Study on the Adsorption of Chromium (VI) Metal Ion from Aqueous Solution by Green Algae Biomass (*Chara fragilis* sp.)

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Abstract: Chromium (VI) is major heavy metal found in textile industry wastewater that cause environmental pollution. Biosorption of heavy metals by using algae biomass has emerged as a cost-effective and efficient alternative technology. This study aims to develop algae (*Chara fragilis* sp) biomass as adsorbent for Cr (VI) metal ion in aqueous solution. In this study, the optimum conditions of the absorption of biomass *Chara fragilis* sp. to Cr (VI) ions was determined on the parameters of the optimum contact time and adsorbent mass. Cr (IV) was analyzed by using AAS and the pattern of adsorption isotherms was determined. The results showed that *Chara fragilis* sp biomass has clear ability in adsorbing Cr (VI) ion in aqueous solution with optimum contact time was 40 min and the adsorbent mass was 1 g. Under those optimum conditions, the percentage of absorption of Cr (VI) were 24% and 27%, respectively. The adsorption isotherm of *Chara fragilis* followed the Freundlich pattern, which showed that adsorption mechanism occured physically.

1. Introduction

Heavy metal contamination has been the greatest concern for their negative impacts on aquatic environments and adverse effects on human health. Heavy metals, particularly chromium (Cr), are released into the environment from anthropogenic activity, such as industrial coatings, leather tanning, paint industry, textile industry, electroplating, battery, mining processing [1-4]. Chromium metal is highly persistent, non-biodegradable, tend to accumulate in the environment, such as in the food chain, and toxic. The adverse health effects following to the exposure of chromium are dependent on its oxidation state. Chromium ions are available in the form of Cr (III) and Cr (VI) ions, where the hexavalent form is considered more toxic than Cr (III) [5]. Hexavalent chromium is a highly toxic as easily penetrates biological membranes and has high oxidizing potential. Furthermore, Cr (VI) reported can cause cancer, epigastric pain, vomiting, and chronic diarrhea [6].

Heavy metals in industrial wastewater poses a number of potential risks to human health, and therefore must be reduced before being discharged into the environment. Development of an efficient removal of heavy metals from industrial discharge is still a major challenge [7]. Various heavy metal removal technologies have been developed, neutralization, reverse osmosis, electrodialysis, electro-Fenton process, ultra filtration and ion exchange resins, reverse osmosis, membrane separation, nanofiltration, etc. [8,9]. However, the above methods has a lot of disadvantages in the aspect of high operational costs, low efficiency.
Bioremoval technology that utilizes microorganisms is an alternative technology. It is a simple technique, but has many advantages in the aspects of low operational cost, high efficiency, biodegradability, etc. Green algae *Chara fragilis sp.* as an abundant resource in Indonesia and potential as biomaterial source for adsorbents. Algae biomass has a high sorption capacity, plentiful availability, high surface area to volume ratio, and the potential for metal regeneration and recovery. Green algae contains cellulose with a high percentage of protein bound to polysaccharides which has many functional groups like amino, sulfate, hydroxyl, and carboxyl.

This research is aimed to develop green algae *Chara fragilis sp.* biomass as heavy metal adsorbent Cr (VI) in simulated waste water. The advantages of using green algae as biosorption are biodegradable, low cost, high efficiency, and do not need additional nutrients. For this reason, this research was carried out.

2. Experimental

2.1 Materials

All the primary reagents used in this study were of analytical grade purchased from Merck, Germany and used without further purification. Nitric acid (HNO$_3$), lanthanum chloride (LaCl$_3$.7H$_2$O), calcium carbonate (CaCO$_3$), 30% hydrogen peroxide (H$_2$O$_2$), aluminum nitrate Al (NO$_3$)$_3$.9H$_2$O, potassium chloride (KCl), HCl, NaOH, metal Cd, potassium bichromate (K$_2$Cr$_2$O$_7$), distilled water, green algae *Chara fragilis sp.*

2.2 Preparation of the membrane

Fresh of algae *Chara fragilis sp.* was thoroughly washed and mashed using a blender, then dried in oven at 110 °C for 1 hr. After drying, the dried chara was powdered and sieved 100 mesh.

2.3 Optimization of contact time

Chara powder was weighed 1 g and then put into 50 ml of solution containing Cr (VI) ion. The solution was then stirred using a magnetic stirer for 5, 10, 20, 40, 50, 60, 70, 80, 90, 100, and 120 min. Furthermore, the absorbance of Cr metal in the solution that has been contacted with chara was measured using UV-Vis spectrophotometry at maximum wavelength.

2.4 Optimization of the adsorbent mass

Optimization was done by varying the weight of the chara adsorbent: 0.5, 1.0, 1.5, 2.5, and 3 g chara powder was weighed and put into 50 ml of a solution containing Cr (VI). The solution was stirred using a magnetic stirer for 1 hr. Furthermore, the absorbance of Cr metal in the solution that has been contacted with chara was measured using UV-Vis spectrophotometry at maximum wavelength.

2.5 Determination of adsorption isotherm

Calculation of reaction isotherms (Langmuir and Freundlich) is based on the results of variations of the concentration of Cr (VI). In the Langmuir isotherm model, a graph was plotted between C and c/m, while in the Freundlich isotherm model, a graph was plotted between log C and log m. Determination of the isotherm model is based on the value of R$^2$ which is close to 1.

3. Results and Discussion

The ability of *Chara fragilis sp.* biomass to adsorb Cr(VI) ion is related to the composition of Chara Fragilis containing cellulose in its cell walls. Judging from its structure, cellulose has the potential to be large enough to be used as an absorber because the bound OH group can
interact with the adsorbate component. The presence of OH groups in cellulose causes polar properties in the adsorbent. Thus cellulose is more powerful in absorbing polar substances. The sorption mechanism that occurs between the –OH group attached to the surface with the positively charged metal ion (cation) is the ion exchange mechanism, which is shown in the following figure:

![Chemical structure of cellulose and ion exchange mechanism](image)

**Fig. 1:** A. Chemical structure of cellulose, describes the presence of abundant OH groups in the compound; B. Mechanisms of ion exchange between chromium (VI) ions and OH groups

From **Fig. 1B**, Y is the matrix on which the –OH group is bound. Interaction between the –OH group and metal ions is also possible through the mechanism of forming the coordination complex because the oxygen atom (O) in the –OH group has a lone electron pair, while the metal ion has empty d orbitals. Pairs of lone electrons will occupy empty orbitals which are owned by metal ions, to form a complex compound.

The adsorption capacity of *Chara fragilis sp.* biomass for Cr (VI) ion can be enhanced by drying in order to remove water from the substance. Drying was performed in an oven at 110 °C for 1 hour which effectively remove the water. If the temperature is too high, decomposition may occur, thus affecting the adsorption ability of *Chara fragilis sp.* biomass on Cr (VI). After drying, the biomass is mashed into powder and sieved with a 100 mesh sieve to expand the absorption area thereby increasing the adsorption capacity.

### 3.1 Optimization of contact time

The effects of contact time of Cr (VI) by *Chara fragilis sp.* biomass ranges from 0–140 min on the adsorption capacity. From Fig. 2, it can be seen that an at the range of 0 to 40 min, the adsorption was increase significantly, and the optimum contact time was achieved after 40 min with adsorption capacity was found to be 24.96%. After that point, the adsorption capacity gradually decreases. This possibly happens because the equilibrium of adsorption and desorption of Cr (VI) was already achieved. After 40 min, process of desorption has occurred. At this point, dichromate ions were transformed into chromate ions. Thus, difficult to be bound by hydroxyl groups on cellulose.
3.2 Optimization of adsorbent mass
From Fig. 3, it can be seen that the optimum mass of adsorbent was obtained by adding 1 g of Chara fragilis sp. biomass, where a maximum reduction of Cr (VI) ion of 27.24% was obtained. This perhaps because the biomass was already saturated with Cr (VI) ion. The more adsorbent mass, means the number of active sites is also increasing, so the ability of biomass to adsorb increases. After 1 g, further addition of biomass did not significantly increases the percentage of absorbed Cr (VI).

3.3 Determination of adsorption isotherm
From Fig. 4, it can be seen that the adsorbent chara has a tendency to follow the Freundlich isotherm model based on its linearity value ($R^2 = 0.9662$). The Freundlich isotherm assumes that the adsorption process between the adsorbent and Cr (VI) ions occurs physically dominant, heterogeneous adsorbent sites, and is reversible. The interaction involves weak forces such as van der Waals.
Fig. 4: Adsorption isotherm of Cr (VI) ion on Chara fragilis sp. biomass

4. Conclusion
The green algae Chara fragilis sp. biomass has an ability to absorb Cr (VI) ion, so it can be an alternative for bioremoval of heavy metal chromium. The optimum condition for the absorption was at 40 min contact time and 1 g of adsorbent mass. The adsorption process followed Freundlich isotherm.

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