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The Relationship of Culture Media Composition and Chemical Composition on *Spirulina* sp for Metal Ion Adsorbent

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Abstract: The analysis relationship of *Spirulina* sp medium with chemical composition has been conducted. Chemical analysis was performed using X-Ray Fluorescence analysis. Furthermore, potention of *Spirulina* sp as adsorbent of metal ions was analyzed using FTIR spectroscopy. The results showed that metals such as Zn, Fe, Mn, Ca, Cu, and Mo were mainly metals in *Spirulina* sp. These metals were not correlated with cultivated medium of *Spirulina* sp. Analysis of potention *Spirulina* sp as metal ions adsorbent showed that *Spirulina* sp has functional groups –C=O and –OH as ligand. Intercation of metal ions Cu(II) and Cr(III) with *Spirulina* sp indicated that metal ions bond to –C=O functional group.

Keywords: Spirulina sp, media composition, chemical content, metal ion, adsorption

Abstrak (Indonesian): Telah dilakukan analisis hubungan komposisi media *Spirulina* sp dengan kandungan kimia yang dimilikinya. Analisis kandungan kimia dilakukan dengan X-Ray Fluorescence. Selanjutnya potensi *Spirulina* sp sebagai adsorben dalam mengikat ion-ion logam dianalisis menggunakan spektroskopi FTIR. Hasil penelitian menunjukkan bahwa logam Zn, Fe, Mn, Ca, Cu, dan Mo merupakan logam utama yang terkandung dalam *Spirulina* sp. Logam-logam tersebut diasumsikan tidak berasal dari medium tumbuh *Spirulina* sp. Analisis terhadap potensi *Spirulina* sp sebagai adsorben logam berat menunjukkan bahwa *Spirulina* sp memiliki gugus fungsional -C=O dan –OH yang potensial sebagai ligan. Interaksi ion logam Cu(II) dan Cr(III) dengan *Spirulina* sp menunjukkan bahwa ion logam terikat pada gugus –C=O.

Kata kunci: Spirulina sp, komposisi media, kandungan kimia, ion logam, adsorpsi

1. Introduction

The presence of heavy metals in the environment is commonly due to human activities such as industrial process, home industry, mining industry, and also hospital activity. These processes are lead to pollution of natural environment. Heavy metals such as mercury, lead, cadmium, copper, zinc, nickel, arsenic have ability to accumulate to the system including human body [1]. Thus treatment of heavy metals in the environment is crucial until this decade.

Several physical, chemical, and biological methods to treat metal ions are available including precipitation, ion exchange, extraction, membrane processing, and also adsorption method [2]. Adsorption is advantages due to low cost, easy process, fast treatment, and green process without byproducts [3]. In order to obtain effective adsorption process, selection of adsorbent is needed. Adsorbent can be found natural and synthetic [4]. Both adsorbents have advantages or disadvantages depending on objectives of the process. In order to adsorb heavy metal ions, adsorbents should be effective and have active functional groups act as ligand to bind metal ions. Thus natural adsorbent such as algae with active site groups is potential for adsorbent of heavy metal ions.

Adsorption of heavy metal ions using algae has been reported in many literatures and know well as biosoption process [5–7]. Algae including microalgae and macroalgae from environment is collected and cultivated to obtain pure species [8]. Thus identification of active sites and chemical composition of algae can be generated. Biosorption using algae as adsorbent involved several mechanisms such as complex formation, electrostatic interaction, ion exchange, and also entrapment process [4].

In this report, microalgae *Spirulina* sp was cultivated in appropriate medium to be adsorbent. *Spirulina* sp is microalgae which common in fresh water lowland ecosystem in Palembang, South Sumatera. Chemical composition of *Spirulina* sp was investigated in relation with medium cultivation of algae. The active sites of *Spirulina* sp was identified using FTIR spectroscopy. *Spirulina* sp bind with artificial heavy metal ions such as Cr(III) and Cu(II) was also checked systematically to identify main functional group bind to metal ions.

2. Experimental Sections

Composition of Culture Media

Composition of culture media was made according to Bold's Basal Medium. The solutions for culture media were prepared with deionized water such as stock solution (100 mL) : $NaNO_3$ (25 mg), $CaCl.2H_2O$ (2.5 mg), $MgSO_4.7H_2O$ (7.5 mg), K_2HPO_4 (10 mg), KH_2PO_4 (17.5 mg), NaCl (2.5 mg). Trace Elements (100 mL) : $ZnSO_4.7H_2O$ (0,882 mg), $MnCl_2.7H_2O$ (0.144 mg), MoO_3 (0.071 mg), $CuSO_4.5H_2O$ (0.157 mg). EDTA Stock (100 mL) : Na_2EDTA (5 mg), KOH (31 mg). Iron Solution (100 mL): $FeSO_4.7H_2O$ (0.498 mg). Boric Solution (100 mL): H_3BO_3 (1.142 mg) [9].

Spirulina sp Cultivation

Into 1 L of Erlenmeyer flask was added 10 mL for each component: stock solution, trace elements, EDTA stock, iron solution, and boric solution. The solution was dilute to 1 L with deionized water to form clear solution. The solution was kept at 100 ^oC into autoclave for 2.5 hours. The culture of *Spirulina* sp was added into Erlenmeyer after cooling the solution. The solution was continuously illuminated by four fluorescent lamps for 14 days together with aerator systems. A green solution was formed at 1 day. *Spirulina* sp was collected by centrifugation at 4000 rpm for 3 minutes. Dry *Spirulina* sp was obtained after dried at 45 ^oC overnight.

Chemical Composition Analysis of *Spirulina* sp

Chemical composition of *Spirulina* sp was analyzed using PANalytical Type Minipal 4- X-Ray Fluorescence.

Identification of Active sites Adsorption of Metal Ion on *Spirulina* sp

Dry *Spirulina* sp (0.5 g) was placed into 100 mL of Erlenmeyer flask equipped with magnetic bar. Chromium(III) (10 mL) was added into the flask. The mixtures were stirred for 1 hour follow with filtration. Residue was dried at 50 ^oC for 5 hours. Dried residue was analyzed using Shimadzu Prestige-21 FTIR spectrophotometer in the range of 300-4000 cm^{-1} [10].

3. Results and Discussion

Figure 1 showed the morphology of *Spirulina* sp. This green alga is a cyanobacterium with spiral form [11]. Cultivation of *Spirulina* sp was kept for 2 weeks under fluorescent lamps in Laboratory to obtain 1 g of dry biomass. In this research, we attempt to see the relationship of medium cultivation of *Spirulina* sp with their chemical composition in order to utilize *Spirulina* sp as adsorbent of metal ions.

Figure 1. Morphology of *Spirulina* sp (400x magnification)

Table 1. Chemical composition of *Spirulina* sp.

Elements	Amounts
P	4.3% ± 0.2
K	2.98% ± 0.07
Ca	6.19% ± 0.04
Cr	0.082% ± 0.002
Mn	9.64% ± 0.04
Fe	28.5% ± 0.2
Ni	0.88% ± 0.02
Cu	4.73% ± 0.06
Zn	38.5% ± 0.5
Mo	1.9% ± 1.4
S	0.7% ± 0.03

The results analysis of dry *Spirulina* sp using X-Ray Fluorescence is shown in Table 1. The main metals in *Spirulina* sp was Zn, Fe, Mn, Ca, Cu, dan Mo. All these metals in cultivation medium is less than 1%. Thus there is no relationship of chemical composition of *Spirulina* sp with their cultivation medium. Metals such as Zn (38.5%) and Fe (28.5%) were probably stays in the *Spirulina* sp without increasing from medium cultivation. Other metals such as Mn, Ca, Cu, and Mo also gave the equivalent effect similar with Zn and Fe. In order to evaluate the ability of *Spirulina* sp as adsorbent, rare earth metals or early transition metals (Sc to Mn) probably appropriate as adsorbate due to elimination of competitive adsorption [12].

The active sites of *Spirulina* sp was identified using FTIR spectroscopy as shown in Figure 2C. The main vibration was appeared at 3400 cm^{-1} assigned as stretching of –OH. Other functional groups were –C=O (1700 cm^{-1}), -C-H (2900 cm^{-1}), and –C-O (1100 cm^{-1}) [3]. In order to know the active sites bond to metal ion, we contacted in separate system metal ion Cu(II) and Cr(III) with *Spirulina* sp for 1 hour then analyzed using FTIR spectroscopy as shown in Figure 2A and 2B.

The results showed that vibration almost similar for Cr(III)-*Spirulina* sp (Figure 2B). On the other hand, vibration of Cu(II)-*Spirulina* sp (Figure 2A) has slightly different from vibration of *Spirulina* sp. The wavenumber at 1400-1600 cm^{-1} splitted into three bands. These vibrations assigned as carbonyl (-C=O) bond with Cu(II). Carbonyl in *Spirulina* sp is active site for metal ion adsorption [13]. Carbonyl is also know well as strong ligand in spectrochemical series can bond spontaneously with metal ions in the environment [14].

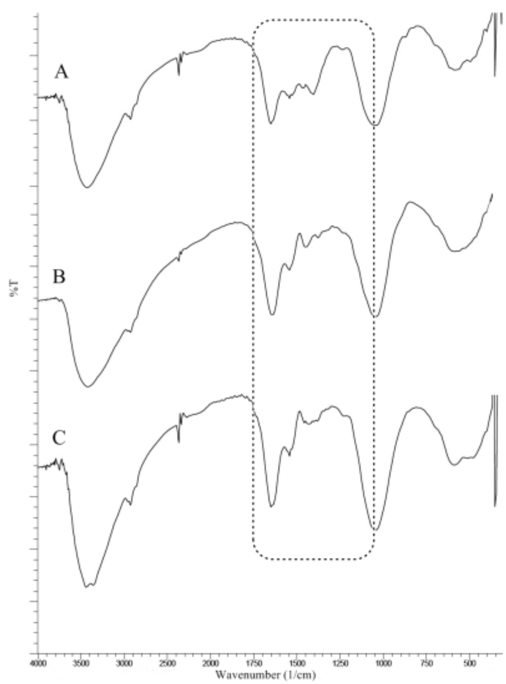

Figure 2. FTIR Spectra of *Spirulina* sp(C) and *Spirulina* sp. bonded with Cr(III) (B) and Cu(II) (A)

4. Conclusion

Spirulina sp has chemical composition did not depending on cultivation medium. Identification of functional groups showed that –OH, -C=O, -CH, and –C-O were found in *Spirulina* sp. Functional group of –C=O was active site for metal ion adsorption in *Spirulina* sp.

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