Removal of Mn (II) from aqueous environment using *Eucheuma spinosum*

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Abstract. *Eucheuma spinosum* is one of the seaweed species that can be found abundantly in Takalar Regency. The biomass of this seaweed has been used to remove Mn (II) ion from the aqueous solution via the adsorption process using *E. spinosum*. The adsorption of Mn (II) ion was studied in various contact time, pH and concentration. An Atomic Absorption Spectrophotometer (AAS) was an instrument used to determine the amount of ion before and after adsorption. Langmuir and Freundlich's equations were used to study the adsorption isotherms of the ion. The results showed that the optimum time obtained was 20 minutes and the optimum pH was 4. The Freundlich isotherm fitted the adsorption of ion Mn (II) using *E. spinosum* with the capacity (Qo) of 4.13 mg/g. The functional group involved in biosorption of Mn (II) metal ions was hydroxyl (-OH) groups.

1. Introduction

Currently, water is a problem that needs serious attention, the quality of water sources has recently declined. This is indicated by the reduced availability of clean water that is able to meet human needs. Water that complies with certain standards is now becoming an expensive item because water has been polluted by various wastes from various products' human activity [1].

Some causes of water pollution include material pollutants such as household waste, industrial waste, hospital waste, dams, etc. examples of water pollution that often occurs today are heavy metal water pollution. One heavy metal which is a pollution source and needs to be removed in waters is manganese metal (Mn) [1]. Manganese can come from mining waste, as well as factories textile processing and alloy making.

Manganese is a heavy metal needed by the body that can become toxic to humans if the metal is in high concentrations in the body [2]. In small amounts, manganese does not cause health problems but in large quantities, this metal can accumulate in the liver and kidneys. According to the World Human Organization [3], the maximum concentration of manganese in drinking water is 0.05 mg L⁻¹. According to Yuliani [4], manganese in high concentrations can cause toxicity such as psychiatric disorders, abusive treatment, hallucinations, forgetfulness and symptoms of brain abnormalities. Therefore, the presence of manganese in water must be reduced to overcome their effects on the environment and healthy humans.

Several methods can be used to reduce pollution heavy metals in waters are chemical and biological methods. The chemical method costly compared to biological methods. Election biological methods are based on the ability to live things and biomaterials to adsorb heavy metal ions, this method is called biosorption.
Various biomaterials derived from microorganisms such as bacteria, yeast, algae, and fungi have now been used successfully as bio-sorbents for remove heavy metals, including the fungus \textit{Saccharomyces cerevisiae}, \textit{Pseudomonas aeruginosa}, \textit{P. putida}, and \textit{K. pneumonia}, and coral algae (\textit{Chara fragilis sp}) [5]. Besides microorganisms, biomaterials obtained from plant waste and biomass can also be used to reduce the content of heavy metals in the aquatic environment. Hasni [6] used tofu pulp to adsorb Mn (II) ions. Seaweed \textit{Eucheuma spinosum} has been used in the biosorption of Cu^{2+} metal ions [7], Pb^{2+} 8; Cr^{6+} [9] and Cr^{3+} [10]. The results show that the seaweed can adsorb metal with the coordination mechanism of coordination covalent bonds [9].

Seaweed is one source of foreign exchange for the country and sources income for people in coastal areas and is one of the commodities. The sea is very popular in world trade because of its wide benefits in various fields. Seaweed such as \textit{E. spinosum} has been cultivated in Sulawesi South. Takalar Regency, especially Punaga Village, Mangarabombang District is one area that is quite potential for cultivation development seaweed \textit{Eucheuma sp}. Potential of \textit{Eucheuma sp} seaweed cultivation is available along the coast with an area of $\pm 13,385$ Ha with cultivation area production which reached 923,832 tons in 2016 [11]. Seaweed is one of the commodities that are exported. Before being exported, seaweed was sorted, and some did not meet the criteria export is discarded and is waste. This waste can be utilized as a biosorbent of metal ions due to the -OH functional groups [12] in the seaweed that can interact with heavy metal ions like Mn (II) ions.

Based on the description above, this research was conducted to find out the ability of \textit{E. spinosum} to reduce the concentration of Mn (II) ions in solution. Biosorption depends on several parameters such as concentration [13], time [14] and pH [15]. Therefore, to get information about optimum time, optimum pH and its capacity, Mn (II) biosorption will be tested at various contact times, pH and Mn (II) ion concentration. Isothermal adsorption will be studied using the Langmuir and Freundlich’s equation. In addition, characterization using a Fourier Transform Infrared (FTIR) spectrophotometer was performed to determine the functional groups that play a role in binding to Mn (II) ions.

2. Methodology

2.1 Materials

All materials in this study were in analytical grades, and solutions were made using double distilled water. The materials consisted of the biomass of \textit{E. spinosum}, MnSO$_4$, H$_2$O (Merck), HNO$_3$ (Merck), and NaOH (Merck).

2.2 Equipment

Equipment used is Atomic Absorption Spectrophotometer (AAS) Buck Scientific model 205 VGP, magnetic stirrer (Fisher type 115), FT-IR Spectrometer Shimadzu Prestige 21, Quantachrome Instruments version 11.0.

2.3 Procedures

2.3.1. Preparation of \textit{E. spinosum} adsorbent. Seaweed (\textit{E. spinosum}) was cleaned using double distilled water to separate it from the dirty materials. After rinsing, the seaweed was dried, crushed, and sieved with 100 and 200 mesh sieves. The adsorbent used was the biomass held on the 200 mesh sieve. The seaweed was then re-dried at 60 °C in an oven to a constant weighted mass.

2.3.2. Analysis of Mn (II) content in \textit{E. spinosum}. Dried seaweed powder was weighed (0.5 g), added and diluted with double distilled water in a 100 mL volumetric flask. The sample was put into a 250 mL beaker, and 5 mL of concentrated HNO$_3$ was added into the beaker, heated to almost dry, cooled, put into a 50 mL volumetric flask by filtering and added double distilled water to the boundary mark. The amount of Mn (II) in the solution was determined using an atomic absorption spectrophotometer (AAS).
2.3.3. Determination of optimum adsorption time. Clean and dried seaweed powder (0.2 g) was put into 6 Erlenmeyer flasks of 100 mL containing 50 mL of Mn (II) solution with a concentration of 10 mg L\(^{-1}\) and stirred by using a magnetic stirrer for 3, 5, 10, 15, 20, and 30 min. The mixture was then filtered and AAS measured the cobalt content in the filtrate. Each experiment was repeated two times. Experiments for blanks were carried out as above but without the addition of adsorbents.

2.3.4. Determination of optimum adsorption pH. Dried seaweed powder (0.2 g) was put into an Erlenmeyer containing 50 mL of a solution of Mn (II) ion with a concentration of 10 mg L\(^{-1}\) at pH 2. The mixture was stirred during the optimum time and then filtered. The utilization of AAS was for measuring cobalt content in the filtrate. The repetition experiments were the same as the one mentioned above. The arrangement of pH to 3, 4, 5, 6, and 7 for the Mn (II) solutions was the experiment conducted for collecting the data to find the optimum pH. The blank experiments were also carried out. The optimum pH is the pH where the most significant number of ions adsorbed.

2.3.5. The effect of concentration on Mn (II) adsorption. Dried seaweed powder (0.2 g) was put into 6 Erlenmeyer flasks of 100 mL, then 50 mL of Mn (II) ion solution with concentrations of 10, 20, 40, 60, 90 and 120 mg L\(^{-1}\) were put successively into different Erlenmeyer flasks. The stirring of the mixture was at the optimum time and the optimum pH. The determination of the Mn (II) content in the filtrate, the experiment repetitions, and the experiments without adsorbent were the same as described before. Freundlich and Langmuir’s equations usually are those for studying the adsorption isotherms; equations (1) and (2) were the linear forms of the equations, respectively,

\[
\log (x / m) = \log k + 1 / n (\log C_e) \quad (1)
\]

\[
\frac{C_e}{q_e} = \frac{1}{Q_a} + \frac{C_e}{Q_o} \quad (2)
\]

where \(x\) is the amount of Mn (II) ion adsorbed on biomass \(E. \ spinosum\) (mg), \(m\) is mass of adsorbent (g), \(C_e\) is the concentration of Mn (II) ion (mg L\(^{-1}\)) when the equilibrium achieved, \(k\) and \(n\) are the Freundlich constants related to the adsorption capacity (mg g\(^{-1}\)) and adsorption intensity (g L\(^{-1}\)), respectively. \(Q_o\) and \(b\) successively indicate the Langmuir constants corresponding to the adsorption capacity (mg g\(^{-1}\)) and the adsorption coefficient (L mg\(^{-1}\)). Plotting \((x/m)\) to \(\log C_e\) for the Freundlich equation or \(C_e/q_e\) to \(C_e\) for the Langmuir equation will result in the adsorption capacities. Intercept in the Freundlich equation produces a value of \(k\) (adsorption capacity) and the slope of the Langmuir equation gives a \(Q_o\) value that is related to the adsorption capacity.

3. Result and discussion

3.1. Analysis of Mn (II) content in \(E. \ spinosum\).

The content of manganese (Mn) metal in \(E. \ spinosum\) obtained from Punaga Village, Takalar Regency measured by atomic absorption spectrophotometry was 0.0031 mg g\(^{-1}\) indicating a tiny amount of manganese in the sample.

3.2. The effect of contact time

The optimum time indicates the time used by the biosorbent to adsorb the maximum amount of metal ions analyzed. The optimum time is the greatest time for adsorbing metal ions by the adsorbent \((C_{\text{adsorption}})\). The optimum time of Mn (II) ion adsorbed by seaweed \(E. \ spinosum\) is determined by counting the number of adsorbed metal ions (\(q_e\)) as a function of time (\(t\)). The amount of Mn (II) ions adsorbed as a function of time is shown in Figure 1.
Figure 1. The amount of Mn (II) adsorbed on E. Spinosum Vs. contact time.

Figure 1 showed that the biosorption of Mn (II) ions increased up to a stirring time of 20 minutes, biosorption of Mn (II) ions increased from a stirring time of 3 minutes to 5 minutes. This can be seen from the increase in the number of Mn (II) ions adsorbed in the 3rd minute by 0.5 mg/g to 0.7 mg/g in the 20th minute. However, after the 20th minute, the amount of Mn (II) ions absorbed has decreased slightly. A relatively small amount of reduction indicates that the active site on the surface of the adsorbent of seaweed E. spinosum is saturated with Mn (II) ions.

3.3. Effect of optimum pH
In the process of adsorption of metal ions with various adsorbents, the pH of the solution plays an important role. The consideration of the solubility product (Ksp) [16] shown that the appropriate pH range for different metal ions is different, namely for Mn (II) at pH 1-7. At pH 1, the concentration of the adsorbed metal ions becomes very low. A pH that is too low or too high is not good for metal adsorption [17]. Therefore, the influence of pH is carried out between 2 and 7 with a stirring time for an optimum time of 20 minutes. The effect of pH on biosorption of Mn (II) ions by biosorbent of seaweed E. spinosum is shown in Figure 2.

Figure 2. The amount of Mn (II) adsorbed as a function of pH.

Figure 2 shows that the amount of Mn (II) ions adsorbed by seaweed E. spinosum at pH 2 is 1.19 mg/g. This amount increases and reaches a maximum at pH 4 with the amount adsorbed 1.58 mg/g. After passing pH 4 the amount adsorbed tends to decrease.

According to Pravasant et al. [16], the adsorption process at low pH will adsorb a low number of ions, too. This is caused by the presence of protons with high concentrations in solution and these
protons are competent with metal ions in the formation of bonds on the active side (functional group) on the biosorbent surface. The existence of this proton will cause protonation that can inhibit the binding process of metal ions. Whereas at high pH, the number of protons is low so that the competition between protons and heavy metal ions also decreases and an increase in the number of Mn (II) ions adsorbed. In addition, the decrease in the number of metal ions adsorbed in the adsorption process at high pH before reaching the pH where the metal ions settle is caused by the formation of dissolved hydroxyl complexes of metal ions so that metal ions can no longer bind to the active groups in the adsorbent [18].

Biosorption of Mn (II) ion as a function of pH was carried out by [19], on biosorption of Mn (II) ions by fungi from Andaman soil at optimum pH 7. Ibrahim [20], adsorbs Mn (II) ions in four species of red seaweed namely Corallina mediterranea, Galaxaura oblongata, Jania rubens and Pterocladia capillacea at the optimum pH of 5. The pH optimum biosorption of the Mn (II) metal in several studies shows different results, depending on the type of bio-sorbent used. In this research, pH 4 is the optimum pH where the maximum Mn (II) ion is adsorbed and the optimum pH is used for further research.

3.4. The effect of the initial concentration of Mn (II) on the adsorption

The amount of Mn (II) ions adsorbed by seaweed E. spinosum biomass as a function of the initial concentration of Mn (II) ions is given in Figure 3. The higher the concentration of Mn (II) ions, the greater the amount of Mn (II) ions absorbed by seaweed E. spinosum biomass. The amount adsorbed in the concentration range used has not reached saturation. Therefore, the adsorption capacity was determined by Langmuir and Freundlich isotherms as shown in Figure 4.

![Figure 3](image-url)

**Figure 3.** The amount of Mn (II) ions adsorbed by the seaweed biomass of *Eucheuma spinosum* vs the concentration of metal ions Mn (II) in the solution after adsorption (time = 20 minutes, pH = 4).

Figure 4 shown that the Freundlich adsorption isothermal model is more suitable for the biosorption of Mn (II) ions by E. spinosum seaweed where the point tends to show a straight line relationship according to the smallest square value where R2 on the Freundlich isothermal curve obtained is 0.998 whereas for the value of R2 on the Langmuir isothermal curve is 0.82. Judging from the value of R2, the Mn (II) ion adsorption model by E. spinosum seaweed is more in accordance with the Freundlich isothermal model compared to the Langmuir isothermal.
Figure 4. Isotherms of Mn (II) adsorption for a) Langmuir and b) Freundlich.

These results are consistent with the results made by Kang [21] that the adsorption of cadmium using seaweed Kappaphycus alvarezii and Eucheuma denticulatum follows the Freundlich isothermal pattern. The suitability of the isothermal adsorption pattern of Mn (II) ions by seaweed Eucheuma spinosum with the isothermal pattern of adsorption of other metals adsorbed using other types of seaweed may be caused by the acidity of active groups in seaweed [7]. Adsorption of Mn (II) ions by seaweed E. spinosum which corresponds to Freundlich's isothermal pattern indicates that adsorption on the surface of the adsorbent occurs at active heterogeneous sites. If it is seen from the functional groups in seaweed which play a role in the adsorption process, namely hydroxyl, carboxyl, and carbonyl groups, then in the Freundlich adsorption isotherm it is assumed that these groups have different absorption potential. From the line equation of the Freundlich isothermal curve, seaweed E. spinosum can be determined relative ability to adsorb Mn (II) ions which is equal to 4.13 mg/gram or 0.16 mmol/g and the strength of the interaction between ions is 1.18 L/g.

3.5. FT-IR analysis of adsorbent E. spinosum
The binding of Mn (II) metal ions to the seaweed biomass of Eucheuma spinosum is possible in the presence of several functional groups in biosorbents (seaweed). These functional groups are found in carbohydrate and protein compounds found in seaweed E. spinosum. Through IR spectra analysis, several functional groups that affect the binding of metal ions can be identified. The absorption band of seaweed E. spinosum before adsorbing Mn (II) ions and after adsorbing 120 mg/L Mn (II) ions can be seen in Figure 5 and the different wavenumbers of the absorption bands.
Figure 5. FT-IR spectra of adsorbent a) before and b) after adsorption of Mn (II) ion.

Some absorption bands in the seaweed biomass of Eucheuma spinosum before and after adsorption experience a shift in wavenumbers when compared to the wavenumbers in the E. spinosum spectrum before adsorption. A large shift is seen in the wavenumber at 3421.72 cm$^{-1}$ to 3448.72 cm$^{-1}$. This shows the interaction of Mn (II) ions with hydroxyl (-OH) bonds found in the biomass of seaweed E. spinosum. While the shift of the wavenumber at 3421.72 to 3448.72 cm$^{-1}$ indicates the -OH bond. Polysaccharides which have functional groups such as carboxyl, carbonyl, and hydroxyl which have a high-affinity form complex with heavy metal ions [22]. Hydroxyl (-OH) bonds in biosorbents are active groups that interact with metals to form stable coordination Mn (II) metal ions can form complexes with four coordination numbers with hydroxyl (OH-) bonds of carrageenan and alginate.

4. Conclusion
The conclusions obtained from this study as follows: contact time and optimum pH biosorption of Mn (II) ions by seaweed Eucheuma spinosum were 20 minutes and pH 4. Biosorption of Mn (II) ions by seaweed E. spinosum met the Freundlich isothermal with a capacitance value of 4.13 mg/g or 0.16 mmol/g and strength of the interaction between ions that equal to 1.18 L/g functional groups involved in biosorption of Mn (II) ions by seaweed E. spinosum, namely the –OH group.

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