Cr^{6+} Metal Ion Adsorption Using Acetobacter xylinum Cellulose

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Cr^{6+} is a metal produced from industrial waste which has a negative impact on the environment. This metal when exposed to the human body can cause acute, chronic poisoning and can cause cancer. One alternative solution in water treatment is adsorption using materials from cellulose. The adsorption process carried out in this study uses Acetobacter xylinum cellulose. The purpose of this study was to determine the ability of cellulose Acetobacter xylinum to adsorb Cr^{6+} heavy metals. The research method used is comparative descriptive research. The water sample used is water from the Citarum river with high levels of Cr^{6+} metal pollution. The results obtained are the levels of Cr^{6+} in river water can be reduced by the adsorption process using cellulose *Acetobacter xylinum*. As for the decrease in the amount of heavy metal Cr^{6+} with the amount of biomass of 5 g by 0.06 ppm, biomass by 6 g by 0.07 ppm and biomass by 7 g by 0.23 ppm. Based on the results of the study showed cellulose *Acetobacter xylinum* can be used as a fairly effective biosorbent.

Keywords: *Heavy metal Cr^{6+}, adsorption, Acetobacter xylinum, Acetobacter xylinum, UV-Vis spectrophotometer.*

Introduction

Industrial development in the era of globalization has an important role for human life, but can also have a negative impact on the environment (Lapik, 2017). Disposing of untreated wastewater is one of the negative impacts of uncontrolled industrial development. Whereas related to waste management obligations already stated in the Government Regulation of the Republic of Indonesia Number 82 Year 2001 regarding Management of Water Quality and Water Pollution Control in article 36 it is mentioned that the study of the impact of waste water disposal is an obligation of the waste producing industry. Waste is simply called the result of dump or stacked waste which in chemical language is called pollutant. Based on its type, waste is grouped into solid, liquid, gas and sound waste. However, based on the source, waste is grouped into industrial waste (effluent) and household waste or domestic sewage. Generally waste disposal is directly discharged or flowed into the river (Setiawan, 2018). The easiest way for naughty industries to handle the waste produced is to dump it directly into the river.

Therefore, industrial waste can be said as one of the most common sources of environmental pollution.

The river is a large, elongated water that flows continuously, often used by living things in this world to fulfill various activities (Andini, 2017). However, today the river has begun to be polluted, mainly by waste products, industrial activities. One of the rivers polluted by industrial waste in Indonesia is the Citarum river. The Citarum River is a very important river for some people who still use the river water, but the Citarum River looks dirty and is no longer suitable for use. The Citarum River is known as the dirtiest river in Indonesia (Sastrianegara, 2018). Even though this river is a source of clean water for residents and also irrigates 420,000 ha of rice fields and generates 2,880 MW of electricity for Java and Bali. The World Bank also declared Citarum as one of the dirtiest rivers in the world, a decade ago (Andina, 2018). Until now, the nickname is still used to describe Citarum.

There are several factors that cause water pollution in the Citarum river, including the large number of houses on the riverbanks making household waste automatically disposed of into the river (Abdussalam, 2018). Industrial waste also participated in polluting the river with a length of about 300 km. Furthermore, livestock and fisheries waste. There are around 1,900 industries around the Citarum watershed. As many as 90% of them turned out to be inadequate Wastewater Treatment Plant. In addition, the Citarum river is also polluted by domestic waste generated by the community, starting from household waste of 20,462 tons / day, 71% of which are not transported to the final landfill. As many as 35.5 tons / day of human waste and 56 tons / day of animal / livestock manure are also discharged directly into the Citarum river.

Industrial waste is also called B3. According to Indonesian Government Regulation No 74 of 2001 Article 1 Paragraph 1, B3 is a material that can endanger the environment, health, survival of humans and other living things. B3 waste has toxic properties that can be toxic. One of the B3 wastes which can be toxic is for example metal hexavalent chromium (Cr^{6+}). Cr is present in rocks, soil, animals and plants. Cr^{6+} and Cr^{3+} are the most stable forms and their exposure to humans is higher (Adhani and Husaini, 2017). Cr^{3+} is an essential essential micronutrient, needed by the body to increase insulin efficiency and can settle to the surface of minerals. While Cr^{6+} is toxic with a carcinogenic effect with toxicity 100x higher than Cr^{3+} (Lapik, 2017). In the Decree of the Minister of Environment numbered Kep 03 / MENKLH / 11/1991 it is stated that the maximum level of total chrome allowed in the waters is 0.1 ppm while the levels of Cr^{6+} 0.05 ppm. In industrial activities, Cr is used for the process of leather coloring, textile manufacturing, chemical concentration, or chrome plating (Wires, 2012).

Handling of waste water that is disposed of should be done through WWTP (Wastewater Treatment Installation), but the fact is that very rarely industries that have WWTP, especially industries with medium to lower scale. So that their waste water is not managed properly and immediately discharged into the drainage that is directly connected to the river. Usually, the handling of metal waste is mostly carried out using membrane separation, cation exchange, chemical precipitation and electro deposition. Alternative processing using membrane separation processes generally use conventional adsorbents such as zeolite, silic gel, bentonite, activated carbon and graphite. The use of adsorbents has good adsorption ability but is a non-renewable natural resource and the price is quite expensive. Currently alternative research is being promoted that comes from nature, because in addition to having good adsorption ability, the adsorbent is also a renewable natural resource (Agustien, 2014). The adsorption process using this type of adsorbent is usually called biosorption. Biosorption is a term used to describe the removal of heavy metals through passive binding to plant biomass or non-living microorganisms from their solution in water (Lapik, 2017; Abdi and Kazemi, 2015). One alternative treatment can use cellulose raw materials sourced from *Acetobacter xylinum*. The manufacturing process that is easy and inexpensive and is biogradable (can be broken down by microbes) is an advantage of these adsorbents. So that the use of cellulose can be used as an alternative method for the lower middle industries in managing metal waste. Based on such characteristics, it is necessary to conduct further research on the ability of cellulose adsorption on Cr^{6+} metal.

Research Method

This type of research is comparative descriptive, can be defined as a study conducted to describe or describe a phenomenon (Notoatmodjo, 2012; Sugiyono, 2017). This research was conducted to obtain information about the ability of cellulose biosorbent Acetobacter xylinum to adsorb Cr^{6+} metal ions. Samples were obtained from Citarum river water around the dense textile industry area so that the Cr^{6+} concentration would be high. This research was conducted in several stages, namely the preparation of Acetobacter xylinum cellulose adsorbents, river water sampling, standard curve making, and sample measurement.

Preparation of Acetobacter xylinum Cellulose Adsorbents

A total of 10 kg of cellulose *Acetobacter xylinum* is washed and blended until the particle size is homogeneous. This is done to enlarge the contact surface area so that the adsorption process will be faster. Cellulose is dried using an oven at 80 ^{0}C to remove the water content in it.

River Water Sampling

River water sampling is done at a depth of one meter and two meters, then put together in a container with a volume of 500 mL. This was done to obtain a comprehensive Cr^{6+} concentration in river water. To the container is added a solution of HNO3 so that the pH of the water becomes acidic.

Making a Standard Curve

Making curves is done by making five $K_2Cr_2O_7$ solutions with concentrations of 0.3 ppm, 0.6 ppm, 0.9 ppm, 1.2 ppm and 1.5 ppm respectively. To each of these solutions 1.5 added diphenyl carbazide was added. Each absorbance was measured using a UV-Vis spectrophotometer at a wavelength of 525 nm.

Measurement of Cr^{6+} Concentration Before Adsorption in Samples

Water samples are filtered to separate the impurities. The filtrate is produced in a centrifuge for 15 minutes and the supernatant is put into a beaker. As much as 2.5 mL supernatant was added with 1.5 diphenyl carbazide solution and the absorbance was measured using a UV-Vis spectrophotometer.

Measurement of Cr^{6+} Concentration After Adsorption in Samples

The supernatant water sample is put into three beakers with each volume of 100 mL. Into the first beaker 5 grams of cellulose Acetobacter xylinum, into the second beaker 6 grams of cellulose *Acetobacter xylinum*, and 7 grams of cellulose *Acetobacter xylinum* inserted. The three beakers are stirred for 1 minute and filtrated. The filtrate is centrifuged for 15 minutes. 2.5 mL supernatant from the first, second, and third beaker was added with a solution of 1.5 diphenyl carbazide and the absorbent was measured using a UV-Vis spectrophotometer.

Results and Discussion

Standard Curves

Making a standard curve is done to obtain a straight line equation that can be used to determine the concentration of Cr^{6+} in the sample. Curves are created by plotting the concentration and absorbance data of each standard solution. The absorbance measurement data can be seen in Table 1.

Table 1. Absorbance Value of Cr^{6+} Standard Solution

Consentration of Cr^{6+} (ppm)	Absorbance
0,3	0,631
0,6	0,74
0,9	0,832
1,2	0,949
1,5	1,076

The data in Table 1 can be plotted to form curves and obtain line equations. Standard solution curves can be seen in Figure 1. Based on the data in Figure 1, the equation of the line y = 0.3663x + 0.5159 is obtained. This line equation will be used to determine the concentration of Cr6 + in the sample. Correlation coefficient values indicate a strong relationship between solution concentration (x axis) and absorbance (y axis). The ideal linear relationship is achieved if $R^2 = 1$ or $R^2 = -1$ (Hasmita in Saputra 2016). The regression coefficient value obtained is $R^2 = 0.9968$, this means the value of R^2 is close to ideal and the equation can be used.

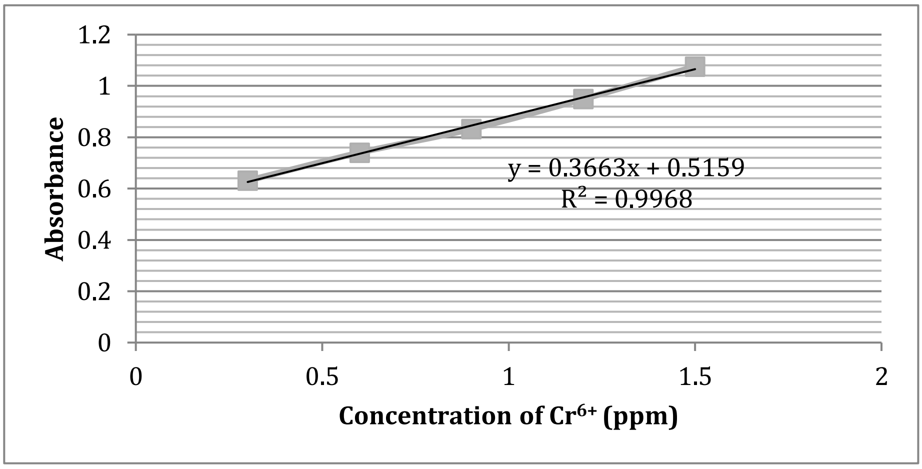

Figure 1 Standard Curve of Cr^{6+} Solution

Measurement of Cr^{6+} Concentration in Samples

Cr^{6+} concentration measurements were carried out in two stages, namely before adsorption and after adsorption. This was done to see the ability of cellulose *Acetobacter xylinum* to adsorb

Cr^{6+} metal. Detailed data from the measurement results can be seen in Table 2. The decrease in Cr^{6+} concentration is proportional to the increasing number of cellulose Acetobacter xylinum used as an adsorbent.

Table 2 Cr^{6+} Metal Concentration Test Results at Various Adsorbent Concentrations

Consentration of Cellulose (g)	Initial Cr^{6+} Concentration (ppm)	Final Cr^{6+} Concentration (ppm)	Decreased Concentration of Cr^{6+} metals (ppm)	Percentage of Decrease (%)
5	1,31	1,25	0,06	4,58
6		1,24	0,07	5,34
7		1,08	0,23	17,55

The biosorption process in this study was based on the amount of variation in the concentration of cellulose used. Judging from the results of the levels before biosorption and after being biosorption, also seen how much the amount of cellulose in the Cr6 + metal decreases. In addition, the pH of the solution must also be considered, in this case the 3-5 pH is the ideal pH. The bond between the function group of the biomass protein and the metal ion involves replacing the proton so that the pH value must match, so that the absorption process can take place optimally. The pH value above the isoelectric point causes a negative charge on the cell wall components and the state of the ligand ion, such as carboxyl, aminone and phosphate groups. Conversely, if the pH is below the isoelectric point, the cell surface charge becomes positive so that it inhibits the approach of cations made by Lapik (2011). According to Agustien (2014), cellulose Acetobacter xylinum has a functional group involved in the process of adsorption of heavy metals, namely the amine C-O and C-N functional groups. This is because free electrons C-O and C-N nitrogen can form coordination bonds with heavy metals. The coordination bond is marked by the reaction equation, $R\text{-}COO^- + Cr^{6+} \rightarrow (R\text{-}COOCr)^{5+}$.

Conclusion

Based on the research that has been done, it can be concluded that Acetobacter xylinum cellulose has the ability to absorb Cr^{6+} metal. With the appropriate amount of cellulose *Acetobacter xylinum* and pH, the adsorption process will be maximal. Based on the results of research, cellulose Acetobacter xylinum can be used as a biosorbent to reduce Cr^{6+} levels properly.

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