The use of activated charcoal from corn cobs as adsorbent of heavy metals from groundwater

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Abstract
Iron (Fe) and manganese (Mn) are heavy metals which are found in high concentration in highly weathered soils, especially in the tropics, resulting in high content of them in groundwater. These metals cause a distinctive odor, reddish brown, yellowish color, and high sediment. This condition could cause health problems when it is used as a source of drinking water. This study was aimed to evaluate the efficiency of activated carbon from corn cobs in reducing the concentrations of Fe and Mn from groundwater adsorption. The adsorption process was performed by applying activated carbon with varying doses of 0.1 g, 0.2 g, 0.3 g, 0.4 g, 0.5 g, 1 g, 1.5 g and 2 g into 100 ml groundwater. Variations of pH were pH 2, pH 3, pH 4, pH 5, pH 6, pH 7 and pH 8, and variations in contact time of 10, 30, 45, 60, 90 and 120 minutes. The results showed that the optimum doses to reduce Fe and Mn concentration from groundwater were 1 g and 0.5 g with the adsorption efficiency of 70.14% and 41.60% respectively. The optimum pH for both Fe and Mn was pH 4 with an adsorption efficiency of 75.44% and 56.52% respectively, while the optimum contact times were 60 and 30 minutes with an adsorption efficiency of 75.44 and 59.29% respectively.

Keywords
Precision agriculture, Activated charcoal, Corn cobs, Adsorption, Heavy metal, Groundwater.

Introduction
Heavy metals such as Fe and Mn are components found in rocks and the earth's crust (García-Mendieta et al., 2009; Hua et al., 2012). In the tropics, highly weathered soils such as Ultisols, Inceptisols and Oxisols contain relatively high levels of heavy metals such as Fe and Mn (Effendi et al., 2015; Shamshuddin and Daud, 2011). Karamina et al., (2019) found the relatively high Fe content in an Ultisol soil at a depth of 0-30 cm and 30-60 cm, which was 62.68 and 83.21 ppm, respectively. In addition, Suhardiyono and Menry (2005), found that the Mn and Fe content in the soil was 22.50 to 59.50 ppm respectively. The relatively high content of Fe and Mn in these soils certainly affects the Fe and Mn content in the groundwater in these soils. Rainwater or groundwater that passes or seeps through soil or rocks containing Fe and Mn can dissolve Fe and Mn so that the Fe and Mn content in groundwater will increase. The quality of groundwater is influenced by the condition of the soil where the groundwater is located.

Groundwater often contains high concentrations of Fe and Mn and exceeds the established quality standards. High concentrations of Fe and Mn metal are often found in groundwater in various parts of the world (Carretero and Kruse, 2015; Weng et al., 2007; Zhai et al., 2021). The presence of Fe and Mn metal in considerable amounts is usually associated with poisoning. Exposure to heavy metals even in small concentrations poses a health risk to humans (Hua et al., 2012). Heavy metals are not degraded into harmless final forms but accumulate in the food chain, causing enormous harm to living organisms (Ucer et al., 2006). Heavy metal pollution has become a serious environmental problem today. Heavy metal poisoning can occur through contamination of drinking water and the food chain (Fu et al., 2011).

Water that contains high Fe and Mn has a characteristic odor, a yellowish brown or reddish-brown color and a sediment that causes high turbidity (Inglezakisa, et al., 2020; Rusydi et al., 2021). Groundwater is an important source of clean water for some people in Jambi City, Jambi Province, Indonesia. However, one of the main problems with using groundwater as a source of clean water is the high content of Fe and Mn. Reducing the content of Fe and Mn in groundwater...
must be done so that groundwater meets the quality standard as a source of clean water for drinking water.

The removal of heavy metals from the environment has already been a concern because of their persistence. Many technologies such as adsorption, precipitation, membrane filtration and ion exchange have been used to remove metal pollution from water (Immanuglu and Tekir, 2008). However, adsorption has been proven to be an economical and efficient way to remove polluted heavy metals from polluted water. Some adsorbents such as activated carbon, silica and graphene can be used for water purification (Immanuglu and Tekir, 2008). Activated carbon has been proven to be an efficient adsorbent for the removal of various inorganic and organic contaminants in the aquatic environment (Bhatnagar et al., 2013). This is due to its high surface area, well-developed porosity structure and the presence of a wide spectrum of surface functional groups so that it is able to distribute pollutants over a large internal surface and make it accessible to reactants (Liu et al., 2010).

Corn cobs are one of the most abundant agricultural wastes in the city of Jambi. The large amount of corn cobs waste has the potential to be used as a source of activated carbon. Corn cobs contain lignocellulose which consists of 45% cellulose, 35% hemicellulose and 15% lignin (Saha, 2003). Activated carbon from corn cobs has a wide specific surface (900-1300 m²g⁻¹) and can adsorb methane (Bagheri and Abedi, 2011). The use of materials that are relatively cheap and easy to obtain is urgently needed to overcome the problem of the availability of clean water for the community's drinking water sources. This study was aimed to evaluate the efficiency of activated carbon from corn cobs in reducing the content of heavy metals Fe and Mn from groundwater through the adsorption process.

Materials and methods

Water sampling

The water samples were collected from groundwater (shallow groundwater) in July 2020, located at Ibrahim Ripin Street, Mutiara Kenali Housing, Kenali Asam Bawah Sub district, Kota Baru District, Jambi City, Indonesia. The collection and preservation of samples were conducted in line with the Standard Methods for the Examination of Water and Wastewater (APHA, 2012). The reagents used included HNO₃, FeCl₃, 6H₂O, CuSO₄·5H₂O, MnCl₂·4H₂O, Pb (NO₃)₂, 0.1 N HCl solution.

Characteristics of groundwater

The content of Fe and Mn in groundwater were 12.74 and 0.53 mg/L, respectively (Table 1). These values exceed the environmental quality standard values of the maximum permissible concentration of Fe and Mn in clean water as a source of drinking water set by the Ministry of Health of the Republic of Indonesia No 32, 2017 which is 1 and 0.5 mg/L for Fe and Mn respectively. The high content of Fe and Mn in groundwater could come from Fe and Mn from the soil where the soil is classified as Ultisol. Ultisols are highly weathered soils that contain high levels of Fe and Mn (Nursyamis and Suryadi, 2000; Kusumaningtyas, et al., 2015; Herviyanti et al., 2011). Dissolution of Fe and Mn from soil by water causes high Fe and Mn content in groundwater.

<table>
<thead>
<tr>
<th>No</th>
<th>Variable</th>
<th>Unit</th>
<th>Value</th>
<th>Quality standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>pH</td>
<td>-</td>
<td>6.38</td>
<td>6.9</td>
</tr>
<tr>
<td>2.</td>
<td>Fe</td>
<td>mg/L</td>
<td>12.74</td>
<td>1</td>
</tr>
<tr>
<td>3.</td>
<td>Mn</td>
<td>mg/L</td>
<td>0.53</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Adsorbent preparation

Corn cobs were obtained from one of the roasted corn sellers in Jambi City. Corn cobs were washed with distilled water until they were free of impurities and dried. The corn cobs were then cut into small pieces using stainless cutters, and oven dried at 105°C until their weight was constant, then crushed using a grinder. The carbonization process was carried out by placing corn cobs into a porcelain dish and putting it in a furnace at a temperature of 300°C for 1.5 hours until carbon forms, which was indicated by no smoke formation. Then the porcelain plate was removed from the furnace until cool in a desiccator and sieved using a 100-mesh sieve. Carbon activation was carried out using a 4 M HCl solution. 50 g of carbon resulted from the carbonization process was activated by adding 500 ml of HCl 4 M solution into a beaker glass containing carbon, then stirred using a magnetic stirrer for 1 hour and left for 24 hours. Furthermore, the activated carbon was filtered using a vacuum filter with whatman filter paper with a diameter of 100 mm, then it was washed using distilled water until the neutral pH. The activated carbon was then dried in an oven at 110°C for 3 hours then cooled and stored in a desiccator.

Determination of characteristics of activated carbon

The surface morphology of the adsorbent was determined using Scanning Electron Microscopy-Energy Dispersive of X-ray Spectroscopy (SEM-EDS) at the SEM-EDS Petrology and Volcanology Laboratory of UPP Chevron Institut Teknologi Bandung (ITB). SEM testing was carried out at 1000X magnification. The functional groups present on the adsorbent surface were analyzed using Fourier Transform Infrared (FTIR)

Adsorption Experiment

Optimum Contact Dose

Determination of the optimum dose was aimed to determine the best dose of adsorbent in adsorbing Fe and Mn from groundwater. It was carried out by applying the activated carbon with different doses of 0.1 g, 0.2 g, 0.3 g, 0.4 g, 0.5 g, 1 g, 1.5 g and 2 g into each 100 ml of groundwater that has been adjusted to pH 5 in a 200 ml erlenmeyer. Then the mixture was stirred using a magnetic stirrer for 60 minutes with a stirring speed of 200 rpm. The mixture was filtered, and the filtrate was analyzed for determination of Fe and Mn with atomic absorption spectrophotometer (AAS). The percentage of Fe and Mn reduction was calculated using the following Equation (Kadir et al., 2014):
Optimizing the pH

For this determination, the optimum dose of activated carbon which had been obtained in the previous experiment was added into each 100 ml of groundwater with varying pH of pH 2, pH 3, pH 4, pH 5, pH 6, pH 7 and pH 8 in 200 ml erlenmeyer. The mixture was stirred using a magnetic stirrer for 60 minutes with a stirring speed of 200 rpm. Then the mixture was filtered, and the filtrate was analyzed to determine the Fe and Mn content with AAS.

Optimum contact time

Determination of the optimum contact time was aimed to determine the best contact time of the adsorbent in adsorbing Fe and Mn metal from water. It was done by applying the optimum dose of activated carbon obtained from the previous experiment into each 100 ml groundwater in each a 200 ml erlenmeyer with a variation of time of 10 minutes, 30 minutes, 45 minutes, 60 minutes, 90 minutes, and 120 minutes. Then the mixture was stirred using a magnetic stirrer for variations in contact time with a stirring speed of 200 rpm. The mixture was filtered, and the filtrate was analyzed for the determination of Fe with AAS.

Table 2. Chemical composition of corn cobs before and after activation with 4 M HCl

<table>
<thead>
<tr>
<th>No</th>
<th>Element</th>
<th>Carbon of corn cob Before activation (%)</th>
<th>After activation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>1</td>
<td>C</td>
<td>76.01</td>
<td>76.22</td>
</tr>
<tr>
<td>2</td>
<td>O</td>
<td>21.57</td>
<td>22.13</td>
</tr>
<tr>
<td>3</td>
<td>Na</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Al</td>
<td>0.06</td>
<td>0.13</td>
</tr>
<tr>
<td>5</td>
<td>Si</td>
<td>0.10</td>
<td>0.64</td>
</tr>
<tr>
<td>6</td>
<td>S</td>
<td>0.02</td>
<td>0.76</td>
</tr>
<tr>
<td>7</td>
<td>K</td>
<td>1.97</td>
<td>0.11</td>
</tr>
<tr>
<td>8</td>
<td>Ca</td>
<td>0.26</td>
<td>-</td>
</tr>
</tbody>
</table>

The characterization of carbon (before and after activation) using FT-IR is shown in Figure 2. There was a change in absorption intensity for several functional groups on charcoal before and after activation. The difference in absorption intensity in the wave numbers in the range of 2800 cm\(^{-1}\) - 2900 cm\(^{-1}\) indicated that the aliphatic carbon chain contained in the activated carbon increased after activation using a strong acid. The absorption peak in the area of 3100 cm\(^{-1}\) to 3300 cm\(^{-1}\) showed that the hydroxyl (O-H) functional group of the carboxylate also increased in intensity on the activated carbon. This was reinforced by the increase in the absorption intensity at the wave number of 1650 cm\(^{-1}\) - 1700 cm\(^{-1}\) which showed that the C = O functional group of the carboxylate compound was more significant. The increased carboxylate group

\[
\% \text{ Removal} = \frac{(C_0-C_f)}{C_0} \times 100
\]

Where:

- \(C_0\) = initial concentration of Fe or Mn (mg/l)
- \(C_f\) = final concentration of Fe or Mn (mg/l)

Optimum pH

The results of the energy dispersive X-ray spectroscopy (EDX) analysis showing the composition of the elements of corn cob carbon before and after activation are presented in Table 2. The activation process significantly increases the carbon element from 76.01% to 76.22%. After the activation process, the remaining chemical compositions are only C, O, Al, Si, S and K, while the Na and Ca elements have been lost. The activation with 4 M HCl causes the impurity elements such as Na and Ca to dissolve. The lost impurities indicate that the pores of carbon produced after the activation process are no longer covered, resulting in a larger pore morphology. The elemental component becomes more concentrated during the carbon activation process. Chemicals such as HCl, H\(_2\)SO\(_4\) and others that are used in the activation process could increase the efficiency of activated carbon adsorption (Ullah et al., 2020).

Figure 1. Morphological characteristics of carbon before activation (a) and after activation (b).
absorption indicated that the lignocellulose breakdown process occurred optimally due to the chemical activation. The termination of lignocellulose bonds (delignification) produces carboxylate groups that can increase the performance of the adsorbent in binding metals during the adsorption process (Abdolali, et al. 2015; Lasheen, et al. 2012). The absorption band above 3500 cm$^{-1}$ indicated free hydroxyl (O-H) of the phenol groups in lignin and the hydroxyl groups in cellulose which were reduced due to chemical activation.

The char activation process using strong acids in this experiment resulted in the breakdown of several aromatic C-H bonds along with free hydroxyl groups which strengthened carboxylate functional groups and increased aliphatic and aromatic fixed carbon as shown in other studies (Demira and Güngor, 2016). Functional groups such as carboxylates (COO$^-$) play a role in increasing the adsorption of metals in water. The negative charge of carboxylates (COO$^-$) increases the availability of surface-active agents that can interact with the positive charge of metal ions (Feng and Guo, 2012; Demira and Güngor, 2016).

![Figure 2. FT-IR spectra of carbon from corn cobs before and after activation.](image-url)

**Figure 2.** FT-IR spectra of carbon from corn cobs before and after activation.

**Determination of the optimum dose of the adsorbent**

The effect of adsorbent dose on the removal of Fe and Mn is presented in Figure 3. The removal of Fe increased with the increasing dose of adsorbent. The removal efficiency of Fe increased rapidly at doses of 0.1 g to 1 g with an increase in removal efficiency from 59.40% to 70.14%. At doses of 1.5 g and 2 g there was still an increase in removal efficiency but was very small, namely 70.76 and 70.97%. This means that the optimum dose of adsorbent for Fe absorption was 1 g. In addition, the optimum dose for adsorbing Mn metal was 0.5 grams with an efficiency of 41.6%. The efficiency decreased with increasing adsorbent dose indicated that the number of ions in the solution adsorbed by activated carbon increases with the increasing number of adsorbents in the system. This occurs due to the presence of a larger surface area with a higher number of functional groups on the surface of the activated carbon (Demira and Güngor, 2016).

The increasing adsorbent doses will cause the number of particles, surface area, and empty pore space to increase so that the metals that are adsorbed in the pore increases. However, the addition of adsorbent showed the amount of adsorbed metal tended to remain constant. This showed that the increase of adsorbent doses had no significant effect on the increase of metal adsorption because the adsorbent reached a saturated state and an equilibrium phase. In addition, the desorption process occurs due to the saturated surface of the adsorbent. The higher dose of adsorbent could cause thickening of the solution so that it was difficult to contact the adsorbent and adsorbate (Ullah et al., 2020).
Determination of the optimum contact pH

The effect of pH on Fe removal in groundwater by activated carbon on corn cobs is presented in Figure 4. It could be seen that the optimum pH for adsorbing Fe metal by activated carbon on corn cobs in groundwater was pH 4. At pH 4 the final concentration of Fe was 2.79 mg/L with an efficiency of 75.44%. This showed that under acidic conditions, at pH 4 the activated carbon has the highest adsorption efficiency. At lower pH, namely pH 2 and 3, the adsorption efficiency value was lower than pH 4. Likewise, at higher pH, namely pH 5, 6, 7 and 8, the adsorption efficiency was lower than pH 4.

Figure 5 shows that the optimum pH for adsorbing Mn metal by activated carbon from corn cobs in groundwater was at pH 4 with a removal efficiency of 56.52% and the final Mn concentration of 0.22 mg/L. At a lower pH, namely pH 2 and 3, the removal efficiency value was lower than pH 4. Likewise, at a higher pH, namely pH 5, 6, 7 and 8, the removal efficiency was lower than pH 4.

An increase in pH or a decrease in pH to more or less than pH 4 caused a decrease in the efficiency of Fe and Mn adsorption, because at low pH (acidic), namely pH 2 and 3 it contains high H⁺ protons. High H⁺ concentrations in solution compete with metal ions such as Fe and Mn for active sorption sites so that adsorption decreases (Boudrahem et al., 2009). When the pH increases, the number of places that are positively charged decreases and the number of negative charges increases, thereby increasing the adsorption of metal ions (Srivastava et al., 2008). When the pH increases, there is a decrease in the concentration of H⁺ ions so that the negative charge on the adsorbent surface increases. This condition causes an increase in metal ion adsorption and removal efficiency. However, when the pH increases, the increasing number of OH⁻ (hydroxyl) ions in the solution reacts with Fe and Mn ions to form insoluble Fe and Mn hydroxide compounds (precipitates) and causes a decrease in the adsorption rate (Huang et al., 2017).

Determination of the Optimum Contact Time

The adsorption of Fe and Mn was carried out at various contact times (10, 30, 45, 60, 90, 120 minutes) using optimum doses of 1 g and 0.5 g for Fe and Mn respectively with pH 4 as the optimum pH. The effect of contact time on Fe and Mn adsorption is presented in Figure 6 and 7 respectively. The initial stage showed that the adsorption of Fe and Mn by activated carbon increased rapidly with increasing time and reached equilibrium at 60 minutes and 30 minutes respectively. Then the adsorption of Fe decreased at 70 to 120 minutes, while for the Mn, it decreased at 49 to 120 minutes. The adsorption efficiency of Fe and Mn were 75.44% and 59.29% respectively. In the early stages there are a large number of places on the surface empty for the adsorption and over time the empty places on the surface are difficult to occupy because of the resistance between the adsorbate molecules present on the solid surface and in the liquid phase. (Boudrahem et al., 2009). The adsorption of metal ions increases with increasing time until equilibrium is reached between the dissolved molecules in the liquid and solid phases (Srivastava et al., 2008). The longer the contact time, the greater the interaction between the adsorbent and the metal ions such as Fe³⁺ ion or Mn²⁺ so that more Fe³⁺ ions or Mn²⁺ are adsorbed by the adsorbent through the ion exchange reaction with H⁺ ions (Ullah et al., 2020).
Conclusions

Chemical functional groups contained in activated corn cobs carbon consist of hydroxyl (O–H), carbonyl (C = O), aromatic (C–C) and aliphatic (C–H). The optimum dose, pH and contact time for the adsorption of Fe metal from shallow groundwater (well water) by activated corncob carbon were 1 gram, pH 4 and 60 minutes with the adsorption efficiency of 70.14%, 75.44% and 75.44% respectively, while for the adsorption of Mn, the optimum dose, pH and contact time were 0.5 gram, pH 4 and 30 minutes with the adsorption efficiency of 41.6%, 56.52% and 59.23% respectively.

References


