Removal of Iron and Manganese in Groundwater using Natural Biosorbent

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Abstract. This study was conducted to measure and compare the concentration of iron, manganese and hardness of the river and groundwater and to determine the effectiveness of iron and manganese removal by using natural biosorbent which is banana peels. The samples of river and groundwater were collected at riverbank filtration site at Jenderam Hilir, Dengkil. Based on the water quality investigation, the concentration of iron and manganese in the samples of groundwater have exceeded the drinking water quality standard which are 0.3 mg/L for iron and 0.1 mg/L for manganese. The removal process of the iron and manganese in the groundwater was done by using 2, 4 and 8 grams of banana peels activated carbon. It is found that with higher amount of activated banana peels, the removal of iron and manganese is more effective. The ranges of percentage of iron and manganese removal are between 82.25% to 90.84% and 98.79% to 99.43% respectively. From the result, banana peels activated carbon can be concluded as a one of the most effective low-cost adsorbent for groundwater treatment.

1. Introduction
Groundwater is the water that fills opening in beds of rocks and sand. Examples of the water that fills in opening beds are rainwater and surface water. Rainwater and surface water infiltrated into the soils and move downward to the water level in the groundwater reservoir which called water table. Groundwater occurs in deeper zone. Deeper zone is the saturated zone which all the pore spaces are filled with water. Groundwater is normally much like a sponge holds water that present in soils and sands and able to hold the water. Groundwater does not commonly occur in lakes, vein and streams that located in underground [7].

Groundwater has been used as the one of important alternative sources of public and commercial water supply in Malaysia especially in fastest developing states such as Selangor. Demand for water supply in Selangor has been increased significantly because of the rapid development in recent years. In addition, the impact of climate change such as drought and dry season and pollution of river have increased the demand for groundwater uses supply. River bank filtration is one of the methods to provide water from the groundwater [5]. Groundwater commonly looked clean and clear since the ground has naturally filters out particulate substance. However, human-induced and natural chemicals can be present in groundwater. Human interferences have strongly affected the groundwater quality such as salt contamination in irrigated areas, leaching of nitrate and heavy metals after clear-cutting or
soil tillage under forest, leaching of nutrients and pesticides under agricultural land and waste water application to agricultural areas [1].

As such, it is imperative to understand the groundwater quality restoration and as it is influenced by the soil it flows through. The behavior and transport of polluting substance in the groundwater has strongly depends on the filtering function of soil as it may affect the quantity of minerals and other constituents in groundwater. Therefore, the objectives of this study are, 1) to investigate the content of iron and manganese in river and groundwater, 2) to remove the amount of iron and manganese in groundwater using activated banana peels.

2. Methodology
In this study, the prominent quality parameters for heavy metal in groundwater chosen to be measured were iron and manganese. The hardness of groundwater sample taken from the site was also selected to be measured. The water samples were collected from a selected river and groundwater’s wells. For the groundwater samples, riverbank filtration has been applied to collect the samples. River water samples were collected by using grab sampling technique and then were put it in the sampling bottles.

For the groundwater samples, the water was collected from the two wells which are MW01 and MW02 by using water pump. The groundwater samples were collected and then put it into the sampling bottles. The water samples were collected for four times. The water samples then were brought to the laboratory for iron, manganese and hardness measurement tests. The result will be getting from the test and the result will be analyzed for the further treatment process.

2.1. Study Area
Jenderam Hilir is located at the southeast state of Selangor. This study area is located at the downstream of Sungai Langat. Dengkil is the nearest town to this study area. Dengkil is a town in the Sepang district of Selangor that located between Cyberjaya and Salak Tinggi. In many years, Dengkil has profited from the development of Putrajaya and Kuala Lumpur which are located nearby this town. This study area was selected because of the high water demand in this study area and groundwater is seen as one of the source with very high potential to be developed as additional source to meet the high public water supply demand [6].

2.2. Laboratory Testing
Water samples that have been collected in the site were brought to the Environmental Laboratory of Faculty Civil Engineering, Universiti Teknologi Mara. In the laboratory, iron, manganese and hardness measurement testing were conducted. If amount of iron and manganese present in water exceeded the water quality standard as presumed, removal of iron and manganese by using activated banana peels will be carried out.

For iron measurement test, 10 ml of water sample was filled into the clean square sample cell. FerroVer Iron Reagent Powder Pillow was added to the sample cell. The solution was swirled to mix. An orange color was form if iron is present in the water sample. The solution then waited for the 3 minutes reaction. For the blank preparation, 10 ml of water sample was filled into another square sample cell. After 3 minutes reaction of water sample with the FerroVer Iron Reagent Powder Pillow, the spectrophotometer was set by the 265 Iron, FerroVer. The blank sample was inserted to the cell holder with the fill line facing right. The start and zero button was pressed. The display was showed 0.00 mg/L Fe. The blank sample was carried out from the cell holder and the sample which has reacted with FerroVer Iron Reagent Powder Pillow was inserted into the cell holder. Read button was pressed and the amount of iron was appeared on the screen.

For manganese measurement test, the blank sample preparation, 10 ml of deionized water was poured into a square sample cell. For the prepared sample, 10 ml of water sample was poured into a square sample cell. The content of one Ascorbic Acid Powder Pillow was added to each cell. Each cell was closed with stopper and was inverted to dissolve the powder. 12 drops of Alkaline-Cyanide Reagent Solution was added to each cell. Each cell was swirled gently to mix. A cloudy solution was
formed. 12 drops of PAN Indicator Solution, 0.1% was added to each sample cell. Each sample was swirled gently to mix. An orange color was developed in the sample if manganese was present in the water sample. The sample was ignored for 2 minutes reaction. After two minutes reaction time expired, the spectrophotometer was set by 290 Manganese, LR PAN. The blank sample was wiped and inserted into the cell holder with the fill line facing right. Zero button was pressed and the displays on screen was showed 0.000 mg/L Mn. The blank sample was taken out from the cell holder. The prepared sample was wiped and inserted into the cell holder with the fill line facing right. The read button was pressed and the amount of manganese was appeared on the screen.

For hardness measurement test, 100 ml of water sample was poured into 100 ml graduated mixing cylinder. 1 ml of Calcium and Magnesium indicator solution was added onto the graduated mixing cylinder using a 1 ml measuring dropper. The cylinder was closed by the stopper and was inverted several times. 1 ml of Alkali Solution for Calcium and Magnesium Test was added into the graduated mixing cylinder using a 1 ml measuring dropper. The cylinder was closed again by stopper and was inverted again for several times. 10 ml of solution in graduated mixing cylinder was poured into each of three square sample cells. For the blank sample preparation, one drop of 1 M EDTA Solution was added to the cell. The cell was swirled to mix the solution. For the magnesium sample preparation, one drop of EGTA Solution was added to the second cell. The cell was swirled to mix the solution. The spectrophotometer was set by the 225 Hardness, Mg and the blank sample was put into the cell holder with the fill line facing right. Zero button was pressed. The display in the screen was showed 0.00 mg/L Mg CaCO$_3$. The blank sample was carried out from the cell holder and the magnesium sample was put into the cell holder. Read button was pressed and the amount of magnesium as a calcium carbonate was appeared on the screen. Magnesium sample in the cell holder was not removed and exit button was pressed. The spectrophotometer was set by 220 Hardness, Ca and the start and zero buttons was pressed. The display on the screen was showed 0.00 mg/L Ca CaCO$_3$. The magnesium sample was removed. Third cell was act as a calcium sample and was put into the cell holder with the fill line facing right. Read button was press and the amount of calcium in the sample was appeared as a calcium carbonate.

In order to remove the metal in the sample as per objective of this study, the banana peels need to be activated. The banana peels were separated from the fruit smoothly and the peels were washed and dried in oven at 110$^\circ$C for 4 hours. The dried banana peels were blended without specific size and then thermally activated (carbonized) at 550$^\circ$C in a muffle furnace for 1 hour to transform the banana peels into activated carbon. Banana peels activated carbons were weighted for 2, 4 and 8 grams and were mixed with 100ml of water samples in the 250ml conical flask. The mixtures were agitated on a mechanical orbital shaker at 200rpm for 30 minutes. Then, the samples were filtered through filter papers and the concentration of iron and manganese were determined by spectrophotometer.

3. Results and Data Analysis
Based on the test results done in laboratory, the data have been tabulated and analyzed.

| Sources   | Manganese concentration (mg/L) | Iron concentration (mg/L) | Calcium concentration (mg/L) | Magnesium concentration (mg/L) | Water hardness (mg/L) |
|-----------|--------------------------------|---------------------------|-------------------------------|--------------------------------|-----------------------|
| River     | 0.376                          | 0.920                     | 0.09                          | 0.256                          | 1.280                 |
| Well M01  | 0.729                          | 5.240                     | 0.24                          | 1.574                          | 7.050                 |
| Well M02  | 0.935                          | 5.600                     | 0.36                          | 0.812                          | 4.230                 |

Table 1 shows the concentration of iron, manganese, calcium, magnesium and hardness in the river and groundwater. Water hardness can be calculated using the water hardness equation:
Based on the data that have been taken, the concentration of manganese and iron in the river are 0.376 mg/L and 0.920 mg/L respectively. The concentration of calcium and magnesium in river are 0.090 mg/L to 0.256 mg/L respectively. The concentration of iron and manganese in river have exceed the water quality standard for drinking water which are 0.1 mg/L for manganese and 0.3 mg/L for iron.

For the concentration of the magnesium and iron which was pumped from well MW01, the results are 0.729 mg/L and 5.240 mg/L respectively and the concentration of calcium and magnesium are 0.24 mg/L and 1.574 mg/L respectively. For the concentration of magnesium and iron which was pumped from well MW02, the concentrations are 0.935 mg/L and 5.600 mg/L respectively and the concentration of calcium and magnesium are 0.360 mg/L and 0.812 mg/L respectively. The concentration of iron and manganese in both groundwater have exceeded the water quality standard for drinking water which are 0.1 mg/L for manganese and 0.3 mg/L for iron.

Using the water hardness formula, the concentration of water hardness in river and groundwater that was pumped in Well MW01 and the groundwater that has been pumped in Well MW02 are 1.280 mg/L, 7.050 mg/L and 4.230 mg/L respectively. Based on the water hardness that have been calculated by the water hardness equation, type of water in river and both groundwater that have been pumped in Well MW01 and Well MW02 are categorized as a soft water.

From the results, the concentration of the concentration of iron, manganese, calcium, magnesium and hardness of the river are lower than the range of concentration in groundwater. These situations occurred due to many possible factors. The high concentration of the iron and manganese in groundwater are caused by the types of soil and rock that have been passed through by the groundwater [4]. Types of rock such as mafic and ultramafic rocks, limestone, greywacke and shale contain high concentration of iron, manganese and calcium which can cause the high concentration of that metal in soil and sediment by weathering process. Microorganism is one of the factors that can cause the mobilization of the iron, manganese, calcium and magnesium in the environment and can increase the concentration of that metal in groundwater [4].

The concentration of iron, manganese, calcium and magnesium in groundwater that has been pumped in Well MW02 are higher than the concentration in groundwater that has been pumped in Well MW01. It is because of the distance between the well and the surface water in that area which is river. Well MW02 is much further in distance compared to Well MW02. Groundwater that has been pumped in Well MW02 has travel passed through more soil and rock compared to the groundwater that has been pumped in Well MW01 and this has probably caused the high contribution of concentration of iron, manganese, calcium and magnesium.

As presumed earlier that the metals content in groundwater is higher than river water, the removal process of the iron and manganese using activated banana peels in both groundwater samples taken for this study has been carried out.
The removal process of the iron in both groundwater samples were done by using 2, 4 and 8 grams of banana peels activated carbon. Figure 1 shows the percentage of iron removal (%) vs weight of banana peels activated carbon. By this removal process, the range of percentage of iron removal by using banana peels activated carbon is between 82.25% and 90.84%. Percentage of removal can be calculated by equation (1) where $P_o$ and $P_f$ is the initial and final concentration of metal respectively.

$$% \text{metal removal} = \left( \frac{P_o - P_f}{P_o} \right) \times 100$$

(2)

The removal process of the manganese in both groundwater samples also were done by using 2, 4 and 8 grams of banana peels activated carbon. From the data in Figure 2, the range of percentage of manganese removal by using banana peels activated carbon is between 98.79% and 99.43% in range. Banana peels was found to be a good sources of pectin, lignin, cellulose, hemicellulose and galactouroninc acid which strong metal adsorbent in aqueous solution [8].

Percentages of iron and manganese removal are dependent on the biosorbent dose of the banana peels activated carbon. The amount of biosorbent dose of the banana peels activated carbon used are 2, 4 and 8 grams. The larger the amount of biosorbtent dose of the banana peels activated carbon, the
higher the percentage of iron and manganese removal because of the increase in the number of binding sites available for biosorption [2].

4. Conclusion

Based on the results obtained from this study, it can be concluded that the concentration of iron, manganese, calcium and magnesium in groundwater are higher than the river because of the existence of soil, rock and weathering process. As a groundwater is one of the important alternative sources for water supply, groundwater’s quality must be made sure not exceeded the drinking water quality standard before supplying to the consumers. If the groundwater’s quality has exceeded the drinking water quality standard, some treatment need to be done. In terms of iron and manganese removal, activated banana peels can be concluded as one of the most effective low-cost adsorbent. The higher the amount of the banana peels activated carbon, the more effectiveness of iron and manganese removal. Banana peels activated carbon might be known as a capable crop-based material available for discovering of alternative uses as well.

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