Heavy Metals (Fe, Cu, and Cr) Removal from Wastewater by *Moringa Oleifera Press Cake*

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Abstract. The consumption of water nowadays is increasing and the wastewater from variety of industry and domestic are increasing as well. If this wastewater is being untreated, it will be wasted and the chemicals inside the water especially heavy metal are harmful to the living organism. There are few conventional method used to treat the wastewater but most of them are costly, hence, natural coagulant is introduced in this study. One of the multipurpose tree *Moringa oleifera*, (MO) which is environmental friendly and low cost become a choice for removal of heavy metal from wastewater. The *Moringa oleifera* press cake (MOPC) are able to remove the heavy metal but the removal efficiency for different metals need to be investigated. Therefore, experiment on heavy metal removal by *Moringa oleifera* press cake was conducted. The wastewater samples and MOPC were collected from Balok River, Kuantan and Mitomasa Sdn. Bhd, Kuala Lumpur respectively. MOPC was immersed in distilled water to remove the oil and different concentration of MOPC solution were made. Jar test were carried out with different concentration of MOPC solution. The initial and final heavy metal (Fe, Cu, and Cr) concentration were measured by Atomic Absorption Spectrometer and the removal percentage was calculated. The MOPC removed 69.99% Fe, 88.86 % Cu and 93.73% Cr at optimum concentration of 10000 ppm, 5000 ppm and 15000 ppm, respectively. The MOPC also reduced 34.94% of COD and 81.6 % of turbidity. However, BOD of wastewater increased from 9.0 ppm to 18.3 ppm. The pH values was not changed with the addition of MOPC. The removal of heavy metal was increased proportionally with MOPC concentration until optimum removal was obtained.

1 INTRODUCTION

Water is very important and essential for human to survive and for all the living organism. Recently, the consumption of water have increased due to the increase of population worldwide. Meanwhile, large amount of wastewater containing contaminant such as suspended solid, pathogens, nutrients and heavy metals which may be harmful and dangerous are generated from the field of domestic and industrial agriculture. If they are kept untreated, safely disposed back to the sea or rivers, many pollution problems will be introduced (Paula et al., 2014). From World Health Organisation 2004, drinking water supplies around the world have been identified to have thousands of chemicals considered potentially hazardous to human health at relatively high concentrations (Vikashni et al., 2012). Besides, pollution of water has received special attention as an environmental issue and causes shortage of water supply especially in the developing and third world countries which have inadequate financial resources (Ali et al., 2009).

One of the contaminant in wastewater is the heavy metal. This wastewater with heavy metals are mainly contributed by anthropogenic sources like electronics assembly and fabrication, textiles, usage of fertilizers and pesticides, and mining activities (Kalavathy and Miranda, 2010). There are mainly 59 elements of heavy metal where cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb) and zinc (Zn) are considered highly toxic (Vikashni et al., 2012). Even at low concentrations, these heavy metals can be toxic to organisms, including humans (Obuseng et al., 2012). Conventional methods used to remove heavy metal ions from wastewaters includes: ultra-filtration, reverse osmosis, ion exchange, solvent extraction, sedimentation and chemical precipitation (Obuseng et al., 2012). However, most of these methods has some disadvantages such as incomplete metal removal and Miranda, 2010). For instance, excess concentration of toxic sludge disposal or treatment problem (Kalavathy and aluminium sulphate

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(alum) which as a chemical coagulant in water treatment has been reported to cause Alzheimer's or other neuro-degenerative diseases (Paula et al., 2014). Cost of the chemical used in conventional method are too expensive for most of the developing country. Besides, for country like Malaysia which has frequent land development and rainy season, the cost of water treatment may be increasing due to unstable quality of water and high turbidity (Ali et al., 2009).

To solve this problem, natural coagulants which are more economical and environmentally friendly are studied. Natural coagulants are biodegradable and can be locally grown. Moreover, they produce less sludge and are safer for human compared to chemical coagulants. Three examples of the natural coagulants that are being tested by Kazi and Virupakshi (2013) are *Cicerarietinum, Seed Moringa,* and *Cactus Opuntiaficus*. It was found that the removal of turbidity by *Cicerarietinum* and *Seed Moringa oleifera* are 90% and 82.02%, respectively. Other research work by Patil et al., (2013) showed that both leave and latex of *Calotropisprocera* can be used in bioremediation of heavy metals. In addition, Sago (*Metroxylon*spp) is found to be one type of coagulant to remove turbidity and heavy metal which grown in Malaysia (Aziz et al., 2000). Since *Moringa oleifera* is one of the best natural coagulant discovered yet, it can be used to replace the conventional methods widely all around the world. It is a small tree which is fast growing and can reach up to 12 meters in height (Araújo et al., 2013). *Moringa oleifera* is one type of tropical multipurpose tree which is adaptable to semi-arid climates. Leaves and seeds of *Moringa oleifera* are also widely used in water treatment since they have no significant side effect and are non-toxic and biodegradable (Ali et al., 2014). Research done by Bodlund, (2013) on MO showed that coagulation activity is similar to the alum. The MO contain cationic polyelectrolytes which have proved to be effective in water treatment as a substitute for aluminium sulfate (Araújo et al., 2013). The flocculation activities of MO adsorb the metal cations based on the electrostatic charge mechanism (Muyibi et al. 2002). The use of *Moringa oleifera* in water treatment also do not have significant effect on pH (Sajidu et al., 2005). In this research, the removal of iron (Fe), copper (Cu) and Chromium (Cr) from wastewater by using *Moringa oleifera* press cake was performed and the efficiency was calculated. The properties of treated water were tested as well such as: pH, Turbidity, BOD, COD.

2 MATERIALS AND METHODS

The wastewater used for the experiment was obtained from the Balok River, Gebeng, Kuantan. While the *Moringa oleifera* Press cake (MOPC) used in the experiment was obtained from MitoMasa Sdn. Bhd., Kuala Lumpur. In order to use the MOPC, it was immersed in distilled water for 24 hours to remove any remaining oil after mechanical press. Then the MOPC was then filtered and stored in the chiller at 4°C.

2.1 Metal Standard Solution Preparation

Different concentration of 0 mg/L, 1 mg/L, 2 mg/L and 4 mg/L of iron, copper, and chromium solution were prepared for calibration curve. A drop of nitric acid was added to the solution for preservation (Vikashni et al. 2012).

2.2 *Moringa oleifera* Solution Preparation

The MO solution was prepared by adding 10 g (dry basis mass) of MO into 500 mL of distilled water to make 20,000 ppm MO solution. The solution was stirred so the MO can be dissolved in the distilled water. Then the solution was further diluted to 10 mL to 1,000 ppm, 5,000 ppm, 10,000 ppm, 15,000 ppm and 20,000 ppm.

2.3 Wastewater Treatment

Each beaker in jar test was filled with 500 mL of wastewater sample. 10mL of MOPC with different concentration prepared were added into each beaker. The stirring speed was set as 200 rpm for 4 minutes followed by 40 rpm for 30 minutes (Lea, 2010).

2.4 Heavy Metal Measurement

The heavy metal removal test was done by using Atomic Absorption Spectrometer (AAnalyst 400. Perkin Elmer). Calibration curve for each type of metal was obtained from the stock solution prepared from each standard at different concentration. The wastewaters obtained after the jar test were filtered by using vacuum pump through a 0.45μm nylon membrane filter before tested by AAS (Ali et al. 2014).

2.5 Turbidity and pH Measurement

The turbidity and pH of wastewater sample were measured by turbidity meter and pH meter respectively.

2.6 Biochemical Oxygen Demand (BOD) Measurement

BOD measurement was done by dissolved oxygen meter. Dilution water was prepared by mixing 3 mL of phosphate buffer, magnesium sulfate, calcium chloride, ferric chloride solution into 3 L volumetric flask. 10 mL of samples after jar test were mixed with 300 mL of distilled water into incubation bottle. Water was added to the BOD test bottle and covered with an aluminium foil. All the bottles were then put into BOD incubator for 5 days at 20°C. The final DO was measured and BOD of each sample was calculated according to Suhartini et al. (2013).

2.7 Chemical Oxygen Demand (COD) Measurement

Spectrophotometer was used to measure the COD. Around 2 mL of de-ionized water (control) and each sample from jar test were added into COD digestion reagent vials. Then, the samples were inserted into COD reactor and heated for 2 hours at 150°C with strong oxidizing agent (potassium dichromate solution). The solutions were then cooled down to room temperature (Kasmawati and Lee, 2007).

3 RESULTS AND DISCUSSION

3.1 Heavy Metal Removal Percentage

The concentration of heavy metal of Fe and Cr metal in the wastewater of the Balok River, Gebeng, Kuantan were approximately to 1 mg/L while Cu concentration was approximately 0.4 mg/L. To determine the optimum dosage or concentration of *Moringa oleifera* solution added into the wastewater, a jar test was done by adding 10 mL of 1000 ppm, 5000 ppm, 10000 ppm, 15000 ppm and 20000 ppm into 500 mL of wastewater. Figure 1 shows the results of the heavy metal concentration of the wastewater from Balok River after the treatment with different concentration of *Moringa oleifera* solution.

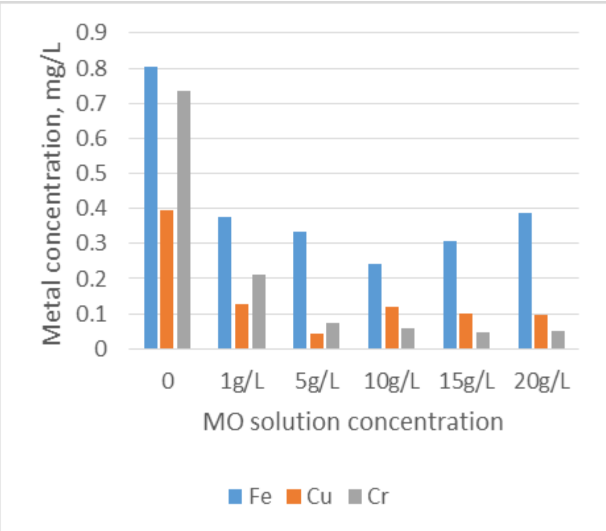

Fig.1. Metal Concentration after Jar test

From the results of the experiment, the heavy metals were successfully reduced after the treatment with the MOPC. The removal percentage of Iron, copper and chromium reached 69.99%, 88.86% and 93.73%, respectively. Generally, the metal removal percentage increase proportionally to the concentration of MOPC solution. Besides, the optimum MOPC concentration for iron, copper and chromium removal were at 10000 mg/L, 5000 mg/L and 15000 mg/L, respectively. The removal of iron in this experiment were lower than the research done by Sajidu et al. (2005), which had a removal of 92.14 %. The removal percentage of chromium in this research was higher compared with the research done by Vikashni et al. (2012), which was only 60% and almost similar to Ravikumar and Sheeja (2013), which was 73%. The copper removal efficiency in this research is approximately similar to the literature statement of Vikashni et al. (2012) which was approximately to 90%.The trend of the removal percentage of copper and chromium were found to be alike as the trend in the research done by (Ali, 2016; Mataka et al., 2010).

The results of the removal percentage of each metal is shown in Figure 2.

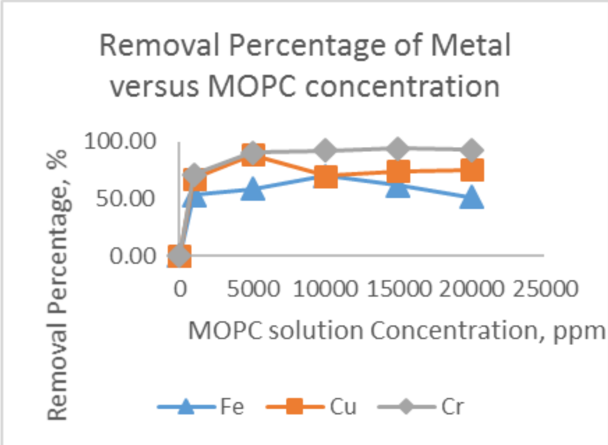

Fig.2. Metal Removal Percentages

3.2 Turbidity

The turbidity of the wastewater was determined by using the turbidity meter and results are shown in the Figure 3

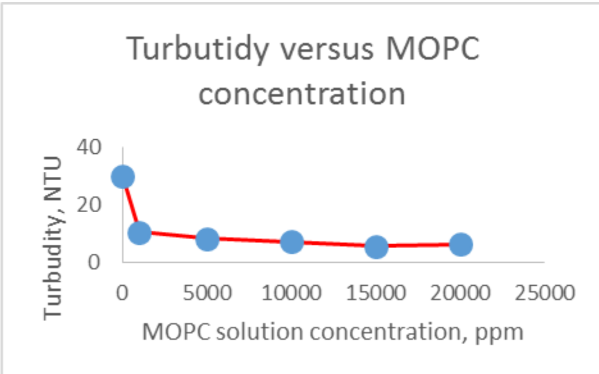

Fig.3. Turbidity of treated wastewater

From the results obtained in the experiment, the wastewater was having turbidity of 30.1 NTU. By adding MOPC, the turbidity was decreased to a minimum value of 5.54 NTU at the optimum concentration of 15000 ppm MOPC solution. Figure 3, shows the trend of decreasing in turbidity as the MOPC solution concentration increase. However, there are a limitation for the turbidity removal and the continue increase of the MOPC will lead to increase residual turbidity. The highest removal percentage of the turbidity was 81.6%.

3.3 pH Value

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The pH value was measured by pH meter and the results are shown in the Figure 4.

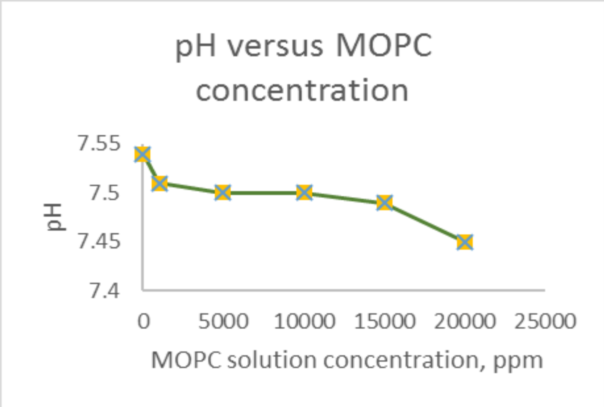

Fig.4. pH value of the wastewater

There was no significant difference in the pH value which is between 7.45 and 7.54 after treatment with different concentration of MOPC as shown in Figure 4, which is in the range accepted by the World Health Organization with permissible limits of 6.5 to 8.5 for drinking water.

3.4 Chemical Oxygen Demand

The COD of the wastewater were determined by using the spectrometer (HACH DR2800) after heating using (HACH DRB200) for 2 hours at 150°C with strong oxidizing agent (potassium dichromate solution) in COD digestion reagent vials. The results of COD are shown in the Figure 5.

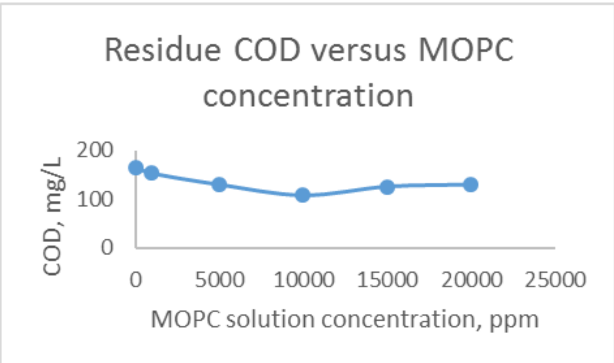

Fig.5. COD of the wastewater

Figure 5, shows that the COD was decreasing by adding MOPC. The COD of the wastewater decrease from 166 mg/L to 108 mg/L at the optimum concentration of 10000 ppm. Then the COD increase slightly with the increase of MOPC solution concentration after it reached the optimum concentration. The maximum COD removal percentage was 34.94 %.

3.5 Biochemical Oxygen Demand

The DO of the wastewater initially and after 5 days were determined by using the dissolved oxygen. The results are shown in Figure 6.

According to the results shown in Figure 6, the DO reduced from 1.31 mg/L to 0.68 mg/L and the BOD value increase as the MOPC solution concentration increase. The BOD had increase from 9 mg/L to 18.3 mg/L when 25000 ppm of the MOPC solution was added to the wastewater. The result are different from the previous research which had shown the removal of the BOD by the *Moringa oleifera*. The increase in BOD indicated the increase of the oxygen demand when higher concentration of the MOPC solution was added to the sample. This is due to the presence of organic compounds in the MOPC, which enable the growth of organism in the water. The decrease in DO value might be caused by the increase in oxygen needed by MOPC to oxidize the organic substance inside the wastewater (Yuliastri et al., 2016).

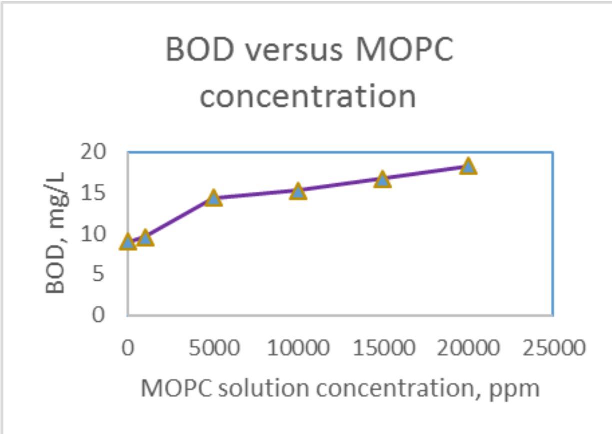

Fig.6. BOD of the wastewater

4 CONCLUSION

The MOPC is a good heavy metal removal. As the MOPC concentration increases the heavy metal removal percentage was increased until the optimum concentration was used. Moreover, the turbidity was reduced as the pH value was not affected, which can be considered as an added value for removal of turbidity and heavy metal where no pH adjustment is needed. MOPC can reduce the COD but the BOD was increased due to presence of some oil in MOPC, and it can suggested to make sure that the oil is totally removed from press cake to reduce BOD. The *Moringa oleifera* press cake can be recommended to be a good coagulant and heavy metal removal.

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