Chromium(VI) Heavy Metal Biosorption in Citarum River Water Sample Using Saccharomyces cerevisiae and Rhizopus oryzae Biomass

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ABSTRACT. The Citarum River was regarded as the World’s dirtiest river in 2018, characterized by a Basin situated adjacent to several textile and electroplating industries. Hexavalent chromium metal (Cr\(^{VI}\)) is a toxic, carcinogenic heavy metal found in the wastes of these industries. Furthermore, biosorption with biological adsorbents, including Saccharomyces cerevisiae and Rhizopus oryzae, is an alternative method for treating water polluted with heavy metals. This study therefore aims to adsorb Cr\(^{VI}\) heavy metals from Citarum River water using S. cerevisiae and R. oryzae biomass in two locations: Nanjung and Pangauban, with various biomass concentration and stirring speeds. For this study, 0.25, 0.5, and 0.75 g of R. oryzae suspension, as well as 250, 500, and 750 µ of S. cerevisiae were used as adsorbent, while rotated at speeds of 250 rpm, 750 rpm and 1500 rpm. Subsequently, the Cr\(^{VI}\) metal content was measured using a UV-Vis spectrophotometer at a wavelength of 525 nm, and calculated based on a standard curve. The results showed S. cerevisiae and R. oryzae are able to reduce the levels of Cr\(^{VI}\) in Citarum river water. The most reduction was obtained with the highest concentration of the adsorbents, 750 µ for S. cerevisiae and 0.75 g for R. oryzae, at the speed of 1500 rpm. S. cerevisiae and R. oryzae have great potential as biosorbents for the in situ remediation of Citarum River contaminated with heavy metals.

Keywords: biosorption; Cr\(^{VI}\) heavy metal; Nanjung; Pangauban; UV-Vis spectrophotometer

INTRODUCTION

The industry 4.0 era led the government to expand the industrial sector, and the textile industry has been discovered to increase in number each year. According to the BPS Jawa Barat (2016), there were about 1062 textile companies within West Java, and most of these companies were located near Bandung Raya. The growth surge experienced in this sector had numerous effects, including rising in production waste (Putra, 2017; Sumantri et al., 2018), often leading to environmental challenges. Furthermore, industrial waste management is habitually ignored by these companies, leading to damage to the surrounding environment. The Citarum River, in this instance, is exposed to hexavalent chromium (Cr\(^{VI}\)) waste.

The study by Komarawidjaja (2016), Putra (2017), Sihombing (2020) reported damage to the aquatic environment to be as a result of pollution by industrial & domestic waste in West Java, while Paramita (2017), Wardani (2018), Priyanto (2019) stated industrial effluents contain heavy metals and are therefore a major cause of water pollution. Textile, electroplating, dyeing, and photographic industries pollute water bodies with Cr\(^{VI}\), and this leads to acute poisoning (Zewail & Yousef, 2014; Kim & Kang, 2016), including vomiting (Kozlowski et al., 2014; Vellaichamy et al., 2017), diarrhea, and indigestion (Jabbo et al., 2016; Igberase et al., 2018; Li & Han, 2019), as well as chronic poisoning, including skin and mucous membrane irritation (Ayob et al., 2016; Fasya, 2018), kidney and liver disorders, leading to lung cancer in industrial workers exposed to chromium (Kozlowski et al., 2014; Proctor et al., 2014; Das et al., 2015).

Industrial waste management is a complicated and expensive process. As a result, the government took action and developed a method to combat pollution degrading the Citarum River water quality. Thus, the LIPI (2019) designed a simpler and faster technique of monitoring the content of textile dyes to reduce the monitoring cost and the results
obtained are of both national and international standards.

Biosorption is a safe, cost-effective alternative for increasing the Citarum River water quality. Furthermore, the technique has a higher metal binding capacity (Chatterjee et al., 2010; Chojnacka, 2010), generates less deposit, recover it into less hazardous forms (Kılıç et al., 2014; Ayangbenro & Babalola, 2017), and utilizes widely available and reusable raw materials (Gürel, 2017; Escudero et al., 2019).

These benefits trigger the increasing efforts to clean water bodies exposed to metal ion waste and encourage further research in order to develop even cheaper, more effective, and efficient wastewater treatment techniques. Utilizing biosorption technique with biological materials is therefore a decent alternative for industrial waste management. Biomaterials, including algae (Son et al., 2018; Ameri et al., 2020), coconut and rice husk (Anirudhan et al., 2011; Gupta et al., 2011; Xu et al., 2013), also filamentous fungi (Dhanakhar & Hooda, 2011; Siddiquee et al., 2015), are effective heavy metal ions adsorbents and have been proven to possess maximum metal-ion absorption capacity.

The benefits of using microorganisms as biosorbents include low operational cost, efficient, high metal binding capacity, minimum deposits, reusability, ubiquity (Bakircioğlu et al., 2011; Abbas et al., 2014; Xie et al., 2020). In fact, Saccharomyces cerevisiae and Rhizopus oryzae is an effective microorganism for biosorption (Fu et al., 2012; Gharieb et al., 2014; Farhan & Khadom, 2015; Tahir et al., 2017; do Nascimento et al., 2019). Sources of S. cerevisiae include natural cultures, bioethanol plant waste and industrial waste containing carbon (Sathvika et al., 2018; Favaro et al., 2019). S. cerevisiae is also a potential material for effective absorption of heavy metals, as a result of the high percentage of cell wall material, serving as binding sites.

This study utilizes S. cerevisiae and R. oryzae for biosorption because the microorganisms’ cell walls are composed of polysaccharides, proteins, lipids, chitin, and chitosan, with carboxylate, hydroxyl, sulfate, phosphate and amino functional groups. In addition, monovalent and divalent ions, including Na+, Mg2+, and Ca2+, are present. These functional groups, particularly carboxylates and amines, are able to bind the metal ion Cr6+, consequently, enabling S. cerevisiae and R. oryzae to function effectively during biosorption. Meanwhile, stirring process is carried out to evenly distribute the biosorbents distributed, leading to maximum adsorption power. Stirring also helps to continuously renew the biosorbent interface concentration gradient using bulk biosorbent, hence, maintaining the adsorbent process.

**MATERIALS AND METHODS**

**Physical and chemical test of Citarum River water samples.** The samples collected from Citarum River in two locations including Nanjung and Pangaugban village. A total of 2 ml of H2SO4 and 0.5 ml 1.5-diphenylcarbazide are added to the Cr6+ standard solution (Lazo, 2009; Rice et al., 2017).

**Rejuvenation and production of Saccharomyces cerevisiae and Rhizopus oryzae.** A total of 0.25, 0.5 and 0.75 g of R. oryzae suspension, as well as 250, 500 and 750 μ of S. cerevisiae were used as adsorbent, while rotated at speeds of 250 rpm, 750 rpm and 1500 rpm.

**Biosorption of Saccharomyces cerevisiae and Rhizopus oryzae.** The Cr6+ metal content was measured by UV-Vis spectrophotometer λ 525 nm. Subsequently, counting was performed using linear regression equation, with standard calibration curve (Zhang et al., 1998; Garg et al., 2007; Stănilă et al., 2015).

**RESULTS AND DISCUSSION**

The concentration of Cr6+ are rather low, thus, the standard calibration curve of Cr6+ solution was reconstructed using a narrower concentration range.

Meanwhile, the standards were measured with a UV-Vis spectrophotometer, at a wavelength of 525 nm. The result (Table 1) showed an increase in standard solution’s concentration, indicating a rise in absorbance.
This is then translated into a calibration curve, using the linear equation $y = ax + b$, where $y$ denotes absorbance value and $x$ signifies concentration. The absorbance of standard solution was then used to determine the sample’s concentration. Fig. 1 dan Fig. 2 shows the calibration curve obtained.

Subsequently, the equation, $y = 0.1163x + 0.0723$, was applied to determine the levels of $\text{Cr}^{6+}$ after biosorption with *Rhizopus oryzae* (Fig. 2).

![Calibration curve for $\text{Cr}^{6+}$](image)

**Fig. 1.** Calibration curve for $\text{Cr}^{6+}$ λ 525 nm with *Saccharomyces cerevisiae*.

The first data and final of biosorption rate using *Saccharomyces cerevisiae* and *Rhizopus oryzae* showed in Table 2 and Table 3. The results presented in Table 2 shows that the highest adsorption was exhibited by 750 µ of *Saccharomyces cerevisiae* in Nanjung and Pangauban village, while the concentration of $\text{Cr}^{6+}$ was reduced less using 250 µ and 500 µ of *S. cerevisiae*.

According to Table 3, the concentration of $\text{Cr}^{6+}$ was discovered to reduce after the adsorption process, and this reduction was observed with an increase in biomass. The highest adsorption was exhibited by 0.75 g of *Rhizopus oryzae* as the biosorbents in both Nanjung and Pangauban village. This indicates an increase in the number of fungi cell wall binding sites leads to increased $\text{Cr}^{6+}$ biosorption. Bennett *et al.* (2013) stated that the majority of the cell wall binding sites were negatively charged, thus the positively charged $\text{Cr}^{6+}$ was attracted to $-\text{OH}$ and $\text{C}=\text{O}$ binding groups which responsible for the adsorption within the fungi biomass. In line with Luo *et al.* (2010), Xu *et al.*, (2012), Espinoza-Sánchez *et al.* (2019) that *Rhizopus* sp. presented biosorption capacities of dry biomass for $\text{Cr}^{6+}$.

### Table 1. Standard calibration curve of $\text{Cr}^{6+}$.

| Concentration (mg/L) | Absorbance |
|----------------------|------------|
| 0.3                  | 0.174      |
| 0.6                  | 0.293      |
| 0.9                  | 0.403      |
| 1.2                  | 0.531      |
| 1.5                  | 0.621      |

### Table 2. The biosorption rate using *Saccharomyces cerevisiae*.

| Location                  | Data          | Biomass 250 µ | Biomass 500 µ | Biomass 750 µ |
|---------------------------|---------------|---------------|---------------|---------------|
|                           |               | Low | Med | Hi  | Low | Med | Hi  | Low | Med | Hi  |
| Citarum River in Nanjung | Absorbantion | 0.931| 0.53 | 0.690 | 0.657 | 0.547 | 0.543 | 0.531 | 0.465 | 0.460 | 0.409 |
| Village                   | Concentration (mg/L) | 1.679 | 0.584 | 1.021 | 0.931 | 0.631 | 0.620 | 0.587 | 0.407 | 0.393 | 0.254 |
| Citarum River in Pangauban Village | Absorbantion | 0.883 | 0.46 | 1.603 | 0.597 | 0.518 | 0.512 | 0.494 | 0.413 | 0.439 | 0.476 |
|                           | Concentration (mg/L) | 1.548 | 0.393 | 3.514 | 0.767 | 0.552 | 0.535 | 0.486 | 0.265 | 0.336 | 0.437 |
The optimum percentage reduction in Cr\textsuperscript{6+} concentration, for the sample obtained from Nanjung village, at the highest stirring speeds, were 84.872\%, and 85.998\%, using 750 µ of \textit{S. cerevisiae}, and 0.75 g of \textit{R. oryzae} respectively. As biosorbent mass increases, the percentage efficiency and competitive of the adsorption process also increases due to the rise in the number of available heavy metal binding sites on the biosorbent’s surface (Li \textit{et al.}, 2016; Mahmoud & Mohamed, 2017). Furthermore, stirring helps to renew the concentration gradient of the biosorbent interface with bulk biosorbate, hence, biosorption occurs continuously. Therefore, an increase stirring speed enlarges the contact zone between the biosorbent and bulk biosorbate.

Based on QS. Ali ‘Imran verse 91 (Kementerian Agama RI, 2019a) that the sky and the earth and all living things on earth are signs of the existence and greatness of Allah swt. to create everything with a specific purpose, nothing is in vain. As intelligent creatures, humans are given the ability to take advantage of the universe and its contents for benefit. One illustration of the use of living things created by Allah swt. namely the use of microorganisms from the fungal group, namely \textit{Saccharomyces cerevisiae} and \textit{Rhizopus oryzae}, as biological agents for the biosorption process. The use of these two microorganisms is a lesson for us always to benefit others and the environment. \textit{Saccharomyces cerevisiae} and \textit{Rhizopus oryzae} with a tiny size can help for the biosorption process, reducing the environmental pollution. Humans should not only be the cause of earth damage, as described in QS. Ar-Rum verse 41 (Kementerian Agama RI, 2019b) but must be a true caliph who has been given a mandate by Allah swt. to provide suitable for the universe, who is responsible for himself, fellow humans, and the ecosystem or environment as implied in QS. Al-Ahzab verse 72 (Kementerian Agama RI, 2019c). Human life cannot be separated from various environmental components. Humans are responsible for maintaining the continuity, balance, and preservation of the environment, which is their life source.

**CONCLUSION**

Chromium(VI) levels in Citarum River water in is decreased by biosorption with \textit{Saccharomyces cerevisiae} and \textit{Rhizopus oryzae}. The optimum percentage reduction in Cr\textsuperscript{6+} concentration obtained, were 84.872\%, and 85.998\%, using 750 µ of \textit{S. cerevisiae} suspension, and 0.75 g of dry residue of \textit{R. oryzae}, respectively. \textit{S. cerevisiae} and \textit{R. oryzae} have great potential as biosorbents for the \textit{in situ} remediation of Citarum River contaminated with heavy metals.

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