POTENTIAL OF USING ROSA CENTIFOLIA TO REMOVE IRON AND MANGANESE IN GROUNDWATER TREATMENT

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ABSTRACT

Groundwater is a source for water supply because of its good natural quality. However, groundwater may be exposed toward contamination by various anthropogenic activities such as agricultural, domestic and industrial. Groundwater quality problems are typically associated with high hardness, high salinity and elevated concentration of iron, manganese, ammonium, fluoride and occasionally nitrate and arsenic. Therefore, groundwater should be treated to an acceptable level before consumption. This study was carried out with the objectives to optimize the feasibility condition of contact time, biosorbent dosage and pH range in removing heavy metal by using Rosa Centifolia (R. Centifolia) and also to determine the water quality of groundwater sources. A dried Rosa Centifolia pretreated before being used as biosorbent. Experiment was done by varying contact time, biosorbent dosage and pH range to get the optimum value. The removal characteristic of iron and manganese by Rosa Centifolia was analyzed using Atomic Absorption Spectrophotometer (AAS). The optimum condition is achieved at 240 minutes, 0.05g/ml and pH 5 respectively. The optimum percentage removal of iron and manganese was found to be more than 70%. The finding indicated that Rosa Centifolia is a promising biosorbent in treating groundwater from RECESS UTHM well.

Keywords: Groundwater, Rosa Centifolia, Fe, Mn, Biosorption

1.0 INTRODUCTION

Most groundwater contains some metal such as iron and manganese which naturally leaches from rocks and soils [1,2,3]. These metals that are found naturally, in soils, rocks, plants and most water supplies are essential for human health [4,5]. Excess amounts of metal in drinking water can cause coloured water, rusty-brown stains or black specs on fixtures and laundry [6,7]. Excess amounts of metal may also affect the taste of beverages and can build up deposits in pipes, heaters or pressure tanks [8]. The accumulation of metal contamination in water has become a concern due to the growing health risk it poses to the public [9,10]. Exposure to heavy metal contamination has been found to cause kidney damage, liver damage, and anemia in low doses [11,12,13].

Due to the severity of heavy metal contamination and potential adverse health impact on the public, efforts must be taken to purify water containing toxic metal ions. However, the conventional methods for removing heavy metals from groundwater such as precipitation and sludge separation, chemical oxidation or reduction, ion exchange, reverse osmosis, membrane separation, electrochemical treatment and evaporation are often ineffective and costly when applied to dilute and very dilute effluents [14,1,15]. Due to this problem, in this study, the biosorption method was used to remove the pollutants. Biosorption is one of the alternative method to remove heavy metal [19,20]. This method was chosen due to its economical and will reduce the production of sludge at the end of treatment process. Recently, researchers have proven
to this alternative method by using many type of biomass waste that provides low cost maintenance but high removal efficiency of heavy metals [21,22]. Most studies prefer on choosing waste biomass that readily discard as waste in compare to costly biomass. R. Centifolia is one of the potential biomass that normally being discarded after extraction of essential oil that can be used as biosorbent to remove Fe and Mn in groundwater.

Commercially, R. Centifolia is used for its aesthetic value in perfumes manufacturing, decoration and healthy purpose. Normally, the number of rose consumptions is approximately 500 to 3000 petals roses in a year [23]. The R. Centifolia biomass that were left after being used is a waste material with no commercial value or other usage. Hence, to reduce the waste of biomass, the R. Centifolia biomass was used as a biosorbent to solve this groundwater problem. The chemical composition of R. Centifolia waste biomass is described later on in this manuscript. In continuation of our investigation, the objective of this study was to determine the water quality of groundwater sources from RECESS, UTHM well. The effects of contact time, biosorbent dosage and pH range on Mn and Fe biosorption are described here in detail.

2.0 MATERIALS AND METHOD

This study consists of comprehensive batch experimental work. Figure 2.1 shows the R. Centifolia that was used in this experiment. Groundwater samples were collected at RECESS UTHM in Parit Raja for the study. The method that was used to collect the groundwater sample is the grab method. In the experimental work, five stages of experiments were conducted.

Figure 2.1: Rosa Centifolia

Figure 2.2 shows the step of experimental work. Firstly, the groundwater quality was tested to determine the culprit heavy metals [24]. At the second stage, the treatment to treat the groundwater pollution was chosen. In this study, biosorption treatment using R. Centifolia in Figure 2.2 was chosen as the biosorbent to treat the groundwater pollution. Third stage is the preparation of R. Centifolia as the biosorbent. The used R. Centifolia was collected and was sun dried in 7 days. Then it was thoroughly washed with running water and three times with distilled water to remove dirt. The washed R. Centifolia was oven dried at 60°C for 72 hours until constant weight. Then, it was cut into small pieces with homogenous known particle size of less than 0.255 mm [25] and turned into powder using mixer. In the fourth stage, optimum condition for the biosorbent to remove the heavy metals was determined by making the biosorbent dosage, pH and contact time as the variables in the batch reactor conducted in the laboratory. Batch study was carried out in this stage. Last stage (5th stage), the optimum condition determined in batch reactor was applied repeatedly to confirm and determine the effectiveness of the removal. The rose waste biomass samples were analyzed using X-Ray Fluorescence (XRF) for trace metals. Kinetic experiments (30–330 min) were performed to evaluate the effect of contact time [46]. The
biomass (at 0.05 g/mL) was added into the conical flasks containing the 100mL of groundwater (100 mg/L) at pH 6. The flasks were agitated at 100rpm. In the dose (0.05–0.45 g/mL), size (less than 0.25mm), 100mL solution was taken in 250mL conical flask and were agitated at 100rpm for the initial contact time was maintained at the optimum value of 240min for Mn and Fe. In order to investigate the effect of pH in groundwater at various initial pH, it were prepared using 0.1M HCl or 0.1M NaOH. The optimum biomass for Mn and Fe (at 0.05 g/mL) was added into the conical flasks containing the 100mL of groundwater (100 mg/L). The flasks were agitated at 100rpm for 240 min. The metal concentrations were measured using atomic absorption spectrophotometer (AAS) (Perkin Elmer Analyst 300). The initial and final concentrations were determined using AAS. The amount of Fe and Mn taken up by rose waste biomass in each flask was calculated using following mass balance Equation 2.1 [26]:

$$\text{Percentage sorption} = \left( \frac{C_i - C_e}{C_i} \right) \times 100$$  
(Equation 2.1)

Where:

- $C_i$ = initial and equilibrium metal concentrations (mg/l)
- $C_e$ = after treatment metal concentration (mg/l).

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**Figure 2.2: Experimental Work**
3.0 RESULTS AND DISCUSSION

The chemical composition of R. Centifolia waste biomass is shown in Table 3.1. The obtained results clearly indicated that the rose waste biomass is cellulosic in nature and have replaceable hydrogen, alkali and alkaline metals. Thus, it can be regarded as potential Mn and Fe adsorbent. The effect of different experimental parameters on Mn and Fe biosorption is described in detail below.

Table 3.1: The elemental and proximate composition of Rosa centifolia waste biomass

<table>
<thead>
<tr>
<th>Metal</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>0.10</td>
</tr>
<tr>
<td>K₂O</td>
<td>62.90</td>
</tr>
<tr>
<td>CaO</td>
<td>9.72</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>8.15</td>
</tr>
<tr>
<td>SO₃</td>
<td>6.52</td>
</tr>
<tr>
<td>S₂O₂</td>
<td>4.38</td>
</tr>
<tr>
<td>MgO</td>
<td>3.30</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.76</td>
</tr>
<tr>
<td>Cl</td>
<td>1.01</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.80</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.44</td>
</tr>
<tr>
<td>MnO</td>
<td>0.42</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.28</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.20</td>
</tr>
<tr>
<td>Rb₂O</td>
<td>0.13</td>
</tr>
</tbody>
</table>

3.1 FOURIER TRANSFORMS INFRARED (FTIR) STUDIES

FTIR analysis is an important analytical tool for determination of functional groups responsible for heavy metal removal by R. Centifolia. Figure 3.1 show the peak frequency of functional group that contain in R. Centifolia.

Figure 3.1: FTIR spectra of R. Centifolia waste biomass.
In order to determine the functional groups responsible for metal uptake, the FTIR was employed as an analytical [27]. Figure 3.1 shows the raw spectrum of waste biomass sample. The spectra indicate the presence of different functional groups which are responsible for metal sorption process for example carboxylic acids display a broad intense –OH stretching absorption from 3300 to 2500 cm$^{-1}$, amines (3393cm$^{-1}$), esters (1065cm$^{-1}$), and alkenyl (1628cm$^{-1}$). The peak observed at 2920.28cm$^{-1}$ are due to vibrations of OH and CO groups belonging to carboxylic acids. Nasir (2007) had pointed out that peak at position 2920.28cm$^{-1}$ shifts towards higher wave number, which indicates involvement of this group in removal metals. Ester groups in the biomass produce carboxylate, which can bind cations. Another study by Padmavathy (2003) further proved that the peak at 1065cm$^{-1}$ also shift towards higher wave number, which indicates involvement of this group in removal metals. It is shown that, chemical functional group in the biomass tends to interact with the metals ion, and it caused stretching, contraction and bending of its chemical bonds. It is expected that functional groups in R. Centifolia have high ability to absorb Fe and Mn.

### 3.2 EFFECT OF CONTACT TIME

The optimum contact time was determined based on the percentage removal efficiencies. The condition which had the highest removal efficiencies of Fe and Mn had been chosen as the optimum condition. Figures 3.2 shows the percentage removal of Fe and Mn at different contact times.

![Figure 3.2: Effect of contact time to the removal efficiencies of Fe and Mn](image)

From Figure 3.2 it was observed that the percentage removal of Fe and Mn ions by R. Centifolia increased with time and at 240min reached a constant value where no more removal increment were observed. At 240min the percentage removal of Fe is about 86.68% where for Mn the percentage removal is reached at 95.73%. At this point, the amount of metals being absorbed onto the biosorbent was in a state of dynamic equilibrium with the amount of absorb from the biosorbent [30]. The state of time required to attain this state of equilibrium was termed as the equilibrium time and the amount of metals absorbed at this equilibrium time reflected the maximum metals biosorption capacity of the biomass under the particular condition.

### 3.3 EFFECT OF BIOSORBENT DOSAGE

The optimum biosorbent dosage was also determined based on the percentage of the removal efficiencies. The condition which had the highest removal efficiencies of Fe and Mn had
been chosen as the optimum condition. Figures 3.3 show the percentage removal of Fe and Mn at different biosorbent dosage.

Figure 3.3: Effect of biosorbent dosage to the removal efficiencies of Fe and Mn

The results from Figure 3.3 shows that the maximum biosorption by immobilized R. Centifolia waste biomass occurred at 0.05 g/100 ml for both Fe and Mn. This shows that the maximum absorption occurs at minimum dose and hence the amount of metals bound to the absorbent and amount of free metals remained constant. After this dose, the uptake capacity (mg/100ml) of biosorbent was gradually decreased with increase in dose. Amount of biosorbent added to the solution determines the number of binding sites available for absorption. Similar results have been reported by Tariq (2010) and Bhatti (2007).

For effective metal sorption, biosorbent dose is a significant factor to be considered. It determines the sorbent–sorbate equilibrium of the system [25]. Moreover, as the biomass concentration rise, maximum biosorption capacity dropped, indicating poorer biomass utilization (lower efficiency). Results could be explained as a consequence of a partial aggregation, which occurred at high biomass concentration resulted to decrease of active sites.

3.4 EFFECT OF PH

Figures 3.4 shows the percentage removal of Fe and Mn at different pH value. From the graph it is shows that the higher the pH the higher the removal of Fe and Mn. Experiments concerning the effect of pH on sorption were carried out within pH range that was not influenced by metal precipitation (as metal hydroxide). The suitable pH ranges for two metal ions were slightly different like in the Figure 3.4 for Mn sorption were performed at the pH range of 1 to 5 and for Fe at pH of 1 to 6.

The biosorption of Mn and Fe on the R. Centifolia distillation sludge biomass was observed to be the function of solution pH. The pH is an important parameter in biosorption from aqueous solution because it influences equilibrium by affecting the speciation of the metal ions, solubility of the metal ions, concentration of counter ions on functional groups of the biomass and degree of ionization of the adsorbate during process (Say, 2003) and (Nadeem,2008). Percentage removal efficiency increased steadily with increasing pH. The most adequate sorption pH was 5 for Mn and 6 for Fe.
The increase in biosorption with increase in pH can be explained by the fact that at low pH, the biosorbent surface became more positively charged thus reducing attraction between the biomass and metal ions. These bonded active sites thereafter became saturated and was inaccessible to other cations [35]. Moreover, as the pH is increased, the ligands such as carboxyl, sulfhydryl, phosphate others groups would be exposed, increasing the negative charge density on the biomass surface, resulting in greater attraction between metallic ions and ligands [35].

### 3.5 BATCH REACTOR PERFORMANCE

From batch experiment the optimum condition result is analysed. The optimum condition for contact time is 240min while for biosorbent dosage optimum condition is 0.05g/100ml for both Fe and Mn. For pH value, the optimum condition for percentage removal of both Fe and Mn is different which pH 5 is for Mn and pH 6 for Fe. For this study, pH 5 was selected to be used as the optimum condition. Table 3.2 showed the percentage removal of all parameter compare with the NDWQS using the optimum condition of contact time, biosorbent dosage and pH range.

#### Table 3.2: Percentage removal of all parameters from optimum condition

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>Groundwater Sample Before</th>
<th>Groundwater Sample After</th>
<th>Percentage Removal (%)</th>
<th>National Drinking Water Quality Standard (NDWQS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>-</td>
<td>6.99</td>
<td>7.12</td>
<td>1.83</td>
<td>6.5-8.5</td>
</tr>
<tr>
<td>COD</td>
<td>mg/l</td>
<td>71</td>
<td>52.38</td>
<td>26.23</td>
<td>10</td>
</tr>
<tr>
<td>BOD</td>
<td>mg/l</td>
<td>52.99</td>
<td>32.28</td>
<td>39.08</td>
<td>1</td>
</tr>
<tr>
<td>TSS</td>
<td>mg/l</td>
<td>16.72</td>
<td>12.35</td>
<td>26.14</td>
<td>25</td>
</tr>
<tr>
<td>Nitrate</td>
<td>mg/l</td>
<td>5.1</td>
<td>26.4</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>Ammonia Nitrogen</td>
<td>mg/l</td>
<td>4.38</td>
<td>33</td>
<td>-</td>
<td>0.1</td>
</tr>
<tr>
<td>Fe</td>
<td>mg/l</td>
<td>2.37</td>
<td>0.009</td>
<td>99.55</td>
<td>0.3</td>
</tr>
<tr>
<td>Mn</td>
<td>mg/l</td>
<td>0.722</td>
<td>0.11</td>
<td>76.73</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Table 3.2 shows that the percentage removals of Fe is higher than percentage removal of Mn with the value of 99.62% and 82.78% for Fe and Mn respectively. Both Fe and Mn are complying with NDWQS [36]. The percentage removal for pH is about 1.83% while for TSS is 26.14%. Both pH and TSS results are comply with NDWQS. Other parameter namely, COD, BOD, Nitrate and Ammonia Nitrogen are higher than acceptable level following NDWQS [37]. These results indicate that biosorbent only effective in removing of inorganic in groundwater sample.

3.5.1 IRON (FE) REMOVAL

Iron (Fe) being the fourth most abundant element and second most abundant metal in the earth’s crust is a common constituent of groundwater [4,13]. According to the value in Figures 3.5, the influent data shows that Fe concentration in average 2.37mg/l. The high presence of iron in groundwater is generally attributed to the dissolution of iron bearing rocks and minerals, chiefly oxides (hematite, magnetite, limonite), sulphides, carbonates and silicates under anaerobic conditions in the presence of reducing agents like organic matter and hydrogen sulphide [39,40]. From Figure 3.5 the Fe concentration before the treatment is high compared to standard and it is out of the compliance range. After the treatment, the concentration of Fe is achieved the compliance range of the standard which is the Fe concentration is less than 1mg/l.

Figure 3.5: Average Iron (Fe) before and after treatment

Figure 3.6 shows that the percentage removal of Fe in this study was very high which is in average of 99.55%. According to Mubashir (2007) has obtained Pb (II) removals of 87.74% and Zn (II) with 73.8%. While Tariq (2010) has reported that Pb (II) removal is increasing to 95.67% by treating immobilized biomass with different chemical reagents (H2SO4, HCl and H3PO4). In this study, the results were in good agreement with previous researcher which is in the range of 70% to 88% ion metals removal [31].
3.5.2 MANGANESE (MN) REMOVAL

Mn is a transition element that rarely exceeds 0.1 milligram per liter (mg/L) in natural water. In most of all the collected water samples there is a slight excessive level of Mn, hence there is an oily taste. According to the value in Figures 3.7, the influent data shows that average value Mn concentration is 0.73mg/l. The high presence of Mn causes adverse health effects in fact, essential to the human diet. However, water containing excessive amounts of Mn can stain clothes, discolor plumbing fixtures, and sometimes add a "rusty" taste and look to the water [42]. The Mn concentration before the treatment is high compare to standard and it is out of the compliance range. After the treatment, the concentration of Mn achieved the compliance with the standard which is the Mn concentration which is less than 0.1mg/l.

Figure 3.8 shows that the percentage of Mn removal in this study is in average of 76.73%. The maximum percentage removal of Mn is 89.93% while the minimum percentage removal is
64.14%. According to previous studies, (Abdul, 2009) have obtained Cu (II) removals of 55.79% and Sayed (2010) have reported Cu (II) 71.24% of removal. In this study, the results were in good agreement with those determined by other researcher which is in the range of 50% to 75% of ion metals removal.

4.0 CONCLUSIONS

This study concluded that R. Centifolia is an effective biosorbent in ferum and mangan removal. The optimum condition of heavy metal removal was found to be at 240min contact time, pH 5 and 0.05g/100ml dosage of R. Centifolia. The highest amount of Fe and Mn removal are 99.55% and 76.73% respectively. In this study parameter such as Fe, Mn, COD, BOD, pH and TSS show a reduce trend after the treatment, while other parameter such as Nitrate and Nitrogen Ammonia show unpromising result. These result show that R. Centifolia is effective to treat inorganic in compare to organic pollutant. The results of Fe and Mn removal in groundwater show that R. Centifolia is a promising biosorbent. Almost all parameter tested using groundwater show that the groundwater is safe to be consumed after treatment process using biosorbent as it follow acceptable level following limit provided by World Health Organization [41].

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