Removal of Fe (II) in groundwater using rice husk-sourced biosorbent in continuous column adsorption

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Abstract. Ferrous is one of the groundwater contaminants that negatively impacts health and the environment. The allowed ferrous content is < 1 ppm in water for daily use. Removal of Fe in groundwater by adsorption using low-cost bio-sorbent from rice husk has been conducted. The process was carried out in continuous mode using two types of rice husk-sourced adsorbents, one was only carbonated at 400 °C and another was followed by a physical activation at 650 °C. To study the effects of physical activation on the surface characteristics, both types of bio-sorbents were characterized by Scanning Electron Microscope and Fourier-transform infrared spectroscopy. The concentration of artificial sample before and after adsorption was evaluated using the Atomic Absorption Spectroscopy. From the results, the adsorption using physically activated sorbent had greater removal efficiency of 74.02% compared to that of without activation treatment, which was only 65.70%. In addition, the concentration of ferrous was successfully reduced to 1,029 and 0.779 ppm from the initial concentration of 3 ppm for the process using the adsorbent without and with activation, respectively. It can be concluded that the physically activated rice husk has the potential to be used for adsorption of Ferrous in continuous column.

1. Introduction

Groundwater is water which sourced from a stream that naturally flows below the surface of the ground [1]. Groundwater is one of the potential sources of raw water that can be utilized by the community for drinking water and other needs [2,3]. However, groundwater cannot be directly consumed by the community due to the high content of contaminants such as heavy metals exceeding the quality standards set by the government [4]. The exceeding concentration of iron (Fe) in water will cause various problems such as technical disturbances such as polluting the tub, sink, toilet, corrosive to the pipe which causes rocking, and physical issues like change of colour, smell, and taste of water [5].

Based on the Regulation of the Minister of Health of the Republic of Indonesia Number 32 year 2017 concerning environmental health, the allowed Fe level in water for sanitation and public bathing is 1 mg/l. Whereas, according to the Regulation of the Minister of Health Number 492 in 2010, the permitted level of Fe is 0.3 mg/L. Therefore, water treatment is needed to reduce the level of Fe in water to meet the quality standard. Adsorption is one of effective water treatment processes which is frequently used to remove heavy metals [6].
Removal of water contaminants by adsorption process involves the use of adsorbent. One of the many materials that can be utilized as activated carbon (adsorbent) is biomass [7-9]. Biomass is the material which sourced from living things like parts of plants or waste [10]. Adsorbents which sourced from the natural source have been widely used and reported to have good sorption performance [11,12].

Rice husk is a lignocellulose biomass consisting of lignin, cellulose, and hemicellulose. Lignin is the main component that forms charcoal, which is useful for the adsorption process [13,14]. Rice husk contains about 32% of cellulose, 21% hemicellulose, 21% lignin, 20% silica and 3% protein [15].

So far, rice husk sourced carbon has been widely used as an adsorbent, but from the previous literature, the use of rice husk adsorbent was reported mostly in batch system adsorption processes. Therefore, in this study rice husk is utilized as an adsorbent for the adsorption process in a continuous reactor system. This study aims to investigate the effects of physical activation on the characteristics and performance of rice husk biosorbent. Biosorbent characterization is carried out to analyse the chemical composition and morphology. In addition, the efficiency and absorption performance of the prepared biosorbent are studied for Fe removal process in a continuous system.

2. Experimental methods

2.1. Rice husk preparation and carbonation
Rice husk was obtained from a rice mill in the Aceh Besar area. Firstly, the rice husk was washed to remove the remaining dirt and then dried in the oven for 24 hours at 80 °C to reduce the water content. After that, the rice husk was carbonated in the furnace by pyrolysis at 400 °C for 1.5 hours. After carbonation, rice husk carbon was crushed to 20-80 mesh.

2.2. Physical activation of rice husk
Preparation of activated rice husk carbon was almost similar to that of the non-activated carbon. The rice husk material was firstly cleaned and dried at 80 °C for 24 hours. Following that, the carbonation process was conducted at 400 °C for 30 minutes and followed by physical activation process by pyrolysis technique at a temperature of 650 °C for 1.5 hours. Then the activated carbon crushed to the smaller size of about 20-80 mesh.

2.3. Adsorption process
The adsorption process was carried out using Fe solution with a concentration of 3 ppm as an artificial sample and 30 gram of adsorbent. The process was conducted in a continuous reactor with a column diameter of 5.4 cm and a column height of 40 cm. The sample was flowed into the vertical column using a centrifugal pump at a flowrate of 1 L/minute.

![Figure 1. Adsorption column.](image-url)
3. Results and discussions

3.1. Characteristic of rice husk carbon
To investigate the effect of physical activation on the chemical composition of rice husk adsorbent, IR analysis was carried out by means of Fourier-transform infrared spectroscopy (FTIR) instrument and results are presented in Fig. 2. From the IR results, it is seen that there is a significant change in the chemical composition of rice husk carbon with and without activation. This change can be observed from the disappearance of some peaks at a wavenumber of 817, 972, 1456, 1698 and 3647 cm\(^{-1}\) on the activated carbon. These peaks are indicators for C-H, C = C, C = O, and OH functional groups which are organic impurities from rice husk material. The disappearance of those groups is due to the removal of impurities at high temperatures in the physical activation process carried out by pyrolysis technique at a temperature of 650 °C.

![Figure 2. IR Spectra of non-activated rice husk carbon (K-O) and physically activated rice husk carbon (K-F).](image)

3.2. Morphology structure
The effect of physical activation on the adsorbent is also studied in terms of morphological structure using microphotograph from scanning electron microscopy (SEM) analysis as shown in Fig. 3.

![Figure 3. SEM microphotograph of (a) Rice husk carbon without activation, and (b) Rice husk carbon with physical activation.](image)
In general, Fig. 3 shows that the rice husk carbon has a rough surface with pore in irregular size. Fig. 3(a) shows that the non-activated rice husk carbon has a smaller pore size than that of rice husk carbon with physical activation as presented in Fig. 3(b). The formation and enlargement of the pore are caused by evaporation of degraded cellulose component and the release by flying substances. Therefore, the carbon with physical activation has clearer surface due to the reduction of hydrocarbon compounds. It is reported that the activation process enlarges the pore by breaking the hydrocarbon bonds or oxidizing surface molecules which leads to improved surface area and adsorption capacity. The porous structure is formed from evaporation and dissolution of non-carbon compounds contained in the raw material caused by the pyrolysis process [16].

3.3. Ferrous adsorption efficiency by rice husk adsorbent

For the performance test, the rice husk adsorbent without and with physical activation was applied in the adsorption process of Fe in water. The adsorption experiment was carried out in a continuous system reactor using 3 ppm Fe solution sample and 50 gram of adsorbent with an operating time of 3 hours, the results are given in Table 1.

Table 1. Data on the efficiency of Fe adsorption using rice husk carbon without and with activation.

| Sampling time (minutes) | Without Activation (ppm) | Sorption Efficiency | Physical Activation (ppm) | Sorption Efficiency |
|-------------------------|--------------------------|---------------------|--------------------------|---------------------|
| 20                      | 1,356                    | 54.81%              | 1,085                    | 63.84%              |
| 40                      | 1,342                    | 55.25%              | 1,050                    | 64.99%              |
| 60                      | 1,084                    | 63.84%              | 0.852                    | 71.61%              |
| 80                      | 1,074                    | 64.18%              | 0.927                    | 69.10%              |
| 100                     | 1,070                    | 64.31%              | 0.896                    | 70.15%              |
| 120                     | 1,064                    | 64.52%              | 0.893                    | 70.25%              |
| 180                     | 1,028                    | 65.70%              | 0.779                    | 74.02%              |

Based on the results given in Table 1, the reduction of Fe content is seen in the first 20 minutes operation for both types of rice husk carbon. In the first 20 minutes of adsorption using rice husk carbon without activation, the level of Fe is reduced from 3 ppm to 1,356 ppm, meanwhile, by using activated rice husk carbon, the reduction of Fe level is slightly higher (1,085 ppm) at the same operating time. As for absorption efficiency, carbon rice husk with physical activation shows a higher efficiency of 74.02% compared to that of without activation of only 65.70%. After 180 minutes of the adsorption process, the level of Fe in the sample is reduced down to 0.779 ppm and 1.028 ppm for adsorbent with activation and without activation, respectively. These results confirmed that physical activation causes rice husk carbon to have higher efficiency in reducing Fe content due to larger pores compared to the rice husk carbon without activation.

4. Conclusion

From the obtained results, it can be concluded that the rice husk carbon has potential as an adsorbent in the removal of Fe in continuous adsorption system. The level of Fe in water has been successfully reduced from 3 ppm to 1.028 and 0.779 ppm by a process using non-activated and physically activated rice husk carbon, respectively. Adsorption process using activated rice husk carbon shows better absorption efficiency compared to using rice husk carbon without activation, which is 74% and 65%, respectively. The overall excellent sorption performance of the activated carbon is due to enlargement of surface pores which provides a larger contact area.
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