The effect of pH, initial concentration, and salinity on the biosorption process of chromium (VI) ions using microalgae Chlorella sp.

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Abstract. The chromium (VII) (Cr⁶⁺) ions are carcinogenic substances, and thus the presence of these substances in water is hazardous for the environment and humans. Therefore, removing Cr⁶⁺ ions in water is required before the water is utilized or discharged into the environment. One of the processes that can be used is the biosorption process which involves microalgae as biosorbents. In this study, a synthetic solution of potassium dichromate (K₂Cr₂O₇) and living microalgae Chlorella sp. was applied in this experiment. The study focused on studying pH, initial solution concentration, and salinity level on removing Cr⁶⁺ ions from the solution. The pH of the solution was varied at 2–6; the initial concentration of the solution was varied at 10–50 ppm; while the salinity level was varied at 2,000–16,000 ppm. The biosorption process was carried out in a batch reactor for 48 hours using white light. Samples were taken and analyzed periodically using a UV-Vis spectrophotometer to determine the decrease of Cr⁶⁺ ions in the solution and a haemocytometer to calculate the number of microalgae in the system. The results showed that 91.79% of Cr⁶⁺ ions could be removed from the solution.

1. Introduction

The economic growth is increasing, supported by adequate technological advances. On the one hand, the current dynamics of national development contribute to improving the quality of life for the community. Still, on the other hand, it also raises concerns about the declining quality of life. This concern is quite reasonable because the reality shows that the environment in this country has not been spared from the threat of pollution due to industrial waste disposal by national industrial companies. Many cases of environmental pollution are caused by carelessness and negligence of the industry by disposing of waste that has not been treated carefully in places such as rivers that are still used by the community, such as the need for bathing, washing, and others.

One of the hazardous wastes is waste in the form of heavy metals. Heavy metals can generally be found in nature at appropriate levels and do not harm living organisms. However, heavy metals have an important role in human life and harm the environment if the level exceeds the designated standards. One of the dangerous heavy metals is chromium (Cr). This metal is generally found in the form of compounds. This metal can be found in aquatic and soil environments. The source of this metal entry generally comes from industrial activities, especially the metal coating industry and the leather tanning industry, combustion, and mobilization of fuels [1]. Chromium is a metal that has high toxicity. The valence of the ion determines the toxicity of this metal. A Cr⁶⁺ ion is a form of heavy metal that is often studied for its toxic properties. The toxic nature of this metal can lead to chronic, acute, and carcinogenic poisoning [2]. Cr⁶⁺ ions are more dangerous and toxic in water than Cr³⁺ ions. The Cr⁶⁺ ion is very active,
and its toxicity will work as a barrier to enzyme work in physiological or metabolic processes of the body. The Cr\(^{6+}\) ion in the body’s metabolism will inhibit the work of the benzopyrene hydroxylase enzyme, which results in changes in cell growth, causing cells grow wildly or known as cancer. This is the basis for classifying chromium metal into a carcinogenic metal group [1].

The wastewater produced in the metal plating industry contains Cr\(^{6+}\) ions in the concentration range of 1–40 ppm (or mg/L) before processing [3]. Meanwhile, the waste generated from the leather tanning industry can contain as much as 100–400 mg/L of chromium [4]. Many conventional methods have been used to treat chromium waste, including chemical precipitation, ion exchange, reverse osmosis, and solvent extraction [5–7]. These techniques are quite expensive and have several drawbacks, including incomplete removal of the chromium ion, requiring many reagents and energy, and producing toxic sludge or other waste products that require separate disposal systems. Therefore, an efficient and environmentally friendly method is needed to reduce the levels of chromium compounds in the waste.

One alternative to the treatment of waste containing heavy metals is the use of biological materials as adsorbents. This process is then referred to as biosorption. Biosorption is one of the alternative methods of biological waste treatment that is still rarely found in Indonesia, so a deeper understanding and study of this process is needed. Biological materials used in the biosorption process include bacteria, fungi, and algae in removing heavy metals in industrial waste. Biosorption is an option that should be taken into account because it has many advantages such as low operating costs, minimum use of chemicals, not producing sludge, and high efficiency [8]. In addition, with the biosorption process, the used biological materials can be reused.

This study focuses on the adsorption process using the microalgae Chlorella sp. This process is applied to synthetic wastewater containing Cr\(^{6+}\) ions. Several parameters affecting the biosorption process, such as solution pH, initial concentration of the solution, and salinity were studied.

2. Materials and method

2.1. Material
Chlorella sp. was obtained from the Center for Study of Water Technology and Waste Management, Parahyangan Catholic University, Indonesia, Walne and F/2 medium as a source of nutrients, K\(_2\)Cr\(_2\)O\(_7\) solution as synthetic waste, Reverse Osmosis (RO) water, HCl, NaOH, H\(_2\)SO\(_4\), 1,5-diphenylcarbazide, and acetone.

2.2. Biosorption process
This study was carried out using a series of equipment consisting of an Erlenmeyer as bioreactor, LED lamp, and aerator. The biosorption process begins by making a solution of chromium metal with various concentrations of 10, 20, and 30 mg/L. Salinity was adjusted by using NaCl with variations of 2,000; 9,000; and 16,000 mg/L. The pH of the solution was varied with values of 2, 4, and 6 at room temperature. Nine hundreds fifty (950 mL) of chromium metal ion solution was then mixed with 50 mL of microalgae at 100,000 cells/mL in an Erlenmeyer, then was sampled periodically at 0, 1, 2, 4, 6, 24, 30, and 48 hours. The liquid phase from sample was separated first and analyzed using a UV–vis spectrophotometer so that the remaining Cr\(^{6+}\) ions content was known.

2.3. Cell density analysis
The density of microalgae Chlorella sp. was calculated using a haemocytometer. Microalgae density was measured daily and plotted in a graph of microalgae cell density against time. The formula for calculating the density of microalgae cells is as follows.

\[
\text{Number of cells} = \frac{x}{80} \times 10,000 \text{cells/mL} \quad (1)
\]

where \(x\) is the number of cells counted in the haemocytometer.
3. Result and discussion

3.1. The effect of pH on the biosorption process of chromium (VI) ions

The first parameter studied in this study is the pH of the solution. This parameter can affect the process of biosorption and the metabolism of microalgae growth of Chlorella sp. The pH variations used in this study were 2, 4, and 6. This condition was chosen for this experiment because, on that pH range (acid condition), chromium (VI) (Cr$^{6+}$) ions will be more stable in solution. Under that condition, the chromium ions will be in CrO$_4^{2-}$ or Cr$_2$O$_7^{2-}$ [9]. Other conditions in this study were maintained at the initial concentration of 30 ppm and salinity of 2,000 ppm. The experimental results are presented in figure 1.

Figure 1. The effect of pH on the biosorption process of Cr$^{6+}$ ions at the initial concentration of 30 ppm and salinity of 2,000 ppm.

Figure 1 shows that the chromium ions biosorption process will run optimally at pH 2. This can be seen from the number of Cr$^{6+}$ ions adsorbed at pH 2 compared to pH 4 and 6. Under these conditions, Cr$^{6+}$ ions can be adsorbed as much as 4.17 ppm or about 14% for 48 hours the process takes place. Thus, the conditions that occur in this study are in line with the study conducted by [10].

Low pH conditions cause the surface of microalgae (cells and/or biomass) as a whole to be positively charged. Therefore, it will affect the biosorption process, both in the active and passive uptake stage. In the active uptake stage, acidic conditions will make it easier for both anions, CrO$_4^{2-}$ or Cr$_2$O$_7^{2-}$, to enter microalgae cells [9]. Meanwhile, functional groups present on the cell surface in the passive uptake stage, such as amine, amide, and carbonate groups, will be protonated. It will interact with chromium ions in the form of Cr$_2$O$_7^{2-}$ and CrO$_4^{2-}$ ions.

3.2. The effect of initial concentration on the biosorption process of chromium (VI) ions

One of the important parameters that need to be studied for the biosorption process is the initial concentration of synthetic wastewater. In this study, the initial concentrations were varied by 10, 20, and 30 ppm. The conditions used are classified as low concentration solutions, because the biosorption process using microalgae is very suitable for that type of solution. On the other hand, high concentration of the solution will make it difficult for microalgae to survive. Other operating conditions, such as pH and salinity, were maintained constant at pH 2 and 2,000 ppm, respectively. The experimental results are presented in figure 2.
Figure 2. The effect of initial concentration on the biosorption process of Cr\textsuperscript{6+} ions at pH of 2 and salinity of 2,000 ppm.

Figure 2 shows that the initial concentration of the solution affects the chromium ions biosorption process where at an initial concentration of 20 ppm, microalgae can remove the most chromium ions, which is 8.90 ppm. However, when viewed from the efficiency of chromium ions uptake, concentration of 10 ppm was the best concentration because it was able to remove chromium ions from the solution by 80.19%. The chromium ion removal efficiency for concentrations of 20 and 30 ppm was only about 44.52 and 13.89%, respectively.

Figure 3. The effect of initial concentration on the growth of microalgae *Chlorella* sp. at pH of 2 and salinity of 2,000 ppm.

The results showed that at high concentrations, the biosorption process was not optimal. This is related to the number of microalgae formed during the biosorption process. Figure 3 shows the results of the calculation of cell density in the biosorption system. Based on that figure, the lowest microalgae density was achieved when the highest solution concentration was used. The density of microalgae cells at a solution concentration of 10 and 20 ppm increased significantly compared to 30 ppm. The increase in cell density at both concentrations can reach 6-8 times compared to cell density at high concentrations when the process lasts for 30 hours. The small number of microalgae formed at this high concentration causes the equilibrium of the biosorption process to be achieved more quickly. This phenomenon is evident in figure 2, where there is no longer an increase in the adsorbed chromium ion between 30 and 48 hours. Even though there are not many microalgae in the system, at the initial concentration of 30 ppm, the biosorption can still take place because the passive uptake stage dominates the mechanism of the biosorption process.
3.3. The effect of salinity on the biosorption process of chromium (VI) ions

As previously explained, this biosorption process's success depends on the growth and number of microalgae in the system. Thus, efforts to multiply microalgae need to be studied. One of the factors that influence microalgae's growth process is the salinity of the solution. In this study, salinity was studied at variations of 2,000, 9,000, and 16,000 ppm. The experimental results are presented in figure 4.

![Figure 4](image)

**Figure 4.** The effect of salinity on the biosorption process of Cr\(^{6+}\) ions at pH of 2 and initial concentration of 10 ppm.

The experimental results show that the higher the salinity of the solution, the better the biosorption process will run. In this study, a salinity level of 16,000 ppm was able to adsorb chromium ions until the remaining chromium ion concentration was 0.82 ppm or 91.79% chromium ions were adsorbed. Increasing salinity will increase the electrical conductivity in the system [10]. Furthermore, a study conducted by Sibi [10] revealed that under conditions of high electrical conductivity, the ability of microalgae to reduce chromium metal would increase so that the effectiveness of removing chromium ions would also increase.

![Figure 5](image)

**Figure 5.** The effect of salinity on the growth of microalgae *Chlorella sp.* at pH of 2 and initial concentration of 10 ppm.

Another thing that causes the biosorption process to get better along with the increase in salinity is the increasing number of microalgae. Figure 5 proves this statement. Salinity affects osmotic pressure and osmoregulation mechanisms directly. As a result, the metabolic process will be affected so that the growth of the microalgae population will improve.
4. Conclusion
The process of chromium ions biosorption using microalgae is influenced by several parameters, such as the pH of the solution, the initial concentration of the solution, and salinity. These three parameters are related to the growth process of the microalgae *Chlorella sp.* so that through the active and passive stages of uptake, the biosorption process will occur. In this study, the lower the pH of the solution and the initial concentration of the solution is, the more efficient the removal of chromium ions will be. On the other hand, increasing salinity in the solution will make more chromium ions adsorbed. The biosorption process that has been carried out shows that the operating conditions that provide the greatest chromium ion removal efficiency are achieved at pH 2. The initial concentration of the solution is 10 ppm, and the salinity is 16,000 ppm. In this condition, the chromium removal efficiency was 91.79%.

5. Reference
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