Zn (II) Removal from River Water Samples of Sembrong, Johor State, Malaysia by Electrokinetic Remediation

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Abstract. Heavy metals pollution has become one of the most serious environmental problems today. The treatment of heavy metals is of special concern due to their recalcitrance and persistence in the environment. Even many physical, chemical and biological treatment processes have been proposed to remove heavy metals from river water, the use of these treatment processes are not efficient and relatively costly. This study focused on the potential application of electrokinetic (EK) remediation in Sembrong River water to remove zinc (Zn²⁺). The physicochemical and biological parameters and water quality index (WQI) of Sembrong River water was characterized. The electrokinetic remediation experiments were performed by controlling pH, and electric density on voltage were observed and investigated. The results indicated that all physicochemical and biological parameters of Sembrong River complied with the standard discharged limit set by the Department of Environment (DOE). However, suspended solids (SS) and pH can be categorized as Class III according to INWQS. The best performance of 88% efficiency of zinc can be achieved EK experiment run at a fixed voltage of 30 V at pH 5.14 after 60 min of the process operate. This technology may be proposed for faster and eco-friendly removal of heavy metals in the environment.

1.0 Introduction
Rapid development of urbanization and industrialization has led to increased disposal of heavy metals into the environment [1]. The use of the heavy metals has increased in many industries over the past few decades, but their effects on the environment are more concern now. The metals are persistent in the environment and posing risks to human health [2]. Trace concentrations of zinc (Zn) are important for the physiological functions of living tissue and regulate many bio-chemical processes. However, similar to other heavy metals, when Zn discharges into natural waters at increased concentrations in sewage, industrial wastewater or from mining operations, it can have severe toxicological effects on humans and aquatic wastewaters before transport and cycling in the natural environment [3-5]. A number of technologies have been developed over the years to remove heavy metals from river water. The important
technology includes chemical precipitation, neutralization, activated carbon adsorption, ion exchange resins, reverse osmosis, solvent extraction and membrane technologies [6]. However, these processes proved to be costly, less efficient and not environmental friendly.

Therefore, the aim of this study is to investigate the potential application of EK remediation in Sembrong River water to remove Zn\(^{2+}\). EK technology represents an interesting approach as it is a simple technique which is environmentally friendly, efficient and substantially higher levels of sustainability. In this study, renovated equipment was used to study the impact of electrokinetic remediation in trapping and removing heavy metals from Sembrong River water. The distribution of pH in an electrolyte solution, contact time and electric density of voltage have been analyzed. This study expected that the effluent complied with the standard discharge limit. However, for this research, EK treatment was introduced for removing heavy metal (Zinc) of water sample from Sembrong River to improve the quality of the water as a water resource.

2.0 Methodology

2.1 Sampling locations and characterization of Sembrong River water

The samples were taken from Sembrong river, located in Air Hitam Johor. The sampling points were selected from two locations i.e., (i) at a point under the bridge of the river and (ii) at a stream flow after discharging from residential area into the river. Several water quality parameters i.e., pH, dissolved oxygen (DO) and temperature were measured in-situ. The measurements of biochemical oxygen demand (BOD), chemical oxygen demand (COD), SS, ammoniacal nitrogen (NH\(_3\)-N), colour and heavy metals analysis were performed at the Laboratory of Micro-Pollutant Research Centre (MPRC) and Environmental Analysis Engineering, Universiti Tun Hussein Onn Malaysia. Table 2.1 shows the analytical methods and the instruments used for measuring the water quality parameters [7].

| Parameter                          | Analytical Methods          | Instruments                        |
|-----------------------------------|-----------------------------|------------------------------------|
| pH                                | Sensor                      | pH meter                           |
| Temperature                       | Sensor                      | YSI Meter                          |
| Dissolved oxygen (DO)             | Sensor                      | DO Meter                           |
| Colour                            | ADMI Weight Ordinate Method | DR6000 Spectrophotometer           |
| Biochemical Oxygen Demand (BOD)   | Dilution Method             | BOD Incubator                      |
| Chemical Oxygen Demand (COD)      | Reactor Digestion Method    | COD digestion reactor              |
| Suspended Solid (SS)              | Gravimetric Method          | Vacuum Filtration                  |
| Ammonia Nitrogen (NH\(_3\)-N)    | Nessler Method              | DR6000 Spectrophotometer           |
| Metals                            | Atomic emission             | Inductively Coupled Plasma Mass Spectrometry (ICP-MS) |

2.2 Dimension and experiment procedure of electrokinetic system

The EK cell (Figure 2.2) is made of acrylic with its dimensions of 35.0 cm length x 9.0 cm height x 8.0 cm width with a capacity of 200 mL samples. Two pieces of fiberglass filter paper (0.45 μm, 80 mm) on the two clapboards were used to separate the river water samples and electrodes in order to enhance the transport of ions toward the electrode compartments and to prevent water particles from flowing into the electrode compartments [8][9].
Aluminium electrodes with a diameter of 8 mm and a length of 12 cm were installed at each side of the river water samples. Aluminium electrode was used to prevent the electrode-electrolysis reaction. A direct current power supply was applied to maintain a constant voltage of 30 V. The experiment was carried out at 25-30°C of room temperature. In order to enhance the effectiveness of the process, the samples were filtered through sand filter filled with fine sand at top, course sand at the middle and peat soil at the bottom of the sand filter (Figure 2.3) to remove any impurities accompanied in the samples. The remaining of filtered samples were put into a Schott bottle and stored in a refrigerator at 4°C for further use.

3.0 Results and Discussions

3.1 Characteristics of Sembrong River
The main characteristics of Sembrong River water are shown in Table 3.1. The results show that all the parameters complied with Standard B as stated in Wastewater Discharge Standards and Raw Water Quality Criteria for Malaysia [10], except for pH and SS.

### Table 3.1: Main characteristics of the Sembrong River water

| Parameters | Unit | H1 | H2 | Standard B |
|------------|------|----|----|------------|
| DO         | mg L\(^{-1}\) | 6.95 | 7.30 | -          |
| Temperature | °C | 28.68 | 30.42 | 40         |
| BOD        | mg L\(^{-1}\) | 3.84 | 3.90 | 50         |
| pH         | - | 3.30 | 3.31 | 5.5 - 9.0  |
| NH\(_3\)-N | mg L\(^{-1}\) | 1.18 | 1.32 | 20         |
| COD        | mg L\(^{-1}\) | 47 | 71 | 100        |
| SS         | mg L\(^{-1}\) | 850 | 800 | 100        |
| Colour     | ADMI | 6.75 | 17.50 | 200        |
| Zn         | µg L\(^{-1}\) | 227.33 | 213.48 | 1000       |
| As         | µg L\(^{-1}\) | 4.61 | 1.99 | 100        |
| Pb         | µg L\(^{-1}\) | 12.45 | 15.88 | 500        |
| Cd         | µg L\(^{-1}\) | 0.51 | 0.51 | 20         |
| Ni         | µg L\(^{-1}\) | 28.26 | 39.51 | 1000       |

Remarks: ^aH1 is a point under the bridge of the river; ^bH2 is a stream flow after discharging from residential area into the river and ^cStandard B is the point of discharge into the river downstream the intake of water for use in the treatment for water supply.

The concentrations of SS are high with a value of 850 and 800 mg L\(^{-1}\) for H1 and H2 sampling points due to land use activities in this region indicate that Sembrong river water containing high organic and inorganic pollutants [11]. The concentrations of Zn considerably higher with the value of 277 and 213 µg L\(^{-1}\) although the value complies with the standard discharge limit while the minor elements of As, Pb, Cd and Ni would be negligible. The Sembrong River water also contains high colour of 17.50 mg L\(^{-1}\) at H2 sampling point as well can affect turbidity. The pH of Sembrong River water is an acidic condition (pH 3.0) due to runoff water from oil palm plantations and modern agriculture probably contains fatty acid composition [12].

#### 3.2 Result analysis based on WQI

Water quality was assessed using the DOE water quality classification based on the water quality index (Table 3.2). The average of WQI from H1 and H2 sampling points obtained is 58.97 and 54.55 respectively. The value of WQI of H1 sampling points shows slightly higher than H2 sampling points, whether is classified as the same class. The overall WQI indicates that Sembrong River is categorized as Class III [10]. It can be seen that Sembrong River still can use as a water supply for extensive treatment required, aquaculture to supports hardened river species and sources for drinking animals. This can be supported by the fact that only a few hardened river fish species can be found in the river [13][14].
### Table 3.2: Water quality index

| Zone | Parameters                          | Sub index and water quality index | Water quality classification based on water quality index |
|------|------------------------------------|-----------------------------------|-----------------------------------------------------------|
| H1   | Biochemical Oxygen Demand (BOD)    | 83.5                              | Slightly polluted                                         |
|      | Ammonical Nitrogen (NH₃-N)         | 52.5                              | Polluted                                                 |
|      | Suspended Solids (SS)              | 29.3                              | Polluted                                                 |
|      | Water Quality Index (WQI)          | 58.98                             | Polluted                                                 |
| H2   | Biochemical Oxygen Demand (BOD)    | 85.7                              | Slightly polluted                                         |
|      | Ammonical Nitrogen (NH₃-N)         | 42.4                              | Polluted                                                 |
|      | Suspended Solids (SS)              | 16.5                              | Polluted                                                 |
|      | Water Quality Index (WQI)          | 54.59                             | Polluted                                                 |

#### 3.3 Effect of current density on voltage and time

Figure 3.1 shows the changes in the electric current during the treatments. The current passing through the system decreases during the EK process. This is due to the loss of ionic strength in the pore fluid since ions migrate towards the electrodes [15][16]. In addition, the resistance in the interface between electrodes and electrolyte might increase due to concentration polarization and water dissociation. During the treatment, more current passed through the system, especially during the 60 min. During this period the enhanced system is the same as the conventional one, apart from the increased cathode compartment length, so it can be assumed that the prevention of OH⁻ ions migrate into the solution enable more Zn ions to be desorbed. More H⁺ ions formed at the implemented anodes and more Zn ions desorbed from the particles contribute to the slight increase in system conductivity [17-19].

![Figure 3.1: Current voltage and contact time during the experiments](image)

#### 3.4 Effect of distribution of pH

The water electrolysis reaction in which H⁺ and hydroxide (OH⁻) are continuously released at the anode and cathode, respectively, is considered to be the predominant reaction under an electric field. During the EK process, OH⁻ can be neutralized by additional H⁺, so the movement of H⁺ would change the Sembrong River water pH drastically.
Figure 3.2: Distribution of pH (a) before and (b) after the EK experiments

Figure 3.2 shows the pH profiles of Sembrong River water in the EK system. The acid front generated at the anode compartment flushed across the Sembrong River water, increasing the pH values from 2.72 to 4.88 and 2.89 to 5.14 for H1 and H2 sampling points respectively with potential voltage of 30 V for 60 min. The pH profiles influenced the forms of the contaminants [20] [21], and the low pH increased the mobility of heavy metals [22]. Decrease in soil pH near the anode is due to water electrolysis which caused by H+ ions formation. Virkutyte et al. [23] reported that metal-hydroxide precipitation was at a minimum if the pH value was below 4.5.

4.0 Conclusions

Based on the study carried out in this research, all the parameters complied with Standard B stated in Wastewater Discharge Standards and Raw Water Quality Criteria for Malaysia, 2009 except for pH and SS and it is categorized as Class III considered polluted bases on WQI analysis. The EK system showed the highest removal efficiency of Zn (88%) occurred at a potential gradient of 30 V, acidic pH (5.14) after 60 min of the EK process. Therefore, the EK treatment may be a better remediation alternatives to accelerate the removal efficiency of heavy metals from river water.

5.0 Acknowledgment

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6.0 References

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