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Research Article

Immobilized algae for heavy metals remediation in textile wastewater

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Abstract. Textile wastewater has characteristics of concentrated color and containing high concentration of COD, BOD, N, P, and heavy metals. Some wastewater treatments have been developed for removal waste contaminant, especially heavy metal such as precipitation, evaporation, electroplating, ion exchange, and membrane process. These methods have disadvantages such as unpredictable of heavy metal, high reagent requirement, and generation of toxic sludge. Biosorption using immobilized algae give the alternative method to removal heavy metal in textile wastewater because of increased stability in the matrix. The main purpose of this research was to determine the adsorption of textile wastewater heavy metal using immobilized microalgae. The best ratio bead: wastewater (v/v) for removal heavy metal by immobilized microalgae of textile wastewater heavy metal in batch system was 1:3. Heavy metal Cu decreased as much as 89% with the highest final concentration of 0.2 ppm. Ability of *Chlorella vulgaris* and *Spirulina platensis* to reduce heavy metals Cr was 89% and 90% with a final concentration of 1.6 ppm and 1.5 ppm. Uptake heavy metal Cu and Cr of textile wastewater by *Chlorella vulgaris* reach 1.9 mg/g and 16.3 mg/g. Meanwhile for *Spirulina platensis* reach 1.7 mg/g and 14.7 mg/g. Based on the Langmuir equation, biosorption by *Chlorella vulgaris* have q_{max} and K_b value of heavy metal Cu was 1,984 mg/g and 0,014 mg/L. On heavy metal Cr, q_{max} and K_b value were 15.873 mg/g and 0.079 mg/L. *Spirulina platensis* have q_{max} and K_b value of heavy metal Cu were 1,798 mg/g and 0,014 mg/L. On heavy metal Cr q_{max} and K_b value were 14.925 mg/g and 0.0445 mg/L.

Keywords: biosorption heavy metal, immobilized microalgae, textile wastewater

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1. Introduction

The textile industry is one of the fastgrowing industries and plays a fairly important in Indonesia. Development is quite promising, which reached 1.48% per year (KEMENPERIN, 2013). It also marks an increase in the risk of environmental damage caused by waste disposal, especially if the waste is not handled properly (Sharma et al., 2023). Textile wastewater color intensity ranges from 50-100 mg/L and BOD and COD values in a row 80-6000 mg/L and 150-12000 mg/L (Holkar et al., 2016). COD and BOD parameter value is very far above the water quality standard threshold of textile industry wastewater required by Ministerial Decision No. LH. 51/MENLH/10/1995 respectively of 300 and 150 mg/L. Textile wastewater containing COD, N, P, and heavy metals that can degrade water quality in the environment. A high content of heavy metals in textile waste originating from the dye at one stage in the production process. To reduce the content of pollutants in wastewater can be used bioremediation process using microalgae as its microorganisms.

Waste Water Treatment Plant (WWTP) textile industry mostly uses activated sludge system in reducing waste contaminants. The advantage of this system can be used on a home scale wastewater treatment to industrial scale. Activated sludge system deficiency that does not remove color from industrial waste and can enhance the color through oxidation, does not eliminate the nutrients that require tertiary treatment, recycling of biomass causes high biomass concentration in the aeration tank so the required residence time is right. Bioremediation is the use of microbes to clean up contaminants in soil and groundwater. Microbes are very small microorganisms, such as microalgae, which lives naturally in the environment. N and P elements that are nutrients for microorganisms. With the basic use of microalgae as a microbe that can absorb elements of N and P in the wastewater. In addition to reducing levels of COD and BOD waste, microalgae can absorb heavy metal content. Textile wastewater treatment using bioremediation systems using microalgae can be used as an alternative to textile wastewater treatment because of its ability to absorb contaminants such as sewage BOD, COD, N, P, heavy metals and color.

In some previous studies on the use of microalgae *Chlorella vulgaris* bioremediation processes because of its ability to reduce heavy metals. But many levels of N, P, COD, and heavy metals that have absorbed maximally only about 60-70% (Fazal et al., 2021). Song et al have experimented with using *Scenedesmus* sp. that has been immobilized to reduce salinity of about 50% and have the ability to live in 100% sea water (Song et al., 2022). By microalgae immobilization, ability to live at high concentrations of wastewater that can be done.

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2. Materials and Methods

2.1 Cultivation of Chlorella vulgaris and Spirulina platensis on textile wastewater

About 10% *Chlorella vulgaris* and *Spirulina platensis* OD_{680} = 0.6 was cultivated in 1000 mL erlenmeyer flask containing the textile wastewater with concentration of 1.5%, 2%, 2.5%, and 3% and added 50% synthetic nutrients. The optical density of microalgae was measured using a spectrophotometer on days 1 to 13.

2.2 Immobilization of microalgae Chlorella vulgaris and Spirulina platensis

Microalgae *Chlorella vulgaris* and *Spirulina platensis* with the amount of 0.6 OD_{680} centrifuged at 3500 rpm for 15 minutes. Microalgae residue dissolved in 50 ml of distilled water demineralization. 4% sodium alginate solution with the same volume is added to obtain a solution of 2% algal-alginate (Liu et al, 2019). Mixture was mixed using a magnetic stirrer in order to have a perfect solution. The solution then inserted into the injection solution and put into a solution of 0.1 M $CaCl_2$ and allowed to stand for 1 hour to stabilize the bead. Having obtained the bead *Chlorella vulgaris* and *Spirulina platensis*, beads were washed in demineralization water to stop the process of coagulation.

2.3 Integrating immobilized microalgae Chlorella vulgaris and Spirulina platensis on textile wastewater

In a 1000 ml Erlenmeyer included immobilization of microalgae with ratio bead:wastewater (v/v) 1:1, 1:2, 1:3 with 24-hour lighting, 18watt, aeration, and room temperature. On day 1, 3, 5, and 7 were measured heavy metal concentration by equation (1).

$$Removal\ heavy\ metal\ (\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where Ci is initial concentration of heavy metal (mg/L) and Cf is final concentration (equilibrium) of heavy metal (mg/L).

2.4 Adsorption of heavy metals by immobilized microalgae

In a 1000 ml Erlenmeyer insert immobilized microalgae on optimal bead ratio: wastewater (v/v) added textile waste with various concentrations of 1.5%, 2%, 2.5%, and 3% with a 18 watt lighting (24 hours) and aeration. Measure the concentration of heavy metals in absorption using AAS on days 1, 3, 5, and 7. The uptake ability of heavy metal was measured by equation (2).

$$(q) = \frac{V(C_i - C_f)}{M} \quad (2)$$

where q is uptake heavy metal (mg heavy metal/g dry weight); V is solution volume (L); C_i is initial concentration of heavy metal in solution (mg/L); C_f is final concentration (equilibrium) of heavy metal in solution (mg/L); and M is total biosorbent in solution (g). Therefore, the maximum adsorption capacity (q_{max}) and bond constant (K_b) were calculated using the following Langmuir formula.

$$q = \frac{q_{max} C_f}{K_b + C_f} \quad (3)$$

where q is absorbed heavy metal on solid phase (mg/g dry wt); q_{max} is maximum adsorption capacity mg/g dry wt); K_b is bonding constant (mg/L); and C_f is final concentration (mg/L).

3. Result and Discussion

3.1 Analysis of chemical content of textile wastewater

Analysis of chemical constituents of textile wastewater can be seen in **Table 1.**

Table 1. Analysis of chemical constituent of textile wastewater

Parameter	Value
pH	9.69
COD (mg/L)	1755
N_{total} (mg/L)	75.87
P_{total} (mg/L)	25.39
Cr (mg/L)	600
Cu (mg/L)	80
As (mg/L)	-
Hg (mg/L)	-
Fe (mg/L)	0.46
Co (mg/L)	-
Pb (mg/L)	-

Based on the chemical analysis of textile wastewater levels were performed in the Laboratory of Healthcare Central Java Province obtained the results that have properties of textile wastewater alkaline with a pH of 9.69, this caused by the process of mercerization, the cloth dipped in a solution of soda (NaOH 20% -25%) in the pressure. This process aims to develop fibers that improve appearance, ability to absorb color and strength. In Table 3.1 shows that the levels of heavy metals Cr and Cu were very high around 600 ppm

and 80 ppm Cu this was very high with the required threshold by Kep. Men. Neg. L.H. No: KEP-51/MENLH/10/1995 about the Wastewater Quality Standard for Industrial. If analyzed in simple terms was very reasonable because of the color of textile waste being analyzed has solid black on the state and on dilution to 30% (v/v) textile waste shows a greenish blue color that is characteristic look of metal complexes of Cr and Cu.

3.2 Growth acclimation of Chlorella vulgaris and Spirulina platensis on textile wastewater

In the study acclimation of *Chlorella vulgaris* and *Spirulina platensis* growth in textile wastewater, 10% microalgae cultivated with 0.6 OD_{680} in textile wastewater with concentration of 1.5%; 2%; 2.5%; and 3% with a 50% addition of synthetic nutrients. Concentration determination was based on the concentration of waste that causes difficult entry of light that would interfere with the process photosynthesis of microalgae. In addition, levels of heavy metals Cr and Cu were high at 600 mg/L and 80 mg/L so as to give toxic effect for microalgae. **Figure 1** shows the OD Chlorella vulgaris and Spirulina platensis in textile wastewater. Cultivation of the results obtained that the cultivation of Chlorella vulgaris in sample C-1,5% had the highest OD on day 5 with a value of 0.36, C-2% had the highest OD on day 7 with a value of 0.38, C-2,5% had the highest OD on day 7 with a value of 0.4, and C-3% had the highest OD on day 10 with a value of 0.30. On the graph can be seen that the highest OD Chlorella vulgaris at a concentration of 2.5% with a value of 0.43 on day 7. On the cultivation of Spirulina platensis in textile waste by dilution of 1.5%, 2%, 2.5%, and 3% the result that the sample S-1,5%, S-2%, and S-2,5% showed the highest OD value on day 12 with a value of 0.35; 0.36; and 0.40. At concentrations of S-3%, *Spirulina platensis* had the highest OD on day 13 with a value of 0.27. **Table 2** showed the growth rate of *Chlorella vulgaris* and *Spirulina platensis* in textile wastewater.

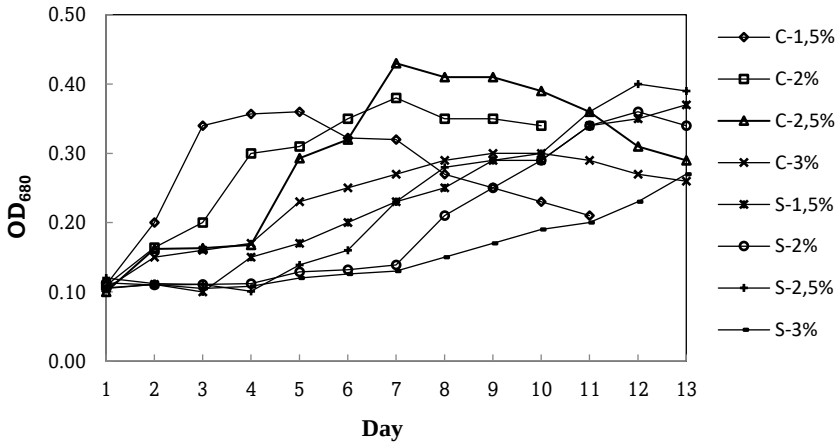

Figure 1. Growth rate of *Chlorella vulgaris* and *Spirulina platensis* in textile wastewater

At low concentrations of 1.5%, 2%, and 2.5% the growth of *Chlorella vulgaris* and *Spirulina platensis* slightly delayed but did not show an effect that is too large this is because the concentration of heavy metals that can still be tolerated by the *microalgae Chlorella vulgaris* and *Spirulina platensis*. At 3% concentration of heavy metal concentrations reached a maximum level that can be tolerated by microalgae. In this experiment the concentration obtained optimum cultivation of *Chlorella vulgaris* and *Spirulina platensis* in textile waste 2.5% with the highest OD *Chlorella vulgaris* obtained on day 7 with OD 0.43 and the highest OD of *Spirulina platensis* obtained at day 12 with OD 0.40**. Table 2** show that there is an increase growth rate of *Chlorella vulgaris* and *Spirulina platensis* with increasing concentrations of textile wastewater. At a concentration of 3% textile wastewater *Chlorella vulgaris* occurs due to large concentrations of heavy metals that cause toxic effects to the growth of *Chlorella*. On *Spirulina platensis* decrease not shown due to the concentration of the growth rate of 3% has not earned OD_{max} on day 13. Lukavsky et al explains that the level of toxicity of some heavy metals Cd>Co>Cr> Cu>Pb>Ni>Zn>Al>Fe, Cr metal has more toxicity than Cu, although both are heavy metal with high toxicity after Cd and Co (Lukavsky et al, 2003). Costa et al explains that the adsorption of chromium on algae *Sargassum filipendula* can reach 67.5% (Costa et al., 2022). Heavy metals Cu concentration has destructive properties at concentration 0.03-1,1 ppm (Shabbir et al., 2020).

Table 2. Growth rate of microalgae in textile wastewater

Mikroalga	Wastewater dilution	OD_{max}	μ
Chlorella vulgaris	1,5%	0.36	0.057
	2%	0.38	0.082
	2,5%	0.43	0.295
	3%	0.30	0.034
Spirulina platensis	1,5%	0.35	0.029
	2%	0.36	0.057
	2,5%	0.40	0.105
	3%	0.27	0.160

3.3 Integrating Immobilized microalgae on textile wastewater

Chlorella vulgaris immobilized with a ratio of 1:3 v/v (beads:wastewater) decrease highest levels of heavy metal Cr and Cu in textile wastewater than ratio 1:1 and 1:2. Ability to absorb the highest Cu are shown in **Figure 2**. with the use of a 1:3 ratio by 89%

types of microalgae *Chlorella vulgaris* and *Spirulina platensis*. By the end of the Cu content in textile effluent 0.2 ppm. This is in accordance with the effluent limits required by the Central Java Provincial Regulation No. 5 In 2012 at 0.8 ppm. Highest ability *Chlorella vulgaris* and *Spirulina platensis* immobilized reduce Cr levels only 89% and 90% by the end of the Cr content of 1.6 ppm and 1.5 ppm. Ability to absorb the highest Cr are shown in **Figure 3.**

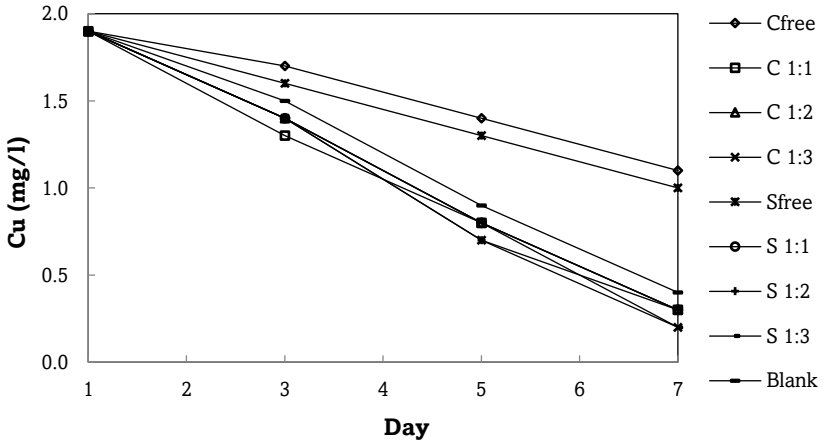

Figure 2. Removal of heavy metal Cu

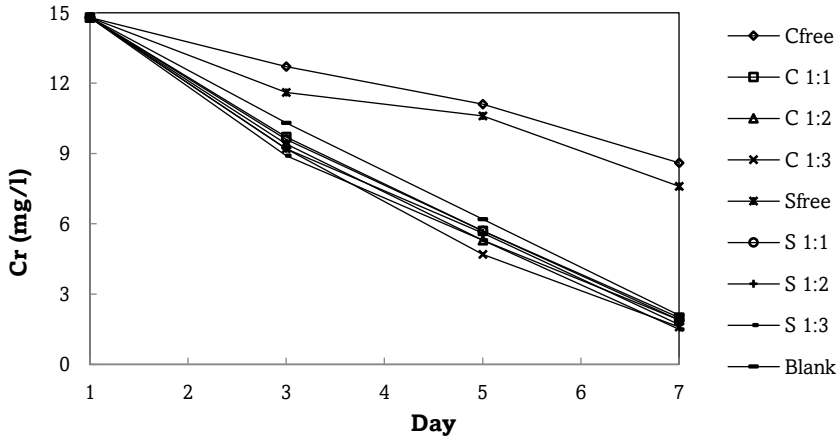

Figure 2. Removal of heavy metal Cr

Table 3. Final concentration and removal percent of Cu and Cr

type	Concentration at day 7			
	Cu (ppm)	% Cu Removal	Cr (ppm)	% Cr Removal
C free	1.1	42	8.6	42
C 1:1	0.3	84	2	86
C 1:2	0.3	84	1.9	87
C 1:3	0.2	89	1.6	89
S free	1	47	7.6	49
S 1:1	0.3	84	1.9	87
S 1:2	0.3	84	1.7	89
S 1:3	0.2	89	1.5	90
Blank	0.4	79	2.1	86

3.4 Biosorption of heavy metals by immobilized microalgae

Bead number is calculated using the assumption that each bead egg-shaped ball with a diameter of 4 mm so that the volume of a sphere formula uses the bead volume gained 33.5 mm3/bead. With a ratio of 1:3 v/v (bead:wastewater) then the number of beads used is 250 ml or equivalent to 250000 mm^3 so the 1:3 ratio is used as the number of beads 7462 bead. Cu uptake ability of Chlorella vulgaris on the initial concentration of 1.5%; 2%; 2.5%; and 3% at 1.2 mg/g; 1.4 mg/g; 1.9 mg/g; and 1.9 mg/g. Cu uptake at same concentration variation by Spirulina platensis heavy metal uptake by 1.1 mg/g; 1.3 mg/g; 1.7 mg/g; and 1.7 mg/g. Cr uptake abilities

shown by *Chlorella vulgaris* in concentration of 1.5%; 2%; 2.5%; and 3% was 9.2 mg/g; 11.9 mg/g; 13.6 mg/g; and 16.3 mg/g. Cr uptake abilities shown by *Spirulina platensis* in same concentration variation was 8.2 mg/g; 10.7 mg/g; 14.1 mg/g; and 14.7 mg/g. Cr absorption capability is greater than heavy metal ion Cu, that was because ion size of Cu (0.96 Å) is greater than the ion Cr (0.63 Å) that is more easily absorbed.

With graphs C_f/q vs C_f will be obtained straight line equation to obtain the value of q_{max} and K_b. **Figure 4** and **5** shows graph of the Langmuir isotherm absorption of Cu and Cr in *Chlorella vulgaris* and *Spirulina platensis* immobilized in alginate. Plotting graphs of the results obtained q_{max} results *Chlorella vulgaris* on Cu were 1.984 mg/g and K_b reach 0.014 mg/l. On Cr heavy metal, *Chlorella vulgaris* has q_{max} and K_b were 15.873 mg/g with K_b reach 0.079 mg/L. Biosorption Cu heavy metal by *Spirulina platensis* has q_{max} and K_b were 1.798 mg/g and 0.014 mg/L. On Cr heavy metal, *Spirulina platensis* has q_{max} and K_b were 14.925 mg/g and K_b reach 0.044 mg/L. Increasing the value K_b will be followed by increase in the value of q_{max} because the bonds between the adsorbent with adsorbate was greater.

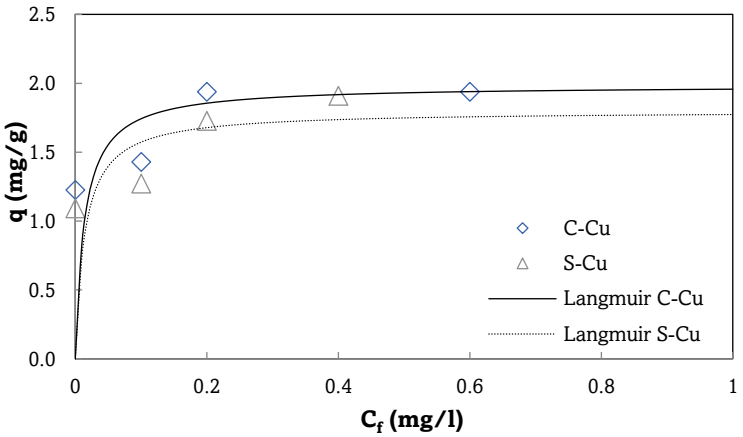

Figure 4. Langmuir adsorption of Cu

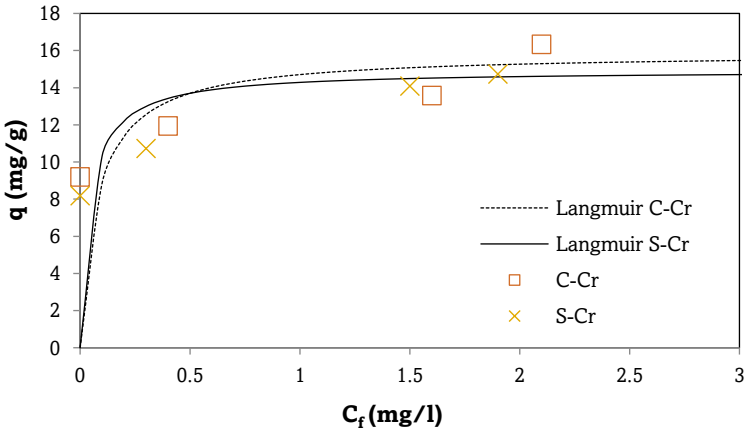

Figure 5. Langmuir adsorption of Cr

Michalak et al conducted a study on the adsorption of Cr using *Spirulina* microalgae and obtained the value of q_{max} 34.6 mg/g (Michalak et al., 2007). This value is higher than immobilized *Spirulina* that only 14.925 mg/g. *Spirulina* q_{max} is lower due to the conditions and characteristics of Cr metal is more poorly absorbed if at high pH conditions. Liu et al explains that the hydrolytic reaction can result in changes in the components and the state of the cell surface (Liu et al., 2019). This resulted in decreased absorption conducted sorbent to metal. Whereas at high pH, the surface of the cells will slowly become negatively charged, so that the power to bind Cr ions become smaller and reduce the absorption capacity. At high pH also occurs Cr ion precipitation to $Cr(OH)_3$ which reduces the solubility of Cr ions in the solution resulted in a reduced number of Cr ions that can be absorbed by the cell surface despite recent precipitation occurred predominantly in the range of pH 9 so that biosorption can no longer be carried out at pH above 9.

4. Conclusion

In the process of acclimation of *Chlorella vulgaris* and *Spirulina platensis* in textile effluent with nutrient addition of 50% obtained that the optimal concentration for the cultivation of microalgae *Chlorella vulgaris* highest OD_{680} occurred on day 7 with a value of 0.43 obtained in sewage dilution 2.5%. Spirulina platensis OD_{680} reached highest on day 12 of 0.4 obtained in 2.5% dilution of textile wastewater. The best ratio decreased color, COD, N, P, and heavy metals textile effluent obtained at a ratio of 1:3. *Chlorella vulgaris* and *Spirulina platensis* reduce heavy metals Cu as much as 89% with the highest final concentration of 0.2 ppm. Highest Cr heavy metal adsorption was 89% and 90% with a final concentration of 1.6 ppm and 1.5 ppm. Plotting graphs of the results obtained q_{max} results *Chlorella vulgaris* on Cu were 1.984 mg/g and K_b reach 0.014 mg/L. On Cr heavy metal, *Chlorella vulgaris* has q_{max} and K_b were 15.873 mg/g with K_b reach 0.079 mg/L. Biosorption Cu heavy metal by *Spirulina platensis* has q_{max} and K_b were 1.798 mg/g and K_b

reach 0.014 mg/L. On Cr heavy metal *Spirulina platensis* has q_{max} and K_b were 14.925 mg/g and K_b reach 0.044 mg/L. Increasing the value K_b will be followed by increase in the value of q_{max} because the bonds between the adsorbent with adsorbate was greater.

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