
Potential Mobility of Heavy Metal in Soil Using Electrochemical Method

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ABSTRACT

This paper investigates the potential mobility of heavy metal in soil using an electrochemical method in hoped to be used as an extraction technique to reduce the number of soil contaminated sites. In this study, the mobility of chromium (Cr) in the fully saturated soil sample with 1000ppm concentration was investigated by checking the changes of pH performance. A total of four different tests were conducted, and each of the tests is divided equally into two sample preparation. Sample preparation 1 and 2 were applied with electric field strength of 5 V/cm and 10 V/cm respectively, which achieved from a DC power supply. The total duration of tests is six hours and the result was taken and recorded at every one hour. Consequently, the pH value of the soil significantly affects the mobility of heavy metal ions. The mobility of chromium (III) from the soil using the electrochemical method was achieved by considering changes of pH values during experimental works. The pH values are slightly increased at the initial experiment, but then start to decrease after four hours for sample preparation 1 and after three hours for sample preparation 2. In addition, the results also showed that the increased experimental time might induce a higher mobility of chromium in soil due to the changes in pH value performance.

1. Introduction

Heavy metals, particularly chromium, lead, nickel, cadmium, mercury, arsenic, and zinc, is a major public health concern at many contaminated sites (U.S. EPA 1995). Heavy metal contamination of soils stills an unsolved problem, although metals are associated with human life and have been widely used for thousands of years. Soil can be contaminated with heavy metals deriving from various sources, including waste from abandoned mines, improper treatment of industrial wastes,

incomplete collection of used batteries, leakage of landfill leachate, accidental spills, and military activities (Kim et al., 2005). When introduced into soils, heavy metal compounds are hazardous pollutants because they are not biodegradable, toxic at the relatively low concentrations, and they may be mobilized under changing physicochemical conditions like, redox potential or pH (Stegmann et al., 2001).

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Lately, there is growing concern worldwide surrounding issues of soil contamination from a large range of pollutants. The accumulation of heavy metal in soil is of interest because of the adverse effect heavy metals may pose to food quality, soil health and the environment. Experimentally, heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. For instance, it's may enter the human body through food, water, air, or absorption through the skin when they come in contact with humans. With increasing of heavy metal contamination in the soil environment due to various human and natural activities, further contaminants will be affecting the ecosystems.

Chromium is one type of heavy metals that usually contribute to the contaminated soil besides others such as lead, iron, zinc, copper, nickel, cadmium, arsenic, and uranium. There are elements, which can be harmful to people, animals and plants. Moreover, the effects of this contamination are often poorly understood because lack of knowledge about these hazards among people. This phenomenon may lead an increase of various problems to the unhealthy ecosystem. Therefore, there is a need to gain better understanding the behaviour of chromium as well as the other heavy metals which may be risk associated with any contaminated sites.

Electrochemical in soil is the moving of substance by applying an electric potential across the soil. This research will assess a basic electrochemical process as a potential method used to move chromium through the soil and then extract it from the soil or concentrate it in small volume soil, which can be more easily and economically to deal it. In this research, laboratory experiments were conducted to investigate the relationship of chromium mobility in soil with respect to pH performance. It is hoped that these experiments will help to produce a proper extraction technique in order to reduce the number of soil contaminated sites, also provide further insight into electrochemical phenomena and the behaviour of chromium in soil.

2. Findings From The Previous Research

Migration of contaminants into non – contaminants sites as dust or leachate through the soil is the example of events that contribute

towards contamination of our ecosystem. The migration of heavy metals contaminants may lead to increase the area of contaminated soils. Mobility of heavy metal, in particular, soil environment is an important factor assessing the risk posed by that site. Generally, the migration of the contaminants should be in a soluble form. If it not in a soluble, it needs to be desorbed, dissolved, or solubilized into the pore solution before it can be adequately transported from the soil. The mobility of contaminants shows the process of migration of the contaminants (Reddy et al., 1997).

Several studies have been done on the extraction of heavy metal from contaminated soils. Most of the studies done more focusing on the method that can be use for remediation at the contaminated sites. Stewart and West (1996) were done an investigation on the enhancement of electrokinetic remediation for arsenic (As) contaminated soils. In that study, Stewart and West (1996) founded that arsenic is typically immobile in agricultural soil, hence accumulates in the upper soil horizons. Thus, the regression analysis of pH, organic matter content, clay content, iron oxide content, aluminum oxide content, and cation exchange capacity versus arsenic (As) mobility was used in order to determine how each parameter affected the arsenic (As) mobility in soil (Stewart and West, 1996). It was founded that iron oxide content is the only soil characteristic significantly positively correlated with arsenic (As) mobility.

In addition, Darland and Inskeep (1997), have noticed that arsenic mobility is more dependent on ligand exchange mechanisms, particularly with iron oxides than the pH-dependant dissolution precipitation reactions that regulate the movement of most other metals in the soil. Darland and Inskeep (1997) found that arsenate (AsO_4) transport through sand containing free iron oxides was very slow at pH 4.5 and 6.5, and significantly more rapid at pH 8.5. It was suggested that liming soil to increase the pH and promote metal precipitation to decrease metal mobility, may actually facilitate the movement of As (Darland and Inskeep, 1997). Moreover, Inskeep et al (2002) was done a research about arsenic mobility by considering their pH value and redox potential (Eh) of the environment (Figure 1). From the research, it is founded that at high pH and Eh values (above the thick line in Figure 1) arsenates predominate

and at the lower pH and Eh values (below the thick line in Figure 1) arsenites predominate. It is important to note that chemical (abiotic) and microbiological (biotic) processes are inextricably linked in these environments, which affect the As species found, the rate and type of interchange taking place (Inskeep et al., 2002).

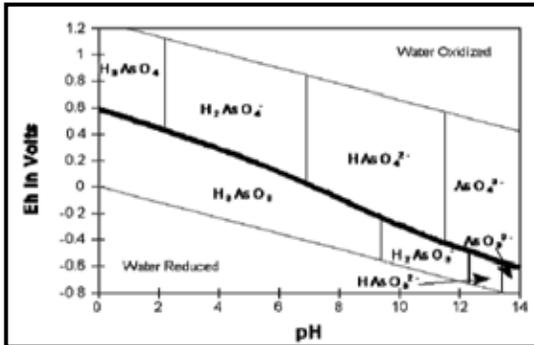


Figure 1: Simplified Eh/pH diagram for arsenic-water system (Inskeep et al., 2002).

3. Theory and Principles of Electrolysis

Electrolysis process is an electrolytic process which decomposes water into oxygen and hydrogen gas with the aid of an electric current as a power source (i.e. battery). The electrolysis cell consists of two electrodes submerged in an electrolyte and connected to opposite poles of a source of direct current (Acar and Alshawabkeh, 1993). The components which have a contact with the electrolyte are called electrodes. One of the electrodes is attached to the negative pole of the battery and supplies electrons to the electrolyte are called the cathode. At the cathode, the area of reduction is taken place (Acar and Alshawabkeh, 1993). While, the other electrode which is attached to the positive pole of the battery and accepts electrons from the electrolyte is called the anode. Oxidation takes place at the anode (Acar and Alshawabkeh, 1993). Hence, when a direct electric current is passed through an electrolyte (such as a molten salt or an aqueous solution of a salt, acid or base), chemical reactions take place at the contacts between the circuit and the solution (Figure 2).

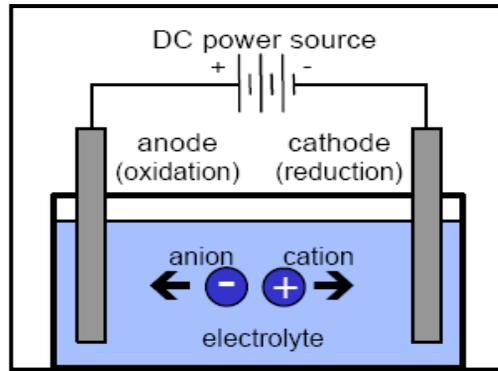


Figure 2: Electrolytic cell

4. Materials, Instruments, Experimental Set-Up And Testing Procedure

4.1 Soil Preparation

Kaolin was selected as a main material for this study. Kaolin is a commercially prepared soil that primarily consists of kaolinite material. Conversely, Chromium III (Cr_2O_3) was used as a chemical reagent in this electrochemical experiment. Those materials have been chosen because of inexpensive, not dangerous and easy to obtain. The soil sample was prepared to be a fully saturated soil by adding a large amount of water to 3kg of kaolin soil until the void contained in the soil is fulfill with water. After that, the soil was tamped into a container using a hand compactor so that the amount of void space was minimized. Then, the static load has been applied vertically to the soil, and the soil was allowed to settle for six days to make sure the soil was fully saturated. The calculated concentration of Cr (III) solution was added to the soil sample by mixing 100g of soil and 100ml of distilled water. The electronic analytical mass balance apparatus was used to measure the quantity of materials needed for the soil sample preparation. The slurry mixture then thoroughly mixed and stirrer to ensure homogenous distribution of a contaminant in the slurry. The final soil sample was spiked with Cr (III) with 1000ppm of concentration. The soil sample was divided into two sample preparation. Both of sample preparation consists with two mixtures. Sample preparation 1 and 2 were applied with electric field strength of 5 V/cm and 10 V/cm respectively, which achieved from a DC power supply.

4.2 Experimental Set Up

The set up basically included an electrochemical cell, two electrodes (carbon), a power supply, and multi-meter. Two cylinder carbon electrodes placed at the cell were used as the working electrodes. Power supply was connected to both electrodes using alligator clips. The power supply was used to supply 5V and 10V D.C current during the process of electrochemical method. Meanwhile, the multi-meter was used to measure the reading of current and voltage at every one hour.

4.3 Electrochemical experiment

The electrochemical method was used to investigate the mobility of chromium in soil and its relationship with respect to pH performance. The basic electrochemical method, which is the electrolysis process, was conducted to investigate and ascertain if it can effectively and efficiently move chromium through the soil. For this study, laboratory experiments will be conducted by passing electric current through the soil sample which had been placed in electrochemical cell. The electrolysis experiment will be done for two types. First, sample preparation 1, was applied with 5V D.C current while the sample preparation 2, was applied with 10V D.C current. The electric current will be applied for specified time periods between three to five hours. At each hour, the pH value, current, and temperature were taken and recorded. Thermometer was used to measure the temperature value while pH meter was used to determine the acidity or alkalinity of the samples. Physical and chemical soil parameters such as pH value and temperature will be tested and monitored throughout the experiment. The small volume of soil for both sample preparations was taken and placed in a plastic container for digestion process. Figure 3 showed the electrochemical experiment set up apparatus that was conducted for this research.

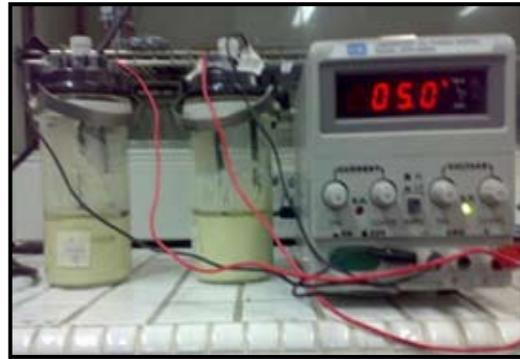


Figure 3: Electrochemical Experiment Set up Apparatus

4.4 Digestion Process

The digestion process is needed in this study, in order to change the slurry form of sample to the liquid form. Digesdahl Digestion apparatus was used to conduct the experiment. All samples taken from the electrochemical experiment were dry using the oven-dry machine. Afterwards, the samples were left for a day in the oven-dry machine before 0.2 grams of dry samples were taken for the digestion process. The samples were placed into 100ml Digesdahl digestion flask and were added with concentrated sulfuric acid and two silicon carbide boiling chips. The silicon carbide boiling chip is the type of hanger granules, which used for a smooth boiling. When the apparatus was properly set up, the temperature dial was turned to a heat setting of 440°C (825°F). Then, the samples were heated approximately about 3 to 5 minutes, and it is important to ensure the samples were not boiled to dryness. About 10ml of 50% hydrogen peroxide is added to the charred sample via the funnel on the fractioning head. After addition of hydrogen peroxide complete, then the excess of hydrogen peroxide will be heating for one more minute. The hot flask was allowed to cool, and the digest sample was diluted with approximately 100ml of deionized water. Finally, the digested samples with visible turbidity, was filtered and placed in the plastic bottles for a further used of the Inductivity Plasma (ICP) experiments.

4.5 Inductivity Couple Plasma (ICP) Experiment

Inductivity Coupled Plasma (ICP) is an analytical technique used for the detection of trace metals in environmental samples. If the

chromium is moveable, then the mobility of chromium will be determined by considering the reduction of concentration value, which can be determined by conducting the Inductively Coupled Plasma (ICP) test. In ICP experiment, the digested samples were placed on the plastic test tube and labelled. Meanwhile, for running the ICP machine, three standard solution and blank solution with varied concentration was prepared. The removal efficiency of the samples will be determined based on the data taken from ICP test. The ICP machine takes at least three hours to complete the whole experiment process. However, it depends on the amount of the digested sample that needed to be tested. The result of the experiment will be displayed on the computer program and print out.

5. Electrochemical Experiment Results

The most pronounced electrochemical effect that occurs during the electrokinetic extraction is probably the generation of the pH gradient in the soil by electrolytic decomposition of water (Hamed et al., 1991). Table 1 showed the data of sample preparation 1, which taken before and during the process of the electrochemical experiments was conducted. Furthermore, in this table, the value of pH, temperature, and current was taken and recorded at each hour until the total of hours taken to run the experiment is five hours. Besides, the pH variation in the sample preparation 1 which consists of the values of two mixtures, which are the mix 1 and mix 2 was clearly shown in the Figure 4. For sample preparation 1, 5V D.C current was applied through the electric current field of the electrochemical experiment.

Table 1: Results of Sample Preparation 1 for Electrochemical Experiment (Applied with 5V D.C current)

Soil mixtures	Time (hour)	Current (Amperes)	pH value	Temperature (°C)
Mix 1	0	0	4.64	23.1
	1	0.029	4.68	27.4
	2	0.022	4.73	28.0
	3	0.014	4.97	28.5
	4	0.011	4.85	29.0
	5	0.060	4.72	29.5
Mix 2	0	0	4.69	23.1
	1	0.029	4.79	27.7
	2	0.022	4.90	28.0
	3	0.014	4.92	28.8
	4	0.011	4.82	28.8
	5	0.060	4.65	29.5

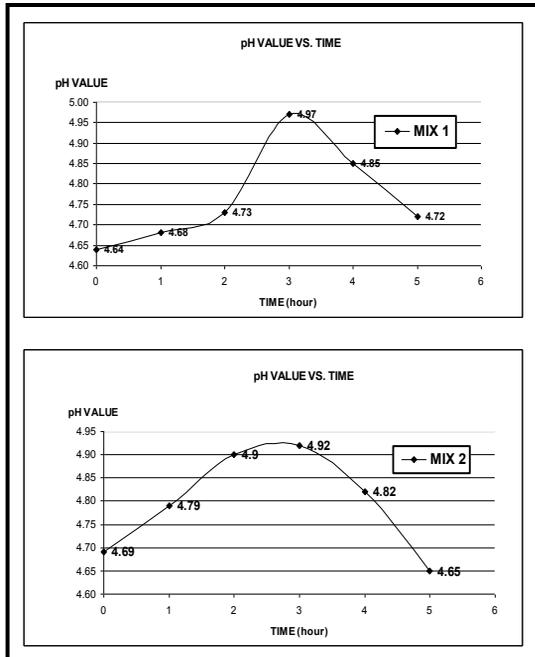


Figure 4: The pH variation in the soil sample preparation 1

In the electrolysis experiment, the changes in pH value and temperature were examined. The value of pH at the first stage was increased from the original pH value of 4.30 to 4.64, and it was continued increasing until achieved the peak pH value of 4.97 for soil sample, which boiled for three-hour durations. However, the pH value started to decrease from 4.85 to 4.72 for soil sample, which boiled more than three hours. This process shows that the samples tried to go back to the original form and become more acidity. Nevertheless, for the mix 2, the pH value of the sample also decreases to 4.65 and achieved the peak value of pH at three hour duration of time.

On the other hand, the pH value of sample preparation 2 was slightly changes (Table 2 and Figure 5) during the electrochemical experiment. From the figure 5, the pH value of sample preparation 2 was achieved peak pH value of 4.74 for mix 1 and 4.70 for mix 2 at the soil sample boiled for two hour duration time. Then, after two hours of duration time, the pH value for both mixes was quickly decreased. From the observation, it is assumed that the mobility of chromium is faster in sample preparation 2 compared to sample preparation 1. This occurred because the amount of power

supply or voltage gradient in sample preparation 2 are higher compared to sample preparation 1.

Table 2: Results of Sample Preparation 2 for Electrochemical Experiment (Applied with 10V D.C current)

Soil mixtures	Time (hour)	Current (Amperes)	pH value	Temperature (°C)
Mix 1	0	0	4.66	29.0
	1	0.042	4.72	29.5
	2	0.073	4.74	29.8
	3	0.071	4.69	30.5
	4	0.053	4.66	31.0
	5	0.051	4.61	31.5
Mix 2	0	0	4.64	29.0
	1	0.042	4.68	29.0
	2	0.073	4.70	29.8
	3	0.071	4.61	31.0
	4	0.053	4.59	31.5
	5	0.051	4.57	32.0

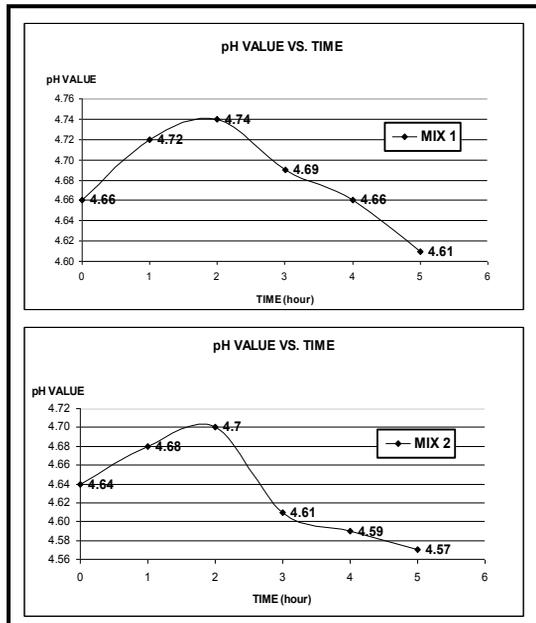


Figure 5: The pH variation in the soil sample preparation 2

By taking consideration of both cases, it can be stated that the pH performance played the important factor to ensure the achievable mobility of chromium in soil. Moreover, the changes in pH value during the experimental works show that the mobility of chromium in soil was occurred when the high pH value of soil sample was achieved after the chromium element is added before it returned to the initial pH value of soil sample. This process showed that the extraction may occur during the

experiment period. Besides, the changes of pH value in the experiment can be clearly presented by taken the average of mixtures for both sample preparations (Table 3 and Figure 6).

Soil Mixture	Time (hour)	Average pH Value	
		Sample Preparation 1	Sample Preparation 2
Average mixture	0	4.67	4.65
	1	4.74	4.70
	2	4.82	4.72
	3	4.95	4.65
	4	4.84	4.63
	5	4.69	4.59

Table 3: Average Value of Sample Preparation 1 and 2

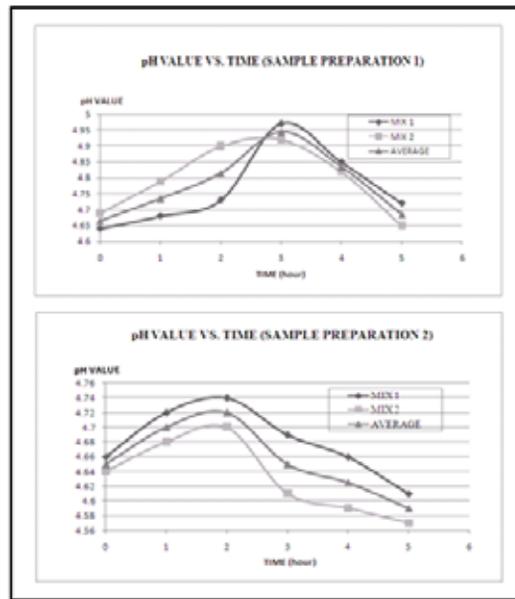


Figure 6: The average pH variation in the soil for both sample preparation

6. Inductivity Couple Plasma (ICP) Experiment

Table 4 and 5 indicated the results taken from ICP experiment for both sample preparations. From Table 4, the concentration of chromium in soil samples was slightly decreased during the experiment. The decreasing of concentration value might be due to extraction of the chromium to the electrodes. Hence, this ensured that the mobility of chromium in soil was occurred during the experimental process. Same goes to the sample preparation 2, the concentration value of this sample also

decreased by a time. Figure 7 clearly showed the changing of concentration value during the ICP test. For sample preparation 1, at the zero hour, the value of concentration is 1754mg/L but after three hours, the concentration started to decrease to 276.5mg/L. Meanwhile, for the sample preparation 2, the initial value of concentration is 2822mg/L and after three hours the value of concentration decreased to 983.1mg/L.

Sample No.	Time (hour)	Conc. (Calibrate) mg/L	Conc. (Sample) mg/L
1	0	1754	1754
2	1	1714	1714
3	2	946.8	946.8
4	3	276.5	276.5

Table 4: Results of Sample Preparation 1 for ICP Experiment (Applied with 5v D.C Current)

Sample No.	Time (hour)	Conc. (Calibrate) mg/L	Conc. (Sample) mg/L
1	0	2822	2822
2	1	2206	2206
3	2	1172	1172
4	3	983.1	983.1

Table 5: Results of Sample Preparation 1 for ICP Experiment (Applied 10V D.C current)

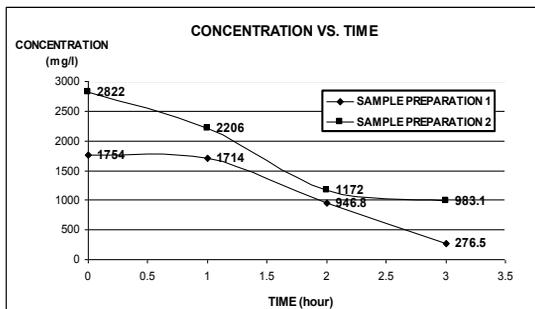


Figure 7: The temperature variation for both samples preparation in ICP experiment

7. Conclusion And Discussion

Based on the result and findings from this research, it can be concluded that:

1. The pH values increased as the time increased, but it will start to decrease at a certain period. The phenomenon occurred shown that the mobility of chromium in the soil sample.

2. The removals of the chromium started to take place when pH value decreasing and returned to the initial pH value of kaolin soil without the present of the chromium elements.
3. The temperature of the sample increasing with respect to time. The existence of chromium lead to the increment of the temperature at each one hour and it became slower at the end of the experiment. It can be concluded that the increases of temperature in the soil sample help to improve the migration or mobility of chromium in electrochemical cell, but it also depends on the element inside the soil.
4. The decrement of the concentration indicated that the mobility of the chromium elements in the soil sample may be occurred and has been removed.
5. For further study on this extraction method could be done in order to understand deeply the concept of the electrolysis and also chemistry. Knowledge in the chemistry and handling apparatus also should be improved to get a better result. It is suggested to use Atomic Absorption Spectrometry (AAS) in order to determine the removal efficiency of heavy metals. This is because Inducted Couple Plasma has restricted limitation of the uses and can only measure the concentration of certain heavy metal only.

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