Test The Effectiveness and Characterization of Quartz Sand/Coconut Shell Charcoal Composite as Adsorbent of Manganese Heavy Metal

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Abstract. The research on the effectiveness and characterization of quartz sand/coconut shell charcoal composite as adsorbent of Manganese (Mn) heavy metal has carried out. Quartz sand was previously activated by using Na₂CO₃ while the coconut shell charcoal was activated by using HCl 4 M. The adsorbent characterization was carried out by Fourier Transform Infrared Analyzer (FTIR), X-Ray Diffraction (XRD), Scanning Electron Microscopy-mapping Energy Dispersive X-Ray (SEM-EDX), and Surface Area Analyzer (SAA). The adsorption experiment of the Mn metal was carried out by varying the composition of quartz sand/coconut shell charcoal. The variations were in the number of 100:0, 0:100, 25:75, 50:50, 75:25 (b/b) at the degree of pH 1-6 and contact time 10, 15, 20, 30, 45, 60, 75, and 90 minutes by using batch method. The measurement of final concentration at the equilibrium phase was carried out by using AAS. The optimum adsorption condition of the Mn metal occurred in the comparison of quartz sand/coconut shell charcoal 50:50 (b/b), the best condition at the degree of pH 5, contact time during 30 minutes with adsorption capacity of 0.56 mg/gram. The type of adsorption isotherm of composite quartz sand/coconut shell charcoal adsorbent towards the metal of Mn followed the Freundlich isotherm theory.

1. Introduction

Water is generally sourced from ground water and naturally contains inorganic elements, such as ferrous metal (Fe), manganese (Mn), zinc (Zn), lead (Pb) and so on. Mn is an essential heavy metal, where its presence in certain levels is needed by the human body, but in excessive levels can cause toxic effects. In drinking water, the allowable manganese level is 0.4 mg/L [1]. According to Purwonugroho research (2013) [2] the Mn content in ground water reaches 0.8 mg/L. Mn in water can cause turbidity, corrosion and hardness. Mn also causes a yellowish tint on the laundry. Manganese can cause toxic effects in the human body if the concentration is too high. The Mn effect mainly occurs in the respiratory tract and brain. Symptoms of Mn poisoning are hallucinations, forgetfulness and nerve damage. Mn can also cause Parkinson's disease, lung disease and bronchitis. Prolonged exposure to manganese can cause impotence [3]. If Mn metal is absorbed by the body it will be difficult to excrete, as well as if contaminated in the eating environment will be difficult to clean. Therefore, the presence of Mn metal needs to be minimized or even eliminated.

Many methods have been developed to reduce levels of heavy metals from water bodies, one of which is the adsorption method [4]. Adsorption is a relatively simple method, the preparation process is simple, the cost is relatively cheap, efficient, can be done at low concentrations and can use natural adsorbents [5]. Adsorbents that are often used in adsorption include zeolites, natural allophane, chitin, chitosan, biosorbents from algal species, fly ash, activated carbon and cellulose [6]. Coconut shell can be used as an
adsorbent because of the availability of abundant coconut shell and is a good adsorbent for purification, removing color, odor, dechlorination, detoxification, filtering, separation and can be used as a catalyst [7]. Coconut shell charcoal also has hydroxyl and carboxyl active groups which influence the adsorption process [8]. Rahmawati and Dony (2016) [9] used activated coconut shell charcoal to adsorb Fe, Mn and Al metals in water up to 20%. Quartz sand has active groups of silanol (Si-OH) and siloxan (Si-O-Si) so that quartz sand can be used as a manganese metal adsorbent (Mn). Quartz sand can be used as an adsorbent as previously reported research which shows quite good efficiency. Lindasari et al (2017) [10] conducted a study on the adsorption of chloride ions in water using quartz sand and had an adsorption capacity of 0.2711 mg/g. However, an adsorbent without pre-treatment if applied as an adsorbent gives less than optimal results. Therefore, this research is conducted to increase the activity of adsorbent.

In this research, in addition to activation, physical mixing of quartz sand and coconut shell charcoal is also carried out so that quartz sand/coconut shell charcoal will be formed. The merger will add active groups to the adsorbent and increase the surface area of the adsorbent so that it is expected to optimize the performance of the composite of quartz sand/coconut shell charcoal in absorbing the metal of Mn.

2. Materials and Methods
2.1. Materials
Quartz sand, coconut shell, distilled water, Mn 1000 ppm mother solution, HCl p.a (Merck), concentrated HNO$_3$ p.a (Merck), Na$_2$CO$_3$ p.a (Merck), ammonia p.a (Merck).

2.2. Preparation of Adsorbent
Quartz sand is cleaned of impurities, sifted and finely ground. After smooth, proceed with sifting using 150 mesh sieve. Then wash with 0.1 M HNO$_3$ while stirring with a magnetic stirrer for 1 hour. Washing is done 3 times and dried by aerated [11]. Coconut shell is cut into small pieces, washed 3 times, dried in the sun, purified with 400 ºC for 1 hour, grinded and sieved using a 150 mesh size sieve [12]. The quartz sand powder and coconut shell which has dried then are identified.

2.3. Adsorbent Activation
Chemical activation is carried out for quartz sand, 165 grams of quartz sand and 135 grams of sodium bicarbonate are mixed and the mixing process is carried out evenly. Then put in a crucible and then heated to a temperature of 1100 ºC for 2 hours. Then the melt is cooled and crushed into powder [13]. Then for the coconut shell, as much as 50 grams of coconut shell soaked with 100 mL of 4 M HCl solution for 24 hours, then filtered and washed with distilled water. The activated carbon produced is then dried in an oven at 110 ºC for 3 hours, then cooled in a desiccators [14]. The activated adsorbent is then characterized by FTIR, XRD, SAA and a specific total acidity test.

The next step is to make variations in the composition of the adsorbent between quartz sand and coconut shell charcoal, which are 25:75, 50:50, and 75:25 (w/w). Mixing each variation of the composition was carried out using stirring for 1 hour. Then after being filtered the solid phase is washed with distilled water. Furthermore, the resulting composition is heated at a temperature of 105 ºC for 4 hours. The dry, solid phase is then crushed with a mortar and sieved with another 150 mesh sieve.

2.4. Adsorbent Effectiveness Test
Optimization of the composition of the adsorbent is done by as much as 0.1 gram of composite quartz sand / coconut shell charcoal with variations in the composition of 100: 0, 75:25, 50:50, 25:75 and 0: 100 (w/w) mixed with 10 mL of solution Mn 6 ppm with pH 5. The solution is stirred for 60 minutes at a constant speed at room temperature. The composite was filtered with Whatman No. filter paper. Filtrate is measured by AAS. The pH optimization of the solution was carried out by as much as 0.1 gram
3. Result and discussion

3.1. Identification of Adsorbent

3.1.1. FTIR Characterization

FTIR characterization is used to determine the functional groups found in raw materials. The results of FTIR analysis of coconut shell charcoal showed the presence of hydroxyl and carboxyl active groups while the results of quartz sand analysis showed the presence of silanol and siloxane active groups. These active groups can be used as adsorbents. FTIR spectra of coconut shell charcoal and quartz sand are shown in Figure 1. Data on functional group analysis is shown in Table 1.

![FTIR spectra of coconut shell charcoal (a) and quartz sand (b)]

Figure 1. FTIR spectra of coconut shell charcoal (a) and quartz sand (b)

of quartz sand/coconut shell charcoal composite at an optimal composition mixed with 10 mL of 6 ppm Mn solution using a buffer variation of pH 1, 2, 3, 4, 5, and 6. The solution was stirred for 60 minutes at a constant speed at room temperature. The composite was filtered with Whatman No. filter paper. Filtrate is measured using AAS.

2.5. Determination of Adsorption Isotherms

There are 0.1 gram of composite quartz sand/coconut shell charcoal at optimum conditions was added with a solution of Mn 2, 4, 6, 8, 10 and 12 ppm as much as 10 mL then stirring with the maximum contact time at room temperature. The adsorption results were filtered with Whatman No. filter paper. Filtrate is measured using AAS. The results obtained were then analyzed by the Langmuir and Freundlich isotherms.
| No | Functional Group | Reference | Wavelength (cm\(^{-1}\)) | Coconut shell charcoal | Quartz sand |
|----|------------------|-----------|--------------------------|------------------------|-------------|
| 1  | O-H              | 3550-2000\([15]\) | 3421                     | 3436                   |             |
| 2  | H-O-H            | 1641\([16]\)             | -                        | 1635; 1437          |             |
| 3  | C=O              | 1705\([8]\)             | 1705                     | -                     |             |
| 4  | C≡C              | 1589\([8]\)             | 1576                     | -                     |             |
| 5  | C-O              | 1300-800\([8]\)         | 914; 1037                | -                     |             |
| 6  | Si-O-Si asymmetric strech | 1076\([17]\)       | -                        | 1022                  |             |
| 7  | Si-O-Si symmetric strech | 771\([17]\)             | -                        | 758                   |             |
| 8  | O-Si-O           | 461\([18]\)             | -                        | 446                   |             |

### 3.1.2. XRD Characterization

XRD characterization was used to determine the mineral content of coconut shell charcoal and quartz sand. The results of XRD analysis showed that coconut shell charcoal contains cristobalite (C), fayalite (F) and manganoan (M) minerals while quartz sand contains quartz minerals (Q). XRD diffractogram is shown in Figure 2.

![Figure 2. XRD diffractograms of coconut shell charcoal (a) and quartz sand (b)](image-url)
3.1.3. **Surface Area and Acidity Analysis**

The surface area will provide an area on the surface of the adsorbent so that the Mn metal can be adsorbed. The specific total acidity analysis aims to show the presence of active sites on the surface of the adsorbent and determine the effect of acidity on the adsorption capacity. More acidic sites indicate that the adsorbent has more active sites so that it will make it easier for the adsorbent to interact with the Mn metal in the adsorption process. The more active sites on the adsorbent, the more likely the adsorption capability will be. The results of surface area and acidity analysis of coconut shell charcoal and quartz sand are shown in Table 2.

| Sample    | Surface area (m²/g) | Acidity (mmol/g) |
|-----------|---------------------|------------------|
| charcoal  | 51,420              | 7,647            |
| quartz    | 17,458              | 9,882            |

3.2. **Adsorbent Effectiveness Test**

3.2.1. **Optimization of Adsorbent Composition**

Optimization of the adsorbent composition was carried out on a comparison of the composition of quartz sand composites: coconut shell charcoal 100: 0, 0: 100, 25:75, 50:50 and 75:25 (w/w). The optimum composition of quartz sand/coconut shell charcoal adsorbent composites is at a ratio of 50:50 (w/w) with an adsorption capacity of 0.573 mg/g and an absorption percentage of 97.02%. These results indicate that the composite of quartz/coconut shell charcoal with a ratio of 50:50 (w/w) supports each other to form more active sites and increase the surface area so that they are able to absorb Mn metals maximally.

3.2.2. **Optimization of pH Conditions**

Optimization of pH conditions aims to determine the optimum pH conditions in Mn metal adsorption. In this study the optimum pH of Mn solution was obtained at pH 5 with an adsorption capacity of 0.556 mg/g and an adsorption percentage of 94.59%. At pH 5 the H⁺ ions contained in the solution are relatively small so that the active group of adsorbent binds more easily to the metal Mn.

3.2.3. **Contact Time Optimization**

The optimum contact time of Mn metal adsorption occurred at 30 minutes contact time with adsorption capacity of 0.56 mg/g and the percentage of adsorption of 94.22%. The longer the contact time of the solution with the adsorbent, the greater the adsorption capacity. However, if the contact time is sufficient, the adsorption capacity will be stable.
3.3. Characterization of Adsorbent Composites Before and After Adsorption

3.3.1. FTIR Characterization

FTIR spectra of adsorbents before and after adsorption are shown in Figure 3.

![Figure 3. FTIR spectra of composite before and after adsorption](image)

FTIR analysis aims to determine the possibility of interaction between the active group on the adsorbent with Mn metal after the adsorption process. The possibility of this interaction can be seen by the shift of the wave numbers in the FTIR spectra. Active groups such as Si-OH /-COOH will interact with Mn metals to form Si-O-Mn /-COO-Mn. A lower wave number shift indicates that the bond strength decreases while a higher wave number shift indicates an increase in bond strength.

3.3.2. SEM-EDX characterization

The SEM test results are shown in Figure 4 while the EDX test results are shown in Table 3. The appearance of the adsorbent surface before adsorption tends to have many open pores that allow Mn metal to fill the empty space on the surface of the adsorbent. After the adsorption process, the pores on the surface of the adsorbent are more closed which is possible because it is covered by Mn metal. The EDX test results of adsorbent composites after adsorption contained more Mn content than before adsorption that is equal to 1.2% which proves that the adsorbent composites are capable of absorbing Mn.
3.4. Determination of Adsorption Isotherms

The adsorption isotherm curve is shown in Figure 5. Based on the isotherm curve, shows that the $R^2$ value for the Langmuir isotherm is 0.935 with an adsorption capacity of 0.304 mg/g while the $R^2$ value on the Freundlich isotherm is 0.994 with an adsorption capacity of 0.661 mg/g. The process of adsorption between Mn metal with quartz sand/coconut shell charcoal composites follows Langmuir and Freundlich isotherm models because the $R^2$ values are equally close to 1. However the Mn metal adsorption capacity is greater in the Freundlich isotherm, so it can be concluded that the adsorption of Mn metal by composite quartz sand/coconut shell charcoal is more dominant in the Freundlich isotherm. The Freundlich isotherm shows that the adsorption process between adsorbents and adsorbates occurs physically through the van der Waals force. Mn metal which has a positive charge will interact with O atoms in the negatively charged Si-OH group so that the distance between Mn ions and O atoms is closer due to dipoles. The interaction between adsorbent and adsorbate occurs by the way Mn metal attaches to the pores of the adsorbent with weak binding energy through van der Waals forces. The existence of a weak pulling force causes the adsorbate to move from one part of the surface to another part of the surface of the adsorbent so that it can form a multilayer.

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**Figure 4.** Composite morphology adsorbent quartz sand/ coconut shell charcoal 50:50 (w/w) before adsorption (a) and after adsorption (b)

**Table 3.** Content of elements in composite adsorbent

| No  | Adsorbent                              | Si  | C    | O    | Mn |
|-----|----------------------------------------|-----|------|------|----|
| 1   | Quartz sand/ coconut shell charcoal composite before adsorption | 9.3 | 38.7 | 46.9 | 0.1 |
| 2   | Quartz sand/ coconut shell charcoal composite after adsorption | 12.6 | 31.6 | 31.6 | 1.2 |

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4. Conclusion

The results of adsorbent characterization showed the presence of active groups which indicated that the adsorbent was able to absorb Mn metal. The quartz sand/coconut shell charcoal adsorbent composite can adsorb Mn metal with the composition of quartz sand/coconut shell charcoal 50:50 (w/w), the best conditions at pH 5, contact time for 30 minutes with adsorption capacity of 0.56 mg/g and the adsorption percentage of 94.22%. Type of adsorption isotherm composite of quartz sand/coconut shell charcoal adsorbent on Mn metal is more dominant in Freundlich isotherm with adsorption capacity of 0.661 mg/g.

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