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The removal of chromium (VI) from tannery waste using Spirulina sp. immobilized silica gel

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Abstract: The use of microalgae biomass is an alternative solution to the problem of environmental pollution due to heavy metals, one of which is Cr metal in leather tanning liquid waste. However, the ability of biomass to adsorb heavy metals has limitations. Therefore, the algal biomass is immobilized with silica gel in order to obtain a stable structure. This research aims to study the absorption efficiency of Cr (VI) metal by the biomass of Spirulina sp. which is immobilized with silica gel from the tannery liquid waste. The preparation stages in this study were adsorbent preparation, immobilization of biomass with silica gel, and preparation of tannery liquid waste. Furthermore, the research treatment was carried out to determine the effect of the independent variable on the adsorption of Cr (VI). Characteristics of functional groups using FTIR show the biomass constituent of Spirulina sp. immobilized containing amino, carboxylate, and hydroxyl groups. The results showed that the optimum contact time required for adsorption of Cr (VI) ions was 60 min of immersion and the optimum pH value was 3. Adsorption of Cr (VI) ions followed Freundlich adsorption isothermal and included in the pseudo second order adsorption kinetics.

Key words: Adsorption, chromium, immobilization, Spirulina sp., tannery waste

1. Introduction

The leather tanning industry is one of the industries that releases a large volume of liquid waste. In tanning 1 ton of wet leather, about 40 m^3 of water is needed and then disposed of as liquid waste mixed with chemical residues of the process and leather components dissolved during tanning [1]. Conventional leather tanning using chrome as a tanning material has an impact on the environment because it brings the remaining chromium into the liquid waste. Although the chromium used in the tanning process is trivalent chromium, hexavalent chromium is always present in the liquid waste [2]. The disposal of chromium with liquid waste is hazardous and toxic contamination, because chromium is a type of heavy metal waste that is difficult to decompose and can accumulate in the body and the environment [3].

Chrome (Cr) is the most widely used tanner in the leather tanning industry and about 85% of the world's leather is tanned using chrome. This is based on the fact that chromium is able to react and form bonds with skin collagen protein amino acids [4]. Cr (IV) is a heavy metal that is toxic, and its toxicity depends on the valence of the ion, and the toxicity of Cr (IV) is about 100 times the toxicity of Cr (III) [5,6]. In addition, Cr (VI) is highly corrosive and carcinogenic. Cr (III) is a nutrient that the human body needs in the amount of about 50–200 μg/day. However, it is feared that in an alkaline environment and the presence of certain oxidizers or certain conditions it is possible for Cr (III) ions to be oxidized to Cr (VI) [7]. Therefore, the Cr metal in the tannery industry liquid waste needs to be handled first before being discharged into water bodies or rivers.

Several species of microalgae have been found to have the potential to adsorb metal ions, both in the living (active) state and in the form of dead cells (inactive biomass) [8]. The use of microalgae biomass for adsorbents aims to reduce the use of nonrenewable inorganic flocculants and synthetic flocculants that are not easily biodegradable [9]. Spirulina sp. is known to be able to adsorb metal ions because there are functional groups in microalgae that can bind with metal ions. These functional groups are carboxyl, hydroxyl, amino, sulfate, and sulfonate groups that are present in the cell wall in the cytoplasm [10]. However, the ability of microalgae to absorb metal ions is very limited by several disadvantages such as very small size, low density, and the algae is easily damaged due to degradation by other microorganisms [11]. To overcome these weaknesses,

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where $\mathbf{q_e}$ is the biomass adsorption equilibrium ions uptake capacity (mg/g), $\mathbf{C_o}$ is the initial ion concentration (mg/L), $\mathbf{C_e}$ is the equilibrium or final ion concentration (mg/L), V is the volume of metal ion solution (L) and **m** is the Spirulina sp. biomass immobilized by silica gel dry weight (g).

Langmuir isothermal assumes the adsorption of a single layer on the surface containing a certain amount of adsorption centers with uniform adsorption energies without displacement of the adsorbate on the surface plane. The linear form of the Langmuir isothermal equation is shown in equation 3 [6]:

$$\frac{C_e}{q_e} = \frac{1}{Q_o k_L} + \frac{C_e}{Q_o} \quad (3)$$

where, $\mathbf{Q_o}$ is the maximum adsorption capacity (mg/g) and $\mathbf{K_L}$ is the langmuir constant (L/mg).

The Freundlich isotherm is most commonly used because it is considered to be better at characterizing the adsorption process [16]. Freundlich isothermal is used at heterogeneous surface energies with different concentrations. The linear form of the Freundlich isotherm is shown by equation 4 [6]:

$$\log(q_e) = \log k_F + \frac{1}{n} \log C_e \quad (4)$$

where $\mathbf{K_f}$ is the adsorption capacity at unit concentration (mg/g); **n** is the intensity of adsorption.

2.7. Adsorption rate kinetics

Determination of the adsorption kinetics model in this study was carried out by varying the absorption time from 30, 60, 90, 120, 150 min at pH value 3 with a concentration of Cr(VI) 20 mg/L. Pseudo first and second order kinetics equations were used to determine the adsorption kinetics order. The determination of pseudo first order kinetics can use the following equation 5 [6]:

$$\ln(q_e - q_t) = \ln q_e - k_{1t} \quad (5)$$

While the determination of pseudo second order kinetics can use the following equation 6 [13]:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \quad (6)$$

where $\mathbf{q_t}$ is the amount of adsorbate adsorbed (mg/g) at time t, $\mathbf{q_e}$ is the amount of adsorbate adsorbed (mg/g) at the best time (0 to t < $\mathbf{q_e}$) and k is the adsorption rate constant.

2.8. Cr (VI) removal from tanning waste industry

Chrome tanning waste is filtered using technical filter paper to remove impurities. The filtrate is used as a sample of liquid waste. As a characterization step, the sample was analyzed to determine the level of Cr (VI), and the results of the analysis were the initial concentration of chromium in wastewater. The final concentration of Cr in the waste was determined by adding 1 gram of Spirulina sp. into 100 mL of liquid waste with optimum pH and stirred with a magnetic stirrer at room temperature for the optimum time. Then filtered with whatman 41 filter paper. The resulting filtrate was analyzed for the Cr (VI) content as the final Cr (VI) content in the waste, while the biomass was characterized using FTIR.

3. Results and discussion

3.1. FTIR characteristics of Spirulina sp. immobilized silica gel

The results of identification of the functional groups of Spirulina sp. immobilized before and after interaction with the Cr (VI) metal ion is shown in Figure 1. Based on the FTIR spectrum, the biomass of Spirulina sp. before the interaction with the Cr (VI) metal ion, it appears that the absorption of the medium around the wave number 3747.95 cm^{-1} is the absorption of the OH-alcohol stretching vibration. The width absorption is around the wave number 3445.95 cm^{-1}, which is the stretching vibration absorption from the primary N-H group and the absorption around the wave number 2365.19 cm^{-1}. This absorption indicates a C-H stretching vibration. The absorption band around the wave number 1648.05 cm^{-1} indicates a stretching vibration of C = O (carboxylate-ester). The absorption around the wave number 1102.24 cm^{-1} indicates an asymmetrical stretching vibration of Si-O. The absorption band around the wave number 468.84 cm^{-1} showed the presence of Si-O stretching vibrations from Si-O-Si, which was obtained from the immobilization of biomass with silica gel [17].
Based on the FTIR spectrum of Spirulina sp. immobilized after interaction with the metal ion Cr (VI), a medium absorption band appears around the wave number 3742.27 cm^{-1}, which is the absorption of the stretching vibration of OH-

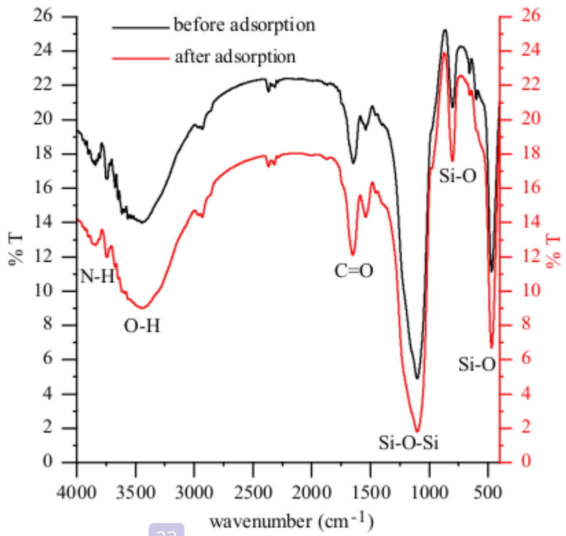

Figure 1. FTIR spectrum of Spirulina sp. immobilized before and after adsorption of Cr (VI).

alcohol. The presence of sharp absorption around the wave number 3445.81 cm^{-1} is the absorption width of the stretching vibration of the primary N-H group and the presence of absorption around the wave number 2366.95 cm^{-1} indicates C-H stretching vibrations. The absorption band around the wave number 1650.01 cm^{-1} indicates a stretching vibration of C=O (carboxylate, ester). The presence of strong absorption around the wave number 469.46 cm^{-1} was identified as the stretching vibration of Si-O from Si-O-Si. The functional groups that experience a shift in wave numbers are assumed to be functional groups that may affect the adsorption process [18].

The process of immobilization of microalgae with sodium silicate solution was carried out using the sol gel method, namely the addition of HCl. The addition of concentrated HCl solution is intended for the process of forming free silicic acid, which can bind to form dimers, trimers and so on through a polycondensation reaction and the release of H_2O molecules.

3.2. Effect of pH value on the Cr (VI) adsorption

The initial pH value of the solution is important for Cr (VI) adsorption because the protonation of the adsorbent configures the active ion exchange site and surface activity [19]. The results of the adsorption of Cr (VI) metal ions with pH variations are shown in Figure 2. The highest percentage of adsorption of Cr (VI) metal ions was achieved when the initial pH value of the solution was at pH = 3. The results of this study are close to the results of Pradhan et al. [6], which obtained the maximum pH absorption of Cr (VI) metal ions by Scenedesmus sp. at a pH = 2.65. At low pH value, the surface of the biomass containing anionic groups such as amines, carboxyl, and hydroxyl is protonated and becomes positively charged (Figure 3). At the same time, through its lone pair, the metal ion Cr (VI), which is present in the acid solution in the form of anionic species, such as tetraoxohydrochromate ($HCrO_4^-$), chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$), relatively easily interacts with the adsorbent, so that adsorbed metal ions are relatively large. The positively charged biomass surface attracts the anionic Cr (VI) species electrostatically, resulting in strong Cr (VI) physisorption to the biomass at lower pH value ranges [20]. Cr VI can form complexes with the NH_2 functional group on Spirulina sp. biomass on an acidified surface by the following reaction:

$$HCrO_4^- + R—NH_2 + H^+ \leftrightarrow R—NH_3^+—HCrO_4^- \quad (7)$$

When the pH value of the solution increases gradually, the biomass surface becomes negatively charged due to the decrease in proton concentration. Negatively charged biomass competes with anionic chromate ions due to electrostatic repulsion, which results in decreased adsorption efficiency at higher pH value ranges [21].

3.3. Effect of contact time on Cr (VI) adsorption

Figure 4 shows that in the initial minutes of interaction, the adsorption progresses faster because the number of active sites in the adsorbent is still quite a lot, after the adsorption process lasts for 60 min, the adsorption is relatively constant. In

Table 1 shows the parameter values in the adsorption isotherm. The $\mathbf{k_f}$ and 1/n values respectively indicate the adsorption capacity and adsorption intensity. The $\mathbf{k_f}$ and $\mathbf{Q_o}$ values are the maximum amount of adsorbate that can be absorbed by the adsorbent in mg. The greater the $\mathbf{k_f}$ and $\mathbf{Q_o}$ values, the greater the adsorption capacity. Based on these data, the biomass adsorbent of Spirulina sp. immobilized had a maximum adsorption capacity of 0.389 mg/g. The magnitude of 1/n gives the adsorption favorability measure. A value of 1/n between 1 and 10 indicates favorable uptake [23]. For this study, a value of 1/n also presented the same result, representing favorable uptake.

3.6. Adsorption kinetics model

Determination of the adsorption rate can be done through a kinetics model approach. These results can be interpreted through adsorption kinetics using two kinetics models, namely pseudo first order and pseudo second order kinetics models. Apart from many alternative models, pseudo first order and pseudo second order remain the most common models for batch processing to evaluate the control mechanism in adsorption systems [24].

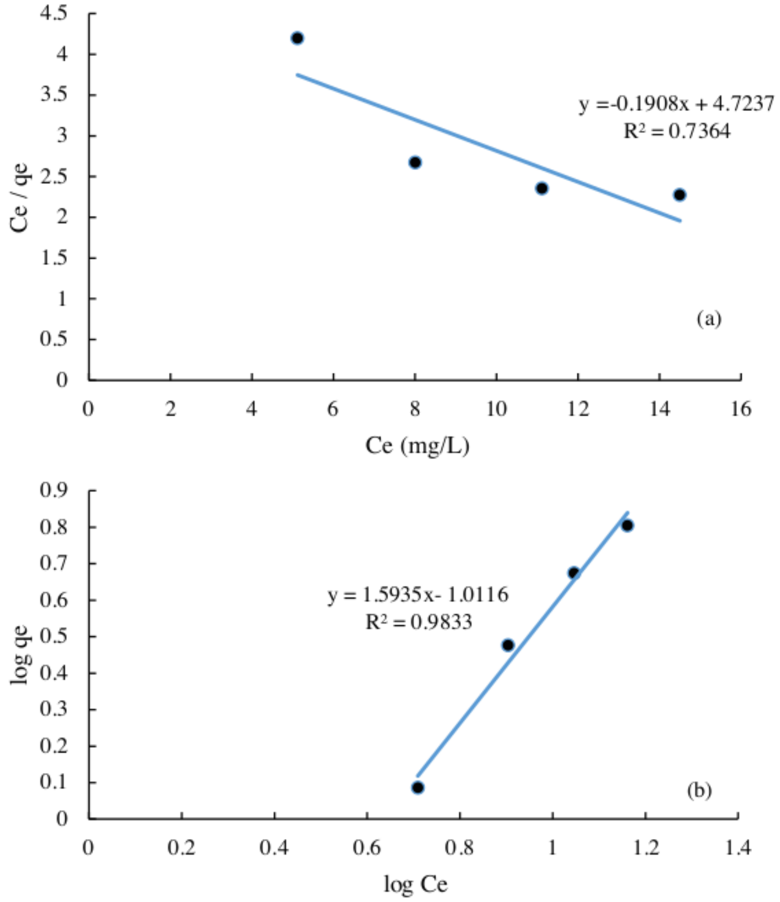

Figure 6. Adsorption isotherm (a) Langmuir and (b) Freundlich isotherm for Cr (VI) adsorption.

Table 1. Langmuir and Freundlich adsorption isotherm parameters.

Freundlich Isotherm			Langmuir Isotherm		
k_f (mg/g)	1/n	R^2	Q_0 (mg/g)	k_L (L/mg)	R^2
0.3895	1.5935	0.9833	5.2411	0.9013	0.7364

The results in Figure 7 show that the pseudo-second order kinetics represent the adsorption rate kinetics in this experiment. This can be seen from the coefficient of determination and the value of q_e. Table 2 shows that the pseudo-second order R^2 value is closer to 1 ($R^2 = 0.9878$) and is higher than the pseudo-first order ($R^2 = 0.2355$). In addition, the calculated q_e value for pseudo second order kinetics of 3.0211 g/mg is closer to the experimental q_e (2.820 mg/g). The results showed that the pseudo-second order adsorption mechanism was dominant. The rate of the adsorption process is controlled by sharing or exchanging electrons between sorbent and sorbate [25].

Removal of Cr (VI) by nonliving biomass occurs through two mechanisms, namely direct reduction and indirect reduction are presented in Figure 8 [26]. Based on this mechanism, Cr (VI) is reduced to Cr (III) by biomass in an acidic environment. Then some of the Cr (III) is adsorbed onto the biomass. The amount of adsorption depends on the nature of the biomass [27].

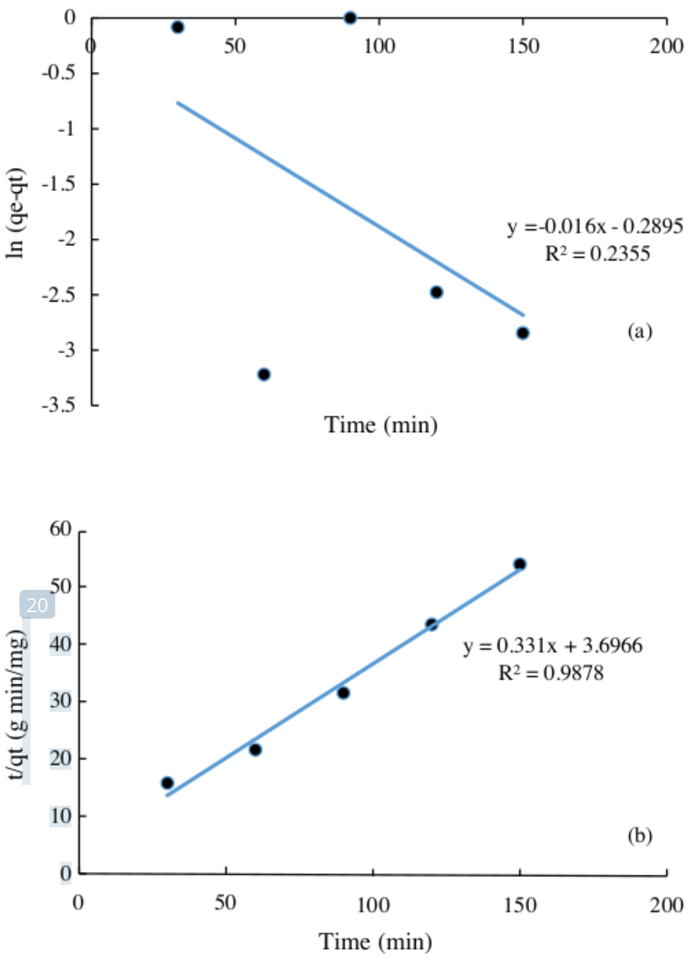

Figure 7. (a) Pseudo first order and (b) Pseudo second order Cr (VI) adsorption by Spirulina sp. immobilized silica gel.

Table 2. Predicted kinetic parameters for removal of Cr(VI).

Pseudo First Order				Pseudo Second Order			
$q_{e\ exp}$ (mg/g)	q_e (mg/g)	K_1 (1/min)	R^2	$q_{e\ exp}$ (mg/g)	q_e (mg/g)	K_2 (g/mg min)	R^2
2.8200	0.9841	0.2895	0.2355	2.8200	3.0211	0.0296	0.9878

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