4]. The vast amount of computer and electronics related products that are being pro-duced in Taiwan has been a major factor in terms of the environmental pollution, especially factories in areas that produce semiconductors show increased arsenic, gallium, and indium contamination [5]. The petrochemical industry is also linked to contribution of pollution by leak-ing or discharging polycyclic aromatic hydro-carbons (PAHs) [6].

Approximately 11 million tons of general waste and 1.26 million tons of hazardous waste have been accumulated in the year 2004 [7]. Fur-thermore, more than 120,000 [8] abandoned industrial sites exist in Taiwan and 102 of the 175 sites surveyed by the TEPA have shown to be seriously polluted. The mercury contaminat-ed area of Zheng-Tai Company, the lead con-taminated area of Jin-Yu Company, and the mercury and dioxins contaminated site of China Petrochemical Development Company [9] are examples for severely contaminated sites.

2.2 Illegal Dumping

In 1987, the TEPA urged the local governments to report all documented dumping sites used for the illegal disposal of waste to create a database. 168 illegal dumping sites were investigated by the TEPA in the year 2004 for the purpose of designing appropriate remediation strategies [10]. Additionally, 175 illegal deposit sites were registered according to data from the year 2009 [11]. 17 of the 175 sites were categorized as A-class, while the remaining 158 sites were ranked as lower contaminating risk classes C and D. The responsibility among others was ascribed to a plastic-stabilizer producing plant that dis-charged wastewater containing cadmium and lead [12]. Moreover, mercury sludge, chemical waste, and numerous drums filled with, upon discovery, unidentified content was found in areas in Taiwan. Remediation of illicit waste sites appears to be challenging since the hazard-ous contaminants are of complex nature.

2.3 Gas Stations and Storage Tanks

Fuel is stored inside underground tanks and is then carried by underground pipelines. The parts can be damaged by earthquakes, rusting and aging, or by unheeding maintenance and operation. These damaging accidents of parts pose a threat to the environment by leaking their contents leading to a contamination of soil and groundwater nearby. A spill may cause contam-ination of BTEX (benzene, toluene, ethylben-zene, xylenes) or other organic compounds since petroleum contains these hazardous chemicals. Generally areas where pipes are disconnected and connected implicate a rising potential for leakage. Taiwan has more than 2,600 [13] gas stations and therefore holds approximately 10,400 underground storage tanks containing fossil fuels, which when leaking, represent a significant danger to the surrounding environ-ment.

To address the aforementioned issue of contam-ination by fuel, the TEPA has been working on strategies for the investigation of gas stations and storage tanks since 2001. In 2002, 191 gas stations [14] and 1,402 large (100 KL) storage tanks [13] have been surveyed. The following year 400 gas stations and 2,171 large storage tanks have been additionally surveyed. Until 2010, a total of 1,837 gas stations have been examined.

The investigations of gas stations and storage tanks were ranked according to the potential risk of leakage or error-proneness. The priority of investigation of sites were determined by the opening year of the gas stations and age of in-stalled equipment, hence the potential of being damaged or malfunctioning. The data show that the soil is mostly contaminated with gasoline related hydrocarbons, whereas groundwater is polluted with benzene [14]. As of December 2015, according to the TEPA, 144 gas stations and 7 storage tanks have shown contamination, while 62 gas stations and 2 storage tanks have already been remediated [1].

2.4 Farmland

The illicit discharge by industry and the wastewater from livestock has contaminated the water supply of paddy fields. Furthermore, the incineration of solid waste leads to heavy metal particles in the air, which can directly come in contact with crops and soil. The polluted soil and irrigation water is then used to cultivate crops, hence heavy metals or organic contami-nants accumulate in crops. If the soil contains excess heavy metals, the poisoning of plants may occur. If contamination exceeding the pol-lution control standards is found in crops, erad-ication or incineration of crops will be executed to prevent them from entering the human food chain. The agricultural agencies are working to-gether with environmental authorities to per-form this task. Furthermore, farmers receive a payment by a fund to compensate the minimiza-tion of income.

The so-called cadmium rice incident of 1982 in Taoyuan, as mentioned in 2.2 Illegal Dumping, led to a significant change in the regulations of pollution. Two nearby polyvinylchloride stabi-lizer producing companies released cadmium and lead through the illegal discharge of wastewater [12]. The initial investigations that examined soil for the heavy metals arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc started 1983. This program con-sisted of a 5-phase program to reveal the extent of contaminated sites and to get an overview of the situation altogether. Based on the appear-ance, regarding quantity and type of heavy metal, contaminated sites were separated into 5 levels, while level 5 equals the greatest concen-tration of pollution. The last phase was per-formed in 2002 and showed that out of the in-vestigated 619 ha level 5 considered sites ap-proximately 282 ha surpassed the soil pollution control standards of heavy metals in soil. Moreover 138 ha reached the soil pollution monitoring standards of heavy metal in soil. Investigations showed that the farmland in Changhua County contains the most infested soil. According to the TEPA, as of December 2015, 931 ha of polluted farmland have been discovered and 542 ha have been corrected [13].

2.5 In General

The soil and groundwater pollution remediation act (SGWPRA) was established in February 2000 containing 57 articles for regulation and combat of the issues of environmental pollution. Various surveys established an improved man-agement of polluted sites and provided for a better understanding of the situations. If inves-tigations show that pollution of soil or ground-water is present, the data is compared to the soil and groundwater monitoring standard and the soil and groundwater control standard. First, should the concentration of pollution exceed the soil and groundwater monitoring standard, the site is declared a soil and groundwater mon-itoring standard and is continued to be ob-served with great attention. Second, if the site exceeds the soil and groundwater control standard, the site is declared as a control site and further measures are taken to manage and remediate the site. Finally if the declared con-trol site bears a danger to national health and environment, the individuals or corporation re-sponsible for the contamination must inform the local authorities who then will review and pos-sibly declare the affected area as remediation site. The perpetrator of the contamination is hold accountable for submitting a remediation plan, the complete remediation process, and its emerging costs. In case of an untraceable perpe-trator, all costs are defrayed by a fund, which consists of collected fees. Manufacturers or im-porters of petrochemical organic compounds are mostly the contributors to these fees.

Correct management practices and installing monitoring equipment are required to achieve higher chances of pollution prevention. Unfor-tunately the process of rehabilitation is protract-ed, since monitoring of soil and groundwater contamination levels is essential to assure their judicious quality after the applied remediation technologies. The TEPA and the local environ-mental protection bureaus have installed moni-toring wells for the routinely observation of groundwater quality [16]. Regional monitoring wells (RGMWs) and site-specific monitoring wells (SSMWs) are two types of wells that are distinguished. 431 RGMWs were installed be-fore the year 2003, while 1,080 SSMWs were finished until 2011. As its label implies, site-specific monitoring wells are installed at high pollution potential representing areas such as industrial parks, illegal dumping sites, gas sta-tions, and large storage tanks.

3. COMMONLY USED TECHNOLOGIES

The selection of the appropriate remediation technology depends on several factors such as the characteristics of hydrogeological environ-ment, chemical and physical properties of the contaminants and financial resources. Due to the occurrence of complex compounds, the ne-cessity of using more than one remediation technology (treatment train) is often the case. Phytoremediation and ISCO are widely used in Taiwan to reassure a safe environment.

3.1 Phytoremediation

Phytoremediation is a biological remediation technology used in-situ or ex-situ to decrease or remove pollution in soil and groundwater by the use of living plants. Although this technology is not commercially used yet, promising results have shown their feasibility. The cultivated spe-cies should have an increased resistance and a high absorption capacity for heavy metals or organic contaminants. Certain heavy metals are necessary micronutrients for plants, but can also pose phytotoxic properties to plants if occurring in increased quantities leading to a retarded growth. As example, arsenic, cadmium, or lead may be entering the plant, although considered non-essential for plants. Therefor, the election of species depends on the occurring contamina-tion at the site. Phytoremediation is further cat-egorized into processes such as Phytodegrada-tion, Phytoextraction, Phytostabilization, Phy-tostimulation, Phytovolatilization, and Rhizofil-tration [17]. These processes involve the extrac-tion, degradation, or metabolization of toxic substances.

Disadvantages may include a slow rate of re-mediation process, difficulties to achieve ac-ceptable levels of contamination, and the feasi-bility only at sites with shallow or sparse con-tamination. Nonetheless, phytoremediation is a cost-effective, environmentally friendly, and aesthetically approach to restore the environ-ment mainly without destructive properties.

3.1.1 Phytoremediation of Heavy Metals

Heavy metals are typically consistent in soil and not degradable, therefor the aimed objective for remediation of soil and groundwater is a high accumulation rate. Phytoextraction is a common technology for the removal of heavy metals. The uptake of heavy metals through transporta-tion from the plants' roots to its shoots is de-sired. Plants with increased accumulation are called hyperaccumulators. The term hyperaccu-mulation [18] plays a significant role concerning phytoremediation, since this property of plants is important for a better result of accumulation of heavy metals. Certain species are able to store high concentrations of heavy metals lead-ing to an increase in transfer and storage of con-taminants without showing signs of toxicity. Plants that are not hyperaccumulators are in-tended to have high biomass or either growth rate to reach efficient levels of phytoextraction.

A study [19] of a cadmium, lead, and zinc con-taminated paddy field investigated the phyto-extraction-capabilities of six high biomass plants and two hyperaccumulators. Results have shown that the two hyperaccumulators Viola baoshanensis and Sedum alfredii, and the high biomass species Rumex crispus, are able to effi-ciently remediate the soil of cadmium and zinc. When comparing the ethylene diamine tetraacetic acid (EDTA) treated plants with the control plants, it is recognizable that the accu-mulation of cadmium of all plant species has not significantly improved.

Certain bacteria and plant hormones are known to accelerate the growth of the plant species to receive faster accumulation results or impact the absorption significantly. As an example, che-lants such as EDTA can aid to sequester heavy metals [20], however the biodegradability of these additives is not always existent. These additives should therefor be biodegradable and pose low toxicity otherwise they will possibly leave contaminants behind and pollute soil or groundwater.

Another field study [21] examined the hyperac-cumulation and metal tolerance of Thlaspi caer-ulescens in cadmium and zinc contaminated sites, while the used species differed in terms of origin. This study displayed that the cadmium uptake of species whose origin were from metal contaminated sites was approximately 100% of species whose origin were from non-metal con-taminated sites. The accumulation of zinc on the other hand, demonstrated an opposite outcome. Zinc was significantly lesser found in shoots of plants whose origin was from metal infected areas.

3.1.2 Phytoremediation of Organic Com-pounds

Compared with heavy metals, organic contami-nants are simpler to degrade or detoxify. The aim of phytoremediation is to transform the pol-lutant as reasonable as possible. A widely ap-pearing organic pollutant is the industrially used degreasing agent trichloroethylene (TCE). TCE is a dense non-aqueous-phase-liquid (DNAPL) and therefor a common pollutant of groundwa-ter. Groundwater appears to be more of a chal-lenge for phytoremediation, since its location is mostly in lower depths. The remediation of groundwater is limited by the size of the root system of plants and trees.

Vroblesky et al. investigated tree cores of dif-ferent species at three sites by coring [22]. The groundwater at these sites was contaminated with chlorinated ethenes. Tree trunks that were located above groundwater contained TCE at all three sites, while cis-1.2-dichloroethene (cDCE) was found at two sites as well and tet-rachloroethene (PCE) was detected at one side. The finding of concentrated cDCE in the inner core, while TCE was more present in the outer core of the trunk, indicates a microbial degrada-tion process. Therefor, tree trunks can serve as indicators for chlorinated ethenes contamination of groundwater even at greater depths.

The bioaccumulation experiment of Boonsaner et al. [23] showed that canna plants (canna x generalis) present an efficient uptake of BTEX. Also notable is that the growth of canna plants in the contaminated soil revealed no substantial restraints when compared to the control plants. Precautions to prevent volatilization of BTEX provided for a more accurate measurement of accumulation. Boonsaner et al. have shown that BTEX can be successfully transported from the canna plants' root zone and rhizome zone to its shoots, without signs of toxicity.

3.1.3 Phytoremediation in Taiwan

Different studies have been carried out to aquire information about the characteristics of various plant species and their phytoremediation behavior. Turnover and dilution or acid washing methods are the common method in Taiwan to remediate sites from heavy metal contamination besides phytoremediation.

Two large case studies regarding the research and viability of phytoextraction of flowers have been performed in Taiwan. The first study [24] involves the in situ phytroextraction using 33 different local flower species to treat a arsenic, chromium, copper, nickel, and zinc contaminat-ed site with an area of 1,3 ha in central Taiwan. The purpose of this study was to figure out twelve species that are most suitable for phy-toremediation to conduct an additional 1,3 ha large field study in central Taiwan [25]. Gener-ally, herbaceous plants storaged higher quanti-ties of metal than woody plants. The selection criterion was the considered importance of the proportion between growth condition to accu-mulation concentration. Out of the initial 33 plants, six woody plants and six herbaceous plants were selected by using a 50% to 50% proportion ratio.

A further study [26] consists of a large scale planting of camphor trees (cinnamomum cam-phora) at a former rice field polluted with cad-mium, chromium, and copper in Taoyuan coun-ty. In 1991, an area of 2 ha was divided and distributed in seven smaller plots, then utilized over a period of 20 years. The trees were cut down in the year 2011. Again, the individual parts of the camphor trees were examined for their heavy metal content and further their met-al accumulation was compared. The trees re-vealed no significant influence in terms of growth by heavy metal pollution when com-pared to the trees of the control site. Results showed that chromium and copper content in soil are less than the current monitoring stand-ards for soil and groundwater at farmland (Ta-ble 1). However, cadmium concentrations still exceeded control standards for farmland (Table 1). The gathered information expresses that camphor trees have as well high potential for phytoextraction purposes, since they accumulate eminent quantities of cadmium in leaves and branches.

Starcluster (Pantas lanceolata Deflers.), French marigold (Tagetes patula L.), Impatiens (Impa-tiens walleriana Hook. f.), Garden verbena (Verbena bipinnatifida Nutt.), and Scarlet sage (Salvia splendens Ker-Gawl.) were grown in a pot experiment [27], artificially contaminated with different cadmium concentrations. Find-ings yielded that French Marigold and Impa-tients accumulated the greatest cadmium amount by far. Nonetheless, only Impatients has hyperaccumulation-potential since its bioaccu-mulation factor (BF = shoot heavy metal con-centration divided by soil heavy metal concen-tration) and translocation factor (TF = shoot heavy metal concentration divided by root heavy metal concentration) are in a range to be regarded as hyperaccumulator (BF and TF ≥ 1).

A phytoextraction survey by Fan et al. [28] re-garding cadmium accumulation and tolerance of mahogany (Swietenia macrophylla) seedlings was carried out and has proven their potential for phytoremediation. Cadmium storage of twigs and leaves were considerably high Alt-hough some leaves of seedlings treated with 30 mg/L cadmium contamination showed signs of chlorosis and presented biomass losses (>75% compared to control seedlings), the tolerance and accumulation of seedlings grown in smaller concentration of cadmium is promising, consid-ering biomass losses are less than 30%. Toler-ance, biomass, and accumulation values of ma-hogany trees are favorable and could be used in the future for cadmium removal of soil and groundwater.

3.2 In situ Chemical Oxidation (ISCO)

ISCO is another alternative technology to re-mediate soil or groundwater of several organic compounds. The contaminants are catalyzed by injecting liquid or gaseous oxidants directly in to the polluted medium. The objective of this technology is to degrade, detoxify, or change the solubility of organic compounds. Further-more, ISCO can be used as pretreatment and coupled with another treatment technology such as bioremediation. Fenton's reagent, ozone, permanganate (sodium permanganate and po-tassium permanganate) and persulfate are most-ly used as oxidants.

3.2.1 Oxidants

The Fenton's reagent uses hydrogen peroxide (H2O2) and iron salts as a catalyst to react with one another. The reaction yields hydroxyl radi-cals (·OH), which are highly reactive and oxi-dize contaminants of soil or groundwater, such as chlorinated solvents. Due to the precipitating properties of iron the ph-level of the medium usually has to be decreased, which may have adverse impact on the ecology. Ozone is a gase-ous fluid that only leaves dioxygen (O2) behind after treatment. Unfortunately this oxidant also reacts easily with other chemicals that are not considered as contaminants. The compounds permanganate (KMnO4) and sodium permanga-nate (NaMnO4) have a lower reaction time, con-tributing in penetration of more volume of the medium and further spread. Sodium persulfate Na2S2O8 has a high solubility and leaves only a small amount of residual compounds. When ap-plying to soil or groundwater, sodium persulfate is activated to derive the kation sulfate radical $SO4^{-}$, which reacts with many contaminants. Persulfate is persistent in soil and less harmful to microorganisms present at the site.

3.2.2 ISCO in Taiwan

Huang et al. [29] demonstrated the decomposi-tion of 2-chlorophenol (2-CP) and H2O2 by three different iron oxides as catalysts. The per-formance of hematite as catalyst showed to be responsible for the fastest degradation of 2-CP, whereas its contribution was the least for the decomposition of H2O2.

Yeh et al. [30] investigated the effects of soil organic matter on the Fenton oxidation.

This study revealed that Fenton's oxidation is also feasible at natural ph levels to remove choloro-phenols. Concentrations of 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) after treatment depended on the appropriate concentration of oxidants and H2O2. As Fe2+ concentration increased, less H2O2 was needed for the reduction of chlorophenols. The soil or-ganic matter was oxidized to some extent, caus-ing the release of earlier absorbed chlorophenols. However, this posed no difficulties, since the contaminants were simply oxidized by the Fen-ton's reagent as well.

The remediation of TCE proves difficulties, when appearing as a DNAPL, since the com-pound sinks deeply into the ground. Since Fen-ton's Reagent requires an ferrous catalyst, it would be beneficial to already have the catalyst on-site. Fenton's reagent showed to be able to directly oxidize TCE as a DNAPL without the addition of a catalyst, since the treated site al-ready contained naturally occurring iron [31]. The utilized soil containing the iron was silica sand, aquifer sand from an illegal dumping site at Kaohsiung, and glass beads as control. Fur-thermore, the ph-level stayed at a natural occur-ring standard. H2O2 could be catalyzed in the aquifer sand by the iron according to the results.

The potential of persulfate to remediate PAHs polluted soil has shown to be present by execut-ing batch experiments [32]. The remediation efficiency of sodium persulfate was compared to the oxidants potassium permanganate and hydrogen peroxide. Moreover, it was the influ-ence of the amount of Fe2+ ions investigated. Results of diesel treated with persulfate indi-cated, that higher persulfate additions equal an increased rate of diesel removal. The Fe2+ con-centration did not matter in degradation effi-ciency, but only affected the rate of degrada-tion, therefor the end result was similar. Thus, this study proofs aswell that under given con-strictions no additional iron catalyst is essential to reach reasonable remediation efficiencies. 50% of diesel was removed in 3 days by using H2O2 (20%), confirming the rapid reaction of Fenton's reagent. Meanwhile diesel degradation with permanganate (6%) was the most efficient.

4. CONCLUSION

Phytoremediation is definitely a promising technology for the rehabilitation of heavy metal contaminated land and it is assumed to be fur-ther developed in the next few years. Several types of plants and trees have already been dis-covered for the efficient removal of heavy met-als. Heavy metal contaminated farmland poses a threat for national health since they easily enter the food chain. Since mostly multiple types of heavy metal occur simultaneously, the selection of species for phytoremediation is not always simple. Additionally, the tropical climate of Taiwan might be an issue of consideration. Nonetheless, the research should be continued

ISCO remediation is capable of degrading vari-ous organic compounds and often used for the removal of contaminants at gas stations. Ac-cording to this research

most common Fenton's reagent is the most common used oxidant in Taiwan. ISCO can be used if an increased con-tamination is present and other technologies might fail. It can be part of a treatment train as well, removing a bigger part of pollution to pre-pare the site for another, cheaper technology
When performing ISCO the risk of elevation of contaminants should be considered.

It is an inevitable necessity to continue research and to periodically hold conferences for the purpose of sharing knowledge and new innova-tions. This ensures a continuous progress in the field of remediation technologies to rehabilitate the environment. A steadily improvement of the monitoring system and implementations of early warning systems to prevent further pollution saves time and money. Finally, the sources of contamination should be clarified and extermi-nated if possible. Altogether, Taiwan has achieved a lot in the past decades to assure a healthy environment for future generations.

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