

## 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 ( $\text{Cr}^{6+}$ ) 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  $\text{Cr}^{6+}$  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  $\mu$  of *S. cerevisiae* were used as adsorbent, while rotated at speeds of 250 rpm, 750 rpm and 1500 rpm. Subsequently, the  $\text{Cr}^{6+}$  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  $\text{Cr}^{6+}$  in Citarum river water. The most reduction was obtained with the highest concentration of the adsorbents, 750  $\mu$  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;  $\text{Cr}^{6+}$  heavy metal; Nanjung; Pangauban; UV-Vis spectrophotometer

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### 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 ( $\text{Cr}^{6+}$ ) 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  $\text{Cr}^{6+}$ , and this leads to acute poisoning (Zewail & Yousef, 2014; Kim & Kang, 2016), including vomiting (Kozłowski *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 (Kozłowski *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 (Dhankhar & 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 (Bakircioglu *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  $\text{Na}^+$ ,  $\text{Mg}^+$ , and  $\text{Ca}^{2+}$ , are present. These functional groups, particularly carboxylates and amines, are able to bind the metal ion  $\text{Cr}^{6+}$ , 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 adsorption 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 Pangauban village. A total of 2 ml of  $\text{H}_2\text{SO}_4$  and 0.5 ml 1.5-diphenylcarbazine are added to the  $\text{Cr}^{6+}$  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  $\mu$  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  $\text{Cr}^{6+}$  metal content was measured by UV-Vis spectrophotometer  $\lambda$  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

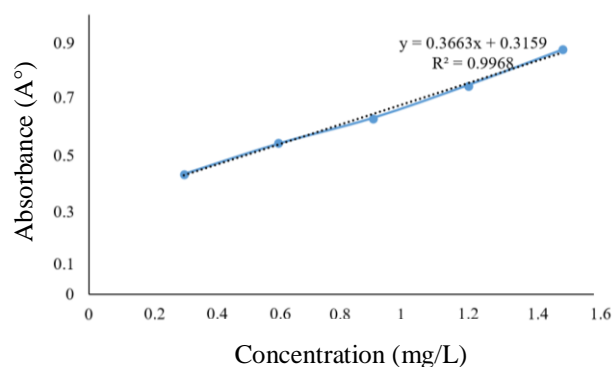
The concentration of  $\text{Cr}^{6+}$  are rather low, thus, the standard calibration curve of  $\text{Cr}^{6+}$  solution was reconstructed using a narrower concentration range.

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.

**Table 1.** Standard calibration curve of Cr<sup>6+</sup>.

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

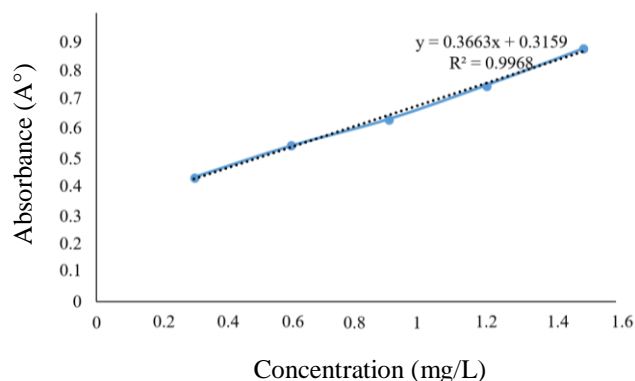
This is then translated into a calibration curve, using the linear equation  $y = ax + b$ , where  $y$  denotes absorbance value and  $x$  signifies concentration. The absorbance of standard solution was then used to determine the sample's concentration. Fig. 1 dan Fig. 2 shows the calibration curve obtained.

**Fig. 1.** Calibration curve for Cr<sup>6+</sup> λ 525 nm with *Saccharomyces cerevisiae*.**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 Village	Absorbantion (A°)	0.931	0.53	0.690	0.657	0.547	0.543	0.531	0.465	0.460	0.409
	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 (A°)	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

According to Table 3, the concentration of Cr<sup>6+</sup> 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 Cr<sup>6+</sup>

Subsequently, the equation,  $y = 0.1163x + 0.0723$ , was applied to determine the levels of Cr<sup>6+</sup> after biosorption with *Rhizopus oryzae* (Fig. 2).

**Fig. 2.** Calibration curve for Cr<sup>6+</sup> λ 525 nm with *Rhizopus oryzae*.

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, while the concentration of Cr<sup>6+</sup> was reduced less using 250 μ and 500 μ of *S. cerevisiae*.

biosorption. Bennett *et al.* (2013) stated that The majority of the cell wall binding sites were negatively charged, thus the positively charged Cr<sup>6+</sup> was attracted to -OH and C=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 Cr<sup>6+</sup>.

**Table 3.** The biosorption rate using *Rhizopus oryzae*.

Location	Data	Biomass 0.25 g			Biomass 0.50 g			Biomass 0.75 g		
		Low	Med	Hi	Low	Med	Hi	Low	Med	Hi
Citarum River in Nanjung village	Absorbantion (A°)									
	0.931	0.233	0.227	0.226	0.231	0.211	0.209	0.112	0.108	0.098
Citarum River in Pangauban village	Concentration (mg/L)									
	1.679	1.382	1.330	1.322	1.366	1.195	1.175	0.341	0.307	0.221
Citarum River in Pangauban village	Absorbantion (A°)									
	0.883	0.280	0.230	0.220	0.231	0.225	0.224	0.127	0.119	0.118
Citarum River in Pangauban village	Concentration (mg/L)									
	1.548	1.786	1.356	1.270	1.365	1.313	1.304	0.470	0.402	0.393

The optimum percentage reduction in Cr<sup>6+</sup> concentration, for the sample obtained from Nanjung village, at the highest stirring speeds, were 84.872%, and 85.998% , using 750 µ of *S. cerevisiae*, and 0.75 g of *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 *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 *Saccharomyces cerevisiae* and *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. *Saccharomyces cerevisiae* and *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 biosorbition with *Saccharomyces cerevisiae* and *Rhizopus oryzae*. The optimum percentage reduction in Cr<sup>6+</sup> concentration obtained, were 84.872%, and 85.998%, using 750 µ of *S. cerevisiae* suspension, and 0.75 g of dry residue of *R. oryzae*, respectively. *S. cerevisiae* and *R. oryzae* have great potential as biosorbents for the *in situ* remediation of Citarum River contaminated with heavy metals.

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