Monitoring Ex Situ Electrokinetic Remediation (EKR) using Nitric Acid as Chelating Agent

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Abstract. Heavy metal has become a serious world crisis due to natural and man-made sources. Zinc contamination in soil is caused by world urbanization and modernization. The Electrokinetic Remediation (EKR) is a green technology aiming at removing zinc contaminated soils. This paper aims to compare the electrokinetic process between Pure System and Nitric acid as chelating agents. The ex situ remediation method using soil box successfully demonstrated that nitric acid which attracted artificial contaminated zinc had been precipitated at the vicinity of cathode terminal in a form of reddish layer. In conclusion, nitric acid is highly recommended as solution for enhancing electroosmosis process.

1. Introduction
Malaysia is moving towards the status of developing country through industrialization and rapid urbanization. By referring to gross statistical value, rate of urbanization has increased from 54.3 percent to 65.4 percent between year 1991 and 2000 [1]. This is expected to increase up to 75 percent by 2020 according to NUP (full form). However, the effects compromise environmental quality as water, air and soil conditions are deteriorating. The National Policy on Environment [2] aims at continuing economic, social and cultural progresses as well as enhancement of quality living through sustainable development. The NEHAP strategies established in Malaysia Plan (MP) 9th by Ministry of Health, later on, developed and implemented in 10th of MP were to achieve objectives of making available a clean, safe, healthy, and productive environment for present and future generations. Therefore, sustainable ecosystem is the most important aspect to keep balance of the environment. Green environment is crucial when it comes to avoiding severe pollutions due to rapid development in Malaysia. Besides, heavy metal pollution in soil and groundwater in fact is a world-wide problem that each country must initiate concern to achieve a sustainable ecosystem. Heavy metals are introduced into the ecosystem by manufacturers and the use of materials containing heavy metals as well as the improper disposal of these wastes.

Heavy metals contribute toward worldwide soil contamination, thus, enhancement program must be kick started to ensure soils are clean and safe for use. In short, a literature review is widely discussed on scientific perspective and a crucial part of investigation regarding the content which may help making the future research engaging and valuable. Environment is an important element when speaking of sustaining the earth. Defined by the Environment Protection Act 1990, Part 1, Section 1(2), the
environment consists of all, or any, of following media such as air, water and land; and the medium of air includes the air within buildings and the air within other natural or man-made structures above or below ground. “Pollution of the environment” means pollution due to release (into any environmental medium) from any process of substances which is capable of causing harm to man or any other living organisms, supported by the environment. Therefore, pollution can be defined as “the introduction by man into the environment of substances or energy liable to cause hazards to human health, harm to living resources and ecological systems, damage to structures or amenity, or interference with legitimate use of the environment [3-4]. Land may be considered as contaminated when it contains a sufficient quantity of toxic or otherwise harmful materials to pose a threat to the health and safety of users of the land or workers engaging in its redevelopment [2].

2. Heavy Metal Contamination in Ecosystem

Heavy metal contamination in ecosystem may include the food chain, river, sediment, soil and air. In Malaysia alone, its 14 states have different types of soil, ecosystem, marine lives and industrial activities. Heavy metal contamination in environment can be divided into two main sources which specifically anthropogenic and natural sources. The natural sources include weathering mineral process, erosion and volcanic activities, and particles released by vegetation. The anthropogenic sources are man made from industrialization and urbanization. For example, Arsenic (As) may be produced from ore mining and smelting, and agricultural activities are also turned adversely when the emission of cadmium (Cd), and copper (Cu)[5]. Therefore, based on anthropogenic analysis conducted in Perlis, there has been found low heavy metal pollution [6]. The state of Perlis involves with anthropogenic activities such as agricultural activities, cement production, and industrialization. The activities highly contribute towards negative changes of pollution loading, decreased biodiversity, simplified structure, and emission of transportation. However, analyses on Cu, Cr, Ni, Cd and Pb concentration found that their levels were lower than allowable limit based on pollution Index (PI). The anthropogenic cycles as shown in Figure 1 [7] above highlighted that leachate from anthropogenic sources may be discharged from factories. The metal ions will aggregate and accumulate inside the soil and groundwater. The contamination in soil will be up taken by plants which are elements of food chain for animals and human beings. Besides, surface irrigations due to rain will flow into the lake and sea. Therefore marine lives are at stake of being endangered.

Marine ecosystem that plays an important role in the entire ecosystem may also involve in heavy metal pollution. A previous study by Othman et al. [8] concluded that Sungai Sedili in Johor contained a low concentration of heavy metal based on Environmental Quality Guideline for freshwater sediment. Had been highlighted heavy metals in the Sungai Sedili were Fe>Al>Zn>Cu>As>Mn>Ni>Pb>Co>Cd and had been studied metal concentration in sediment layer were found to be Fe>Al>Mn>Zn>Pb>Cu>As>Ni>Co>Cd>Ag. A survey by Shaikah et al. [9] had been conducted at aquatic, seawater and sediment in Teluk Sengat and Pulau Setindan. The investigation proved that tissues of Strombus Canarium (siput gonggong) contained lower concentrations of plumbum (Pb) and Zinc (Zn) based on permissible limits recommended by Food and Agriculture Organization (FAO) and World Health Organization (WHO). Therefore, consumption should be controlled due to reason that 25 percent (%) of total Pb intake will remain in human blood and it has neurotoxic effects [10]. However, sediments of both locations recorded high concentrations of Pb and Zn which, thus, they had been declared as slightly polluted with Pb at 45.572 µg/g dry weight. Soft tissues inside clam (kerang) also contained some amounts of heavy metals. The data had been confirmed by Hossen et al. [11] based on Malaysia Food Regulation (1985) that levels of heavy metal concentration depended heavily on species of clam and locations of 34 sites around Malaysia. Sustainability management for soil and groundwater is in safe hands under the Environmental Quality Act 1974. However, there is no specific regulation with respect to soil and groundwater contamination according to Department of Environment (DOE), and Standard and Industrial Research Institute of Malaysia (SIRIM).
3. Methodology
Electrokinetic remediation (EKR) can be defined as a process of physicochemical transport of charged particles, initiated by electric potentials on formation and fluid transports in porous media. The EKR is also highly depends on types of soil, cation exchange capacity (CEC), applied current voltage, pH soil, and duration.

3.1. Artificial Zinc Contamination in Soil
Soil sampling is vital for soil classification and scientific analysis. However, in terms of laboratory studies, artificial contamination is sufficient and controllable to represent the real condition. Moreover, there are difficulties and related circumstances when it comes to extracting contaminated soil. Hence, the chemical sample should be similar to original pollutant such as arsenic, cadmium, lead, chromium, copper and zinc at the concentration of 0.5% or 5000 mg/kg [12]. The clayey soil had been mechanically mixed with dilution of zinc powder in nitric acid of close to 3269 ppm, under acceptance amount in environment 5100 ppm [13] based on Equation 1 below. The sample was successfully homogeneous within at least 24 hours before the remediation had been studied.

\[ g = \text{MM}_s \times M \times V \]  

in which
- \( g \) is the mass or soil (in g)
- \( \text{MM}_s \) is the mole of chemical (g/mol)
- \( M \) is the molarity of the solution (mol/L)
- \( V \) is the volume of solution (in L)

Spiked soil is an approach for laboratory scale due to constrains to supply contaminated soils from real sites. Therefore, related heavy metals should be mechanically mixed based on environmental guideline as recorded in Table 1. Zinc nitrate-6-hydrate is a white crystal compound soluble in water molecules. The compound Zn(NO$_3$)$_2$.6H$_2$O has molecular weight 297.49 g/mole. Consequently, the clay sample had been mechanically mixed into 0.1M zinc nitrate. The ratio
of the clay soil to 1M of zinc nitrate to distilled water (DW) followed Equation 1. Secondly, the soil sample had been mechanically mixed into dissolved zinc powder with 10 percent of nitric acid. As a result, the soil increased homogeneity after at least 24 hours mixing process. The chemical reaction for dissolution of zinc metal in 10 percent nitric acid was as shown in Equation 2.

\[
\text{Zn}^{2+} + \text{H}^+ + \text{NO}_3^- \rightarrow \text{Zn}^{2+} + \text{NO}_2^- + \text{H}_2\text{O}
\]  

Solution of Nitric acid

3.2. Electrokinetic Remediation (EKR) Laboratory Set Up

There are various heavy metals highly possible to remediate through electrokinetic process such as arsenate, cadmium, soluble copper [14], and zinc. In addition, the electrokinetic can also remove saline from greenhouse. Figure 2 shows a comparison of soil box dimension in which the electric supply is about 20 Volts across 20 cm of electrode distance. There is an acrylic tanks with three separate compartments containing a soil sample in the middle. The electrode could be in a shape of tube well or plate with good electric conductive such as titanium, platinum and graphite. However, steel plate is highly effective in terms of low cost and good conductivity. Electrolyte reservoir aims to continuously supply for electroosmosis process.

**Figure 2.** Comparisons of electrokinetic remediation (EKR) soil box dimensions 
(A= Suzuki [15]; B= Rojo [14]; C= Jo S-U [16])

Figure 3 demonstrates electrokinetic remediation (EKR) set up with regards to ex situ analysis. The soil box had been adapted from previous researches [14]-[16] with volume of 1100 cm³ (22cm x 5cm x 10 cm) for the main compartment, placed in the middle. Electrolyte will be placed at the anode and cathode compartments whilst height, width, and length were 10 cm, 10 cm, and 5 cm respectively.
4. Monitoring Ex Situ Electrokinetic Remediation (EKR)
Ex situ remediation had been divides into two important systems which were pure system and nitric acid as a chelating agent. The principle of chemical reaction is based on the electrolysis of water, which is reduced at the cathode terminal and oxidized at the anode terminal [17]. Therefore, it is proven that the electrolysis of water happened during Pure System for uncontaminated soil as presented in Figure 4(a) and Figure 4(b) in which there were 8 percent of soil moisture at the vicinity of cathode terminal and 19 percent increment at the vicinity of anode terminal as tabulated in Table 1. However, the electrokinetic process for uncontaminated soil using nitric acid contradicted the pure system. This was for the reason that at the vicinity of cathode (nitric acid as catholyte), bubbles appeared and they affected the soil to increase its moisture level up to 40 percent. Hence, at the vicinity of anode, soil moisture only decreased at 6 percent.

The artificial contaminant by zinc nitrate could be categorized as heavy metal. However, zinc nitrate contamination may occur from the nitrogen gas release into soils. Figure 4(c) and Figure 4(d) illustrate variations of soil moistures for Pure System by comparing electric gradients of 50V/m and 150V/m. Physical observation showed that distilled water at cathode terminal remained constant after 7 days of electrokinetic process. Next, at vicinity of anode terminal, white precipitation appeared at electric gradient 50V/cm on a second day of process while 150V/m white precipitate accumulated on third and fourth days of electrokinetic process. Therefore, the electrokinetic process using 10 Voltage of power supply equalled to 50 V/m of electric gradient, was an efficient voltage as mentioned by Bradl [17] that in fine grained soils, electroosmotic could be achieved by applying electric gradients of 100V/m.

The zinc nitrate had been neutralized by using a chelating agent aimed at determining nitric acid should be placed as catholyte or anolyte at electric gradient 50V/m. Therefore, the variations of moisture contents (mc) depicted in Figure 4(e) and Figure 4(d) resulted in accumulated white precipitate at the vicinity of cathode terminal with different soil moistures of 66 percent and 33 percent, respectively. Moreover, at the vicinity of anode terminal, it was recorded that the soil moisture became lesser than before as mentioned in Table 1. The reverse osmosis occurred through electrokinetic process placed nitric acid as catholyte, meanwhile, during third day remediation, soil moisture increased, but decreased on seventh day of soil remediation. Therefore, related electrokinetic process agreed with the fact that a period of three days was occupied to remediate 20 cm of soil sample at 50V/m of electric gradient.
Figure 4. Graph of variations of moisture content (mc) for (a) Pure system for control sample under 10 Volt; (b) Nitric acid as a chelating agent for control sample under 10 Volt; (c) Pure system to remediate zinc nitrate-contaminated soil; (d) Nitric acid as a chelating agent to remediate zinc nitrate-contaminated soil; (e) Nitric acid as anolyte to remediate zinc nitrate-contaminated; (f) Nitric acid as catholyte to remediate zinc nitrate-contaminated; (g) Pure system to remediate artificial zinc-contaminated soil; and (h) Nitric acid as a chelating agent to remediate artificial zinc-contaminated soil.
Table 1. Observation data of ex situ analysis

| EKR System                  | Voltage (Volt) | Anode | Cathode | Remarks                                                                 |
|-----------------------------|----------------|-------|---------|--------------------------------------------------------------------------|
| Uncontaminated soil (Control Sample) |                |       |         |                                                                          |
| Pure System (DW-DW)         | 10             |       |         | The vicinity of terminal was high moisture of about 19 percent increment  |
| Chelating agent (Nitric acid) | 10             |       |         | The vicinity of terminal was dry, of about 8 percent decrement.          |
| Artificial Contaminated (Zinc Nitrate) soils |        |       |         |                                                                          |
| Pure System (DW-DW)         | 10             |       |         | DW – the level had been reduced from initial level.                      |
| Chelating agent (Nitric acid) | 10             |       |         | Nitric acid- bubbles appeared                                            |
| Artificial Contaminated (Zinc metal) soils |        |       |         |                                                                          |
| Pure System (DW-DW)         | 10             |       |         | White precipitate (process happened on 2nd day)                         |
| Chelating agent (Nitric acid as anolyte) | 10             |       |         | At the vicinity of cathode terminal, the moisture was high and DW level remained the same. |
| Chelating agent (Nitric acid as catholyte) | 10             |       |         | White precipitate with high moisture content of about 66 percent (%)     |
| Artificial Contaminated (Zinc metal) soils |        |       |         |                                                                          |
| Pure System (DW-DW)         | 10             |       |         | Level of DW reduced/ Dried White Precipitate                            |
| Chelating agent (Nitric acid) | 10             |       |         | Level of DW reduced/ Dried White Precipitate As Figure 5(a).            |

Nitric acid was successfully employed as enhancement solution.
The electric gradient of 50V/m became a constant parameter to analyze the electrokinetic process for zinc metal artificial contaminant soils. This study performed a comparison between Pure System and Chelating agent as enhancement solution. The electrokinetic process showed that white precipitate which was nitrate ion had been accumulated at the vicinity of anode terminal for both systems with dried region as pictured in Figure 5(a). Meanwhile, at the vicinity of cathode for both systems, there was high soil moisture. The accumulation of reddish layer proved that the anion of zinc, Zn\textsuperscript{2+} had been attracted towards the cathode terminal as visually presented in Figure 5(b) below.

5. Conclusion
Based on physical observation which had been discussed, it was verified that 10 Voltage of power supply was the most efficient compared to 30 Voltage. The right method for artificial zinc-contaminated soil was by using dilution of zinc powder with molecular weight of 64.38 based on periodic table. The white precipitation at the vicinity of anode terminal was expected to be nitrate precipitation. Therefore, spectrometry analyses such as X-Ray Diffraction (XRD), and Ion Chromatography (IC) should be conducted. In addition, analyses should be extended on electrolyte and soil particles on the electrode (steel plate). In conclusion, the method for artificial contaminated soil was succeeded in respect of ex situ electrokinetic remediation (EKR); accordingly, it should become a guideline for in situ application.

6. References
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