Biochar-coated aluminium electrodes for Cr, Mn and Fe removal in electrochemical treatment for polluted river water remediation

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Abstract. Biochar (a by-product of biomass pyrolysis) is developed as a renewable, low-cost, and promising carbon-based electrode for electrochemical remediation of Cr, Mn and Fe in polluted river water. The biochar - electrode were prepared with two types of tailored sieved size medium (2.0 mm) and fine (150 µm). The effect of the different sieved size on the electrochemical reactor was set at 60V of voltage supply, 6 cm inter-electrode distance within 105 minutes electrolysis operational time. The results indicated that the highest removal efficiency for Cr was achieved at 95% after 105 minutes followed by Mn at 99.9% in 65 minutes and Fe at 92.76% in 105 minutes. Interestingly, the electrode with larger sieved size showed the highest removal efficiency for all three elements. These results emphasize the importance of tailoring the porous structure of the biochar electrode material as a function of the specific size of adsorbate ions to improve the electrochemical water treatment performance for polluted river water.

1. Introduction

Water pollution caused by heavy metals is a global problem and have received worldwide attention. Since late 20th century, contaminated river water has become a very critical task that needs to be taken care of, due to the public expectation of producing water that are clean, free of color, turbidity, taste, odor and other harmful metal ions. Heavy metal containing water should be managed properly, or it could lead to serious damage to the environment which will result in long term effect on human health.
and other living creature [14]. There are many techniques used in water remediation of contamination, they are physical, biological, photolytic, chemical, and electrochemical.

Of these, electrochemical processes have gained lots of attentions and interests in recent years as a cost efficient and accomplished technology for the treatment of contaminated water [20]. Meanwhile, it offer several advantages over other techniques [19] due to its operation at ambient temperature and pressure as well as robust performance and capability to adjust to variations in the influent composition and flow rate. The method itself is considered to be capable of degrading a notable wide range of contaminants, including phosphate [22], PFAAs [23], phenolic compounds [8], arsenic [4], nitrate [14], methyl orange (MO) [18] and heavy metal [2][9][15][16][17][19][21][25]. The nature of the electrochemical process involves the application of electricity to pass a current through an aqueous metal solution, which also contains a cathode plate and an anode. The treatment is the precipitation of the heavy metals in a weakly acidic or neutralized electrolyte as hydroxides. In that manner, the choice of the electrode material does not only provide specific application options but also play a significant role in improving the method proficiency against various type of contaminated compounds [2].

The biochar, otherwise known as charcoal, are widely used as adsorbent material for heavy metal removal in water [3] due to its considerable heavy metal removal capacity. It has feature such as cost effective, large surface area, stable chemical properties, high conductivity, availability, structure adjustable and is emerging as an economical substitute to the activated carbon to remove diverse organic and inorganic contaminants. Biochar normally used in adsorption for water treatment but the disadvantages of this technique alone are its low efficiency [9]. Accordingly, it should be very interesting to use the biochar fabricated with aluminium electrode in an electrochemical cell to investigate its removal performance. The main objectives of the research were to:

- study the efficiency in removing Cr, Mn and Fe using integrated EC-adsorption system and,
- investigate the effects of different biochar sieved size on the removal of metals.

2. Experimental

2.1. Electrode preparation

A mixture of biochar (150 µm and 2.0 mm sieved size) with 9:1 mass ratio was prepared using methanol (99.99% assay; Fisher Scientific) as solvent. The mixture was sonicated for 1 hour and then binded with cyanoacrylates using a doctor knife on a 7 × 7 cm aluminium plate then placed in an oven for 4 hours. Two sets of electrodes were made from each tailored biochar sample to verify removal efficiency for Cr, Mn and Fe metal from polluted river water.

2.2. Analytical technique

The polluted river water used in this research was obtained from Senggarang river, Johor, Malaysia. The pH of the river water was determined to be 3.51 by using pen type pH meter (PH-8061, Huixia). Quantitative analysis of Cr, Mn and Fe in the river water before and after the electrochemical process were determined by using an atomic absorption spectrometer (AAS, Perkin Elmer A Analyst 800 (Flame and Furnace AAS); USA). The linearity and sensitivity check was done for Cr (5 ppm; 4 ppm), Mn (2 ppm; 2.5 ppm) and Fe (5 ppm; 5 ppm); respectively. The river water was diluted 10 times prior to analysis with three replicate measurements to quantify metal content in the samples. Both anode and cathode were dissembled and dried overnight after electrochemical operation, and then surface structure was analysed by scanning electron microscopy (SEM, HITACHI SU1510). The elemental composition change on the electrode surface was analysed by energy-dispersive spectroscopy (EDS).
2.3. Determination of Cr, Mn and Fe removal efficiency

The removal efficiency of Cr, Mn and Fe at time t, were determined using following equation:

\[
\text{Removal efficiency} = \frac{C_o - C_t}{C_o} \times 100\%
\]

where \(C_o\) and \(C_t\) are the metal concentration in water (mg/L) before and after (at time t) the electrochemical experiment (mg/L), respectively.

2.4. Electrochemical reactor setup

An electrochemical cell was designed with biochar coated aluminium electrodes for both anode and cathode to treat the capacity of a 500 mL river water containing 0.49 mg/L of Cr, 0.78 mg/L of Mn and 10.7 mg/L of Fe. The experimental setup is shown schematically in Figure 1. All experiments were carried out at room temperature, normal pressure; an original pH value of the water (pH value of 3.51), supply energy of 60 V current and no additives were added. During the process, hydrogen and oxygen were generated at cathode and anode due to the half-cell reaction. Those generated gasses pushed most of the created sludge to the surface of the aqueous phase while the other remained in the body water (Tran et. al., 2017). The different sizes of sieved biochar affect the value of the process and result in different removal efficiency. During the 2 h of treatment, the samples were drawn every 5 minutes for monitoring the metal ion concentration of the water together with measuring collected heavy metals of the cathode.

3. Results and discussion

3.1. Characterisation of biochar electrode

Figure 2 shows the surface morphology of the 150 µm and 2.0 mm sieved size biochar electrodes after heavy metal removal studies. While the 150 µm biochar electrode surface cover with darker surface area, the 2.0 mm surface can be seen accumulated with more shining area. EDS analysis (Figure 3) shows that significant amounts of Cr, Mn and Fe element was detected on the surface of each used electrodes, confirming the deposition of the metals while Table 1 represents the atomic percentages of concerned elements from EDS analysis.
Figure 2. SEM image for (a) coated biochar with 150 µm sieved size and, (b) coated biochar with 2.0 mm sieved size.

Figure 3. EDS spectrum for (a) 150 µm sieved size biochar electrode and, (b) 2.0 mm sieved size biochar electrode after the electrochemical treatment.

Table 1. Listed the atomic percentages of each heavy metal based on EDS spectrum analysis.

| Element | 150 µm | 2.0 mm |
|---------|--------|--------|
| C       | 68.10  | 62.17  |
| O       | 31.30  | 35.30  |
| Cr      | -0.04  | -0.04  |
| Mn      | 0.08   | 0.36   |
| Fe      | 0.56   | 2.22   |
3.2. **Elemental analysis in water**

As could be shown in Figure 4, with increasing the size of biochar, the efficiency of the metal removal with aluminium electrodes increases too. Explicitly, with 150 µm biochar electrode, Cr, Mn and Fe were removed 82.54%, 90.55% and 84.03%, respectively. All the metal removal could be enhanced by increasing the sieved size of biochar. It shows that higher Cr, Mn and Fe removal efficiency of 95%, 99.9% and 92.76% respectively, was achieved with the 2.0 mm biochar coated electrode. Furthermore, with increasing time, the removal efficiency increases too. The highest removal is attributed to the Mn, whereas the lowest is for Cr and Fe. This can be explained by the element with higher reduction potential has a tendency to gain an electron and be reduced by the oxidation process. Due to the more positive standard reduction potential value, manganese would be treated and removed out of the solution followed by chromium and iron [21].

![Graph (a)](image1.png)

![Graph (b)](image2.png)

**Figure 4.** Variation of Cr, Mn and Fe removal efficiency during electrochemical every 5 minutes sample collection for 105 minutes (a) biochar coated 150 µm (b) biochar coated 2.0 mm.

4. **Conclusion**

The biochar electrode with 2.0 mm sieved size removed more metals compared to the 150 µm sieved size after 105 minutes operating time. Of the three elements (Cr, Mn and Fe) Mn was found to be the highest removal for both biochar electrodes. This happened based on the value in standard reduction potential table. Mn has the power of reducibility 1.51 V which is higher than Cr (1.33 V) and Fe (0.77 V) that makes Mn get deposited first and removed faster. This study was conducted with a single cell (one cathode and one anode) to demonstrate the suitability of the integrated system for heavy metal removal. It is recommended that future studies use multiple cells connected in series to continuously and more efficiently remove heavy metals.

5. **References**

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