Adsorption of metal ion, Co(II) on Eucheuma spinosum

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Abstract. Eucheuma spinosum is one of the seaweed species that found abundantly in Takalar Regency. We used the biomass of the seaweed as an adsorbent for the removal of metal Co(II) ions from an aqueous solution. The adsorption of Co(II) ion by E. spinosum biomass was carried out in various contact time, pH, and concentration. The concentration of metal ion Co(II) before and after adsorption was determined using the Atomic Absorption Spectrophotometer (AAS). The adsorption capacity of Co(II) ions by E. spinosum seaweed was determined using the Langmuir and Freundlich isotherms. The results showed that the optimum time was 20 min, and the optimum pH was 3. Adsorption of metal ion Co(II) using E. spinosum seaweed was in parallel to the Freundlich isothermal model with the adsorption capacity ($Q_o$) of 3.46 mg g$^{-1}$. The functional group involved in adsorption of Co(II) metal ions was C-OH groups.

1. Introduction
Current technological developments result in very rapid development in various fields of life. The development has not only a positive impact on life but also a negative impact, i.e., the damage on the environment, both on land and in the aquatic environment. Environmental pollution, usually created by industries or households, can cause damages to the water environment because of their waste. They discharged the waste into the water without any treatment. One of the wastes produced in the industry as well as domestic waste is heavy metals [1]. Therefore, it is necessary to reduce their existence in the environment.

One of the heavy metals that can pollute the environment is cobalt. Cobalt is an essential metal, but high concentrations of cobalt can be dangerous for living organisms [2]. Disposal of cobalt waste into the environment can cause a variety of toxic effects on all living creatures, including plants, animals, and microorganisms [3]. The tolerance limit of cobalt in drinking water is 0.05 mg L$^{-1}$ [4]. Excessive concentrations can result in hypotension, paralysis, bone cancer, lung irritation, diarrhea, neurotoxicology, and genotoxicology problems [4,5].

An alternative in processing wastes containing heavy metals is the use of biological materials as adsorbents. This process is biosorption. Biosorption shows the ability of biomass to bind heavy metals from the solution through metabolic or chemical and physic steps [6]. Many studies have reported the use of various types of biomasses for the removal of heavy metals, such as Saccharum bengalense for removing Co(II) ions [1], Broussonetia papyrifera [7] for recovering Cd and Cu in metals-containing solution. Cossich et al. [8] have successfully adsorbed chromium (III) by using biomass from Sargassum sp.
One of the biomass used to reduce heavy metal pollution is seaweed. The adsorption of copper, zinc, and cadmium was conducted using two dried seaweeds *Ecklonia maxima* and *Laminaria pallida* [9]. Nonliving *Ulva* seaweed can act as biosorbent of Cd, Zn, and Cu [10]. Xiaou *et al.* reported the utilize of *Laminaria japonica* as biosorbent of Pb(II), Cd(II), and Fe(III) [11]. Mwangi and Ngila [12] used ethylenediamine-modified green seaweed (*Caulerpa serrulata*) to adsorb Cu, Cd, and Pb. Tandigau *et al.* reported the use of Arabica coffee fruit biomass to adsorb Ni(II) ion [13]. *Eucheuma spinosum* is one species of seaweed that can remove heavy metals from aqueous solution. People in Takalar Regency, especially Punaga village in South Sulawesi cultivated *E. spinosum* regularly. The potential for seaweed cultivation is available along the coast with a cultivation area of ± 13.385 ha with production reaching 923.832 tons in 2016 [14]. The seaweed is one of the exported commodities. Before being exported, seaweed cultivators sorted and disposed of those that did not meet the export criteria. The waste can be useful as a metal ion biosorbent due to the presence of functional groups, such as sulfonate, -OH, and –COOH, which can interact with metals [15]. Researchers reported the use of *E. spinosum* in adsorption of Pb$^{2+}$ [16], and Cr$^{3+}$ [15].

Based on the description above, we recently studied the adsorption of Co(II) ions using *E. spinosum*. Adsorption using the seaweed biomass depends on several parameters such as time, pH, and concentration [17]. Therefore, the adsorption study of Co(II) ion was at various contact times, pHs, and Co(II) ion concentrations. Furthermore, a Fourier Transform Infrared (FT-IR) spectrophotometer used to determine the functional groups that played a role in the interaction of Co(II) ions with the seaweed.

### 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 *E. spinosum*, Co(NO$_3$)$_2$.6H$_2$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, Scanning Electron Microscopy (SEM).

#### 2.3 Procedures

##### 2.3.1. Preparation of *E. spinosum* adsorbent.
Seaweed (*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 $^\circ$C in an oven to a constant weighted mass.

##### 2.3.2. Analysis of Co(II) content in *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 Co(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 Co(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 Co(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 Co(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 Co(II) adsorption. Dried seaweed powder (0.2 g) was put into 6 Erlenmeyer flasks of 100 mL, then 50 mL of Co(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 Co(II) content in the filtrate, the experiment repetitions, and the experiments without adsorbent were the same as described before. Freundlich and Langmuir equations usually are those for studying the adsorption isotherms; equations (1) and (2) were the linear forms of the equations, respectively,

\[ \log \left( \frac{x}{m} \right) = \log k + \frac{1}{n} \log C_e \]  
\[ \frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \]  

where x is the amount of Co(II) ion adsorbed on *E. spinosum* biomass (mg), m is mass of adsorbent (g), Cₑ is the concentration of Co(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. Q₀ and b successively indicate the Langmuir constants corresponding to the adsorption capacity (mg g⁻¹) and the adsorption coefficient (L mg⁻¹). Plotting log (x/m) to log Cₑ for the Freundlich equation or Cₑ/qₑ to Cₑ 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 Q₀ value that is related to the adsorption capacity.

3. Result and discussion

3.1. Analysis of Co(II) content in *E. spinosum*.
The content of cobalt (Co) metal in *E. spinosum* obtained from Punaga Village, Takalar Regency measured by atomic absorption spectrophotometry was 0.003 mg g⁻¹ indicating a tiny amount of cobalt in the sample.

3.2. The effect of contact time
The optimum time is the time used by adsorbent to adsorb the maximum amount of metal ions analyzed. The optimum time is the time at which the adsorbed concentration is the greatest. Figure 1 shows the amount of Co(II) ion adsorbed on the adsorbent as a function of time (t).

The adsorption of Co(II) ions increases with the increase of time from 3 to 20 min. However, after 20 min, the adsorption tends to decrease. This result shows that the longer the time used, the more solutes can be adsorbed. However, the amount of adsorbed solute will reach the maximum limit at the specified time. This fact is because the adsorbent surface has achieved the equilibrium. A desorption process can cause a decrease in the adsorption amount after the optimum time, which shows the reversible process of adsorption-desorption [18]. Therefore, the optimum adsorption time was 20 min. Vilvanathan and Shantakumar [19] obtained the optimum contact time of 60 min in the adsorption of
metal Co(II) using *Chrysanthemum indicum*. The optimum contact time for metal adsorption of Co(II) in the two studies was different, depending on the type of adsorbent used.

![Graph](image)

Figure 1. The amount of Co(II) adsorbed on *E. Spinosum* Vs. contact time.

The kinetic model of Co(II) adsorption was studied using pseudo-first-order, and pseudo-second-order equations. Data of the contact time effect on the amount of Co(II) adsorbed were used in this study. By comparing the least-squares of the equations obtained, the corresponding adsorption pattern was obtained. Figure 2 illustrates the adsorption kinetics model based on pseudo-first-order and pseudo-second-order equations. Table 1 gives the values of R², k₁ (pseudo-first-order constant), k₂ (pseudo-second-order constant), along with the calculated and experimental qₑ values.

![Graph](image)

Figure 2. Kinetic study of Co(II) adsorbed using a) pseudo-first-order and b) pseudo-second-order equations.

| Parameter | Pseudo-first-order | Pseudo-second-order |
|-----------|--------------------|---------------------|
| R²        | 0.903              | 1.000               |
| qₑ calculated (mg g⁻¹) | 0.010              | 0.947               |
| qₑ obtained from experiment (mg g⁻¹) | 0.949              |                     |
| Rate constant | 0.070 min⁻¹        | 49.02 g mg⁻¹ min⁻¹  |

Table 1. The value of R², k₂, k₁, qₑ calculated from the experiments in adsorption of Co(II) ions on *E. spinosum*.

Figure 2 shows that the adsorption fits the pseudo-second-order equation because the R² value obtained by using the pseudo-first-order equation is 0.903, whereas the value obtained by using the pseudo-second-order equation is 1.000. The qₑ value calculated using the pseudo-second-order equation that is almost the same as the one obtained from the experiment supports this result (Table 1). The pseudo-second-rate constant (k₂) calculated from the regression equation is 49.02 g mg⁻¹ min⁻¹.
This finding shows that there is a chemical adsorption process between metal ions and adsorbents through electron-electron transitions between adsorbates and adsorbents [20].

### 3.3. The effect of pH on adsorption of Co(II)

In the adsorption process of metal ions with various adsorbents, the pH of the solution plays an important role. The results of the solubility product [21] showed that the pH range was suitable for a variety of different metal ions. At pH 1, the adsorbed metal ion was very low. At the very low pH or very high pH, the adsorption of metal ions is also low. Therefore, the influence of pH was carried out between 2 to 7 at the optimum time of 20 min. Figure 3 gives the effect of pH on adsorption of Co(II) ions on *E. spinosum* biomass.

![Figure 3. The amount of Co(II) adsorbed as a function of pH](image)

The amount of Co(II) ions adsorbed by *E. spinosum* biomass at pH 2 is 1.12 mg g⁻¹. This amount increases and reaches a maximum at pH 3 with an adsorbed amount of 1.31 mg g⁻¹. Above pH 3 the amount adsorbed tends to decrease. According to Pasavant *et al*. [21], at low pH, the adsorbent will adsorb a low amount of ions. This result is due to the presence of protons with high concentrations in solution and these protons compete with metal ions in the formation of bonds on the active side (functional groups) on the adsorbent surface. The existence of these protons will cause protonation, which can inhibit the binding process of metal ions. Whereas a high pH results in a low number of protons so that the competition between protons and heavy metal ions also decreases and an increase in the number of Co(II) ions adsorbed. The decrease in the amount of metal ions adsorbed in the adsorption at a high pH before the formation of precipitates is caused by the formation of dissolved hydroxyl complexes from metal ions so that metal ions can no longer bind to the active group on the adsorbent.

The adsorption of Co(II) ion as a function of pH was carried out by Pal *et al*. [3] on fungi from Andaman soil at pH 7. Ibrahim [22] adsorbed Co(II) ions in four species of red seaweeds, *Corallina mediterranea*, *Galaxaura oblongata*, *Jania rubens* and *Pterocladia capillacea* at the optimum pH of 5. The optimum adsorption pH of metal Co(II) in several studies showed different results, depending on the type of adsorbent used. In this study, pH 3 was the optimum pH where Co(II) ions were maximally adsorbed, and this optimum pH was the one used for further research.

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

Figure 4 shows the amount of Co(II) ions adsorbed on *E. spinosum* biomass as a function of the initial concentration of Co(II) ions. The higher the concentration of Co(II) ions, the higher the amount of Co(II) ions adsorbed by *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 5.

The Freundlich model is more suitable for adsorption of Co(II) ions on *E. spinosum* biomass with $R^2$ of 0.9838. This result is parallel to the results of Kang, *et al*. [12] in adsorption of cadmium using
seaweeds *Kappaphycus alvarezii* and *E. denticulatum*. From the regression equation of the Freundlich isotherm, the adsorption capacity of the biomass was 3.46 mg g⁻¹.

**Figure 4.** The amount of Co(II) adsorbed as a function of the equilibrium concentration.

![Graph showing Co(II) adsorption](image)

**Figure 5.** Isotherms of Co(II) adsorption for a) Langmuir and b) Freundlich

### 3.5. FT-IR analysis of adsorbent *E. spinosum*

Binding of metal ions Co(II) to *E. spinosum* is possible to occur with the presence of several functional groups in adsorbents (seaweed). These functional groups are found in carbohydrate and protein found in the seaweed. By analysis of IR spectra, several functional groups that influence the binding of metal ions can be known. Figure 6 gives the absorption bands of *E. spinosum* before and after adsorbing Co(II) ions with a concentration of 120 mg L⁻¹.

Some absorption bands in *E. spinosum* biomass before adsorption shift after adsorption of Co(II). A significant shift is at the band with the wavenumber of 3416 cm⁻¹. After adsorption, the absorption band shifts to 3443 cm⁻¹. This observation shows that there is an interaction of Co(II) ions with hydroxyl (-OH) bonds found in the seaweed. The shift of wavenumbers at 1033, 1072, and 1259 cm⁻¹ to 1026 and 1261 cm⁻¹ indicates the possible interaction of C-O bonds with Co(II) ion. The functional groups are found in carrageenan and alginate that can interact with the metal ion used in this study. The functional groups can form complex compounds with heavy metal ions. Hydroxyl bonds (-OH) in adsorbents are active groups that interact with metals to form stable compound [23]. The Co(II) ions can form complexes with six coordination numbers with hydroxyl (-OH) bonds from carrageenan and alginate. Figure 7 illustrates the possible compound formed as a result of the interaction between metal Co(II) and (-OH) bonds.
Figure 6. FT-IR spectra of adsorbent a) before and b) after adsorption of Co(II) ion

![FT-IR spectra](image)

Figure 7. The possible complex formed between Co(II) ion with carrageenan and alginate compounds found in *E. spinosum*

Besides using an FT-IR spectrometer, the SEM instrument was also used to study the adsorption of Co(II) on *E. spinosum*. Figure 8 shows the SEM images of *E. spinosum* biomass before and after adsorption.

a) b)

![SEM images](image)

Figure 8. SEM images of *E. spinosum* a) before and b) after adsorption

The imaging results show that pores of the biomass of *E. spinosum* seaweed before adsorption covers by Co(II) ions after the adsorption. This observation indicates that the seaweed adsorbs Co(II) ion, which supports the results of the adsorption ability and the FTIR data.
4. Conclusion
The conclusions obtained from this study are as follows: the adsorption of Co(II) achieved the equilibrium after the contact time of 20 min at the optimum pH of 3. The adsorption in line with the Freundlich isotherm with an adsorption capacity of 3.46 mg g\(^{-1}\). The kinetic adsorption follows the pseudo-second-order equation with the rate constant of 49.02 g mg\(^{-1}\) min\(^{-1}\). The functional groups involved in the adsorption of Co(II) ions on *E. spinosum* seaweed was -OH groups.

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