

Research Article

Biosorption of Heavy Metal Cu²⁺ and Cr²⁺ in Textile Wastewater by Using Immobilized Algae

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Abstract: The objective of this research was to utilize microalgae *Chlorella* sp. and *Spirulina* sp., as biosorption agents for heavy metals removal available in textile waste water. The biosorption of Cu and Cr ions from textile waste water solutions by immobilized algae (*Spirulina* and *Chlorella*) were tested under laboratory conditions as a function of waste concentration (15-50% dilution) and ratio of bead and waste water (1:1-1:3). Experimental results showed that the Langmuir adsorption models were suitable for describing the short-term biosorption of by all algal species. The best ratio of bead: wastewater (v/v) for removal heavy metal in textile wastewater was 1:3. The maximum Cu removed from the waste was 89% while Cr was removed with 90% by using *Chlorella* sp. The algae *Spirulina* showed a higher removal capacity of 90%. The maximum absorption capacity of Cu was achieved at 16.2 and 13.6 mg/g by using *Spirulina* and *Chlorella*, respectively, while the maximum sorption capacity for Cr was achieved at 1.95 and 1.45 mg/g for algae *Spirulina* and *Chlorella*, respectively.

Keywords: Biosorption, heavy metal, immobilized microalgae, textile wastewater

INTRODUCTION

The textile industry is one of leading industries in Indonesia and its development is quite promising, which reach growth rate of 1.48% per year. This increase of textile industries leads to an increase in risk of environmental due to its heavy metals present in waste disposal, especially when the waste is not handled properly. The most common problem of this waste is the presence of heavy metals ions of Cu and Cr. These ions are originated from dye processing during textile production. Water polluted by heavy metals is very toxic in nature and could accumulate in food chains which cause harmful for mankind. Cu and Cr ions are very toxic due to its presence in the waste could severe environmental problem and its high concentration is eventually threatening living organism, especially when the ions available in oxidized form. Besides, textile waste water has also high COD content of 150-12000 mg/L which is much higher than Indonesian regulation, 300 mg/L.

To reduce heavy metals contaminant, textile industry mostly uses conventional treatment i.e., chemical precipitation, coagulation, adsorption, membrane separation. These methods are either too expensive in initial set up or having problems in final sludge treatment (Lau *et al.*, 1998). Bioremediation has been considered as an alternative of innovative technologies to recover heavy metals and nutrient

(nitrogen and phosphor) present in the waste water. Compared to the conventional methods, bioremediation offer several advantages such as low operating cost, very efficient to detoxify waste and least nutrient requirements (Hameed and Ebrahim, 2007; Jianlong *et al.*, 2002).

Microalgae, besides other microbial species: bacterial and fungus, has been reported to have high metal sequestering ability through their active metal uptake and ability to accumulate metal ions inside the cell (Volesky, 1990). Therefore, microalgae also have potential as bioremediation agent. For industrial applications, the use of immobilized algae has more advantages than freely suspended biomass. The advantages of immobilized algae biomass are resistance to chemical environment, easy separation of cells and waste, higher mechanical strength, minimal clogging in continues system and possibility to repeat in many adsorption cycle (Hameed and Ebrahim, 2007; Horváthová *et al.*, 2009). Cell entrapment is the most widely used technique for immobilization. In this technique, the cells are enclosed in a polymeric matrix which is porous enough to allow diffusion of substrate to the cells. Alginate has been successfully used for cell entrapment and widely used for heavy metals removal from aqueous solution.

The cell immobilization is not merely utilized for heavy metals recovery, but it may possible to improve the removal of nutrients available in the waste

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(Jimenez-Perez *et al.*, 2004). Jimenez-Perez *et al.* (2004) found that the Phosphor uptake is higher by using immobilized algae than free-cell of algae, however they concluded that no effect of immobilization on cell growth. Chevalier and De la Noüe (1985) found that there was no significant difference of the growth between immobilized and free cell of algae *Scendesmus* in waste water.

The objective of this research was to investigate the efficiency of using immobilized algae for removal of Cu and Cr ions from textile waste. The algae used for this study was *Chlorella vulgaris* and *Spirulina platensis* which are entrapped in alginate matrix polymer. The biosorption of Cu and Cr ions from textile waste water aqueous solutions by algae was studied in a batch biosorption system as a function of a contact time. The Langmuir adsorption model was applied to describe biosorption capacity of heavy metals.

MATERIALS AND METHODS

Textile waste water: Textile waste water was obtained from a textile company in Semarang, Central Java, Indonesia. The characteristic of waste was analyzed at Environmental Laboratory, Diponegoro University with following properties (Table 1).

Cultivation of *Chlorella vulgaris* and *Spirulina platensis* in textile wastewater: Microalgae *Chlorella vulgaris* and *Spirulina platensis* with OD₆₈₀ 0.6 were cultivated in 1000 mL erlenmeyer containing the textile wastewater. The initial culture was set at 10% of total volume. The waste water was varied for its diluted concentration (15-30%). The concentration of cell was monitored by measuring its OD at 680 nm. During cultivation, the light was exposed constantly by using 4×60 Watt fluorescent tubes and culture was mixed by aeration.

Immobilization of microalgae *Chlorella vulgaris* and *Spirulina platensis* in alginate: *Chlorella vulgaris* and *Spirulina platensis* with OD₆₈₀ = 0.6 was centrifuged at 3500 rpm for 15 min. Microalgae residue was dissolved in 50 mL distilled water. About 4% sodium alginate solution with the same volume was added to obtain a solution of 2% algal-alginate. Mixture was mixed using a magnetic stirrer in order to have a perfect solution. Inserted into the injection solution and put in to a solution of 0.1 M CaCl₂ 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.

Bead number was calculated using the assumption that each bead egg-shaped ball with a diameter of 4 mm so that the volume of a sphere formula used the bead volume of 33.5 mm³/bead. With a ratio of 1:3 v/v

Table 1: Analysis of chemical constituents 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)	-
Color	Greenish

(bead: wastewater) then the number of beads used was 250 mL or equivalent to 250000 mm³. This led to number of beads used was 7462 bead.

Adsorption of heavy metals immobilized microalgae:

The adsorption of metal ions by using immobilized algae was conducted by variation of bead: waste water ratio = 1.5 to 3% in 1 L Erlenmeyer. The experiment was illuminated with 18 watt lighting for 24 hour while mixing was supplied by aeration. The concentration of metal ions in the solution was determined by the AAS. The amount of metal ions adsorbed by used immobilized algae was obtained by using the following expression:

$$q = \frac{V(C_i - C_f)}{M} \quad (1)$$

where,

- q = The amount of metal ions adsorbed onto the unit amount of the biosorbents (mg/g)
- C_i and C_f = The initial and equilibrium concentrations of the Cu²⁺ or Cr²⁺ (mg/L) after biosorption, respectively
- V = The volume of the adsorption medium (L)
- m = The amount of the biosorbent (g)

Biosorption isotherm model: The amount of metal ions adsorbed by used biosorbent was obtained by using Langmuir model as follow:

$$q = \frac{q_{\max} C_f}{k_b + C_f} \quad (2)$$

where,

- q = The amount of absorbed heavy metal on solid phase (mg/g dry wt)
- q_{max} = The maximum adsorption capacity (mg/g dry wt)
- k_b = The bonding constants (mg/L)
- C_f = The final concentration (mg/L)

RESULTS AND DISCUSSION

Microalgae growth in textile wastewater: The growth evaluation of microalgae *Chlorella vulgaris* and *Spirulina platensis* in textile wastewater medium has been conducted in 15-30% dilution. Figure 1 presents

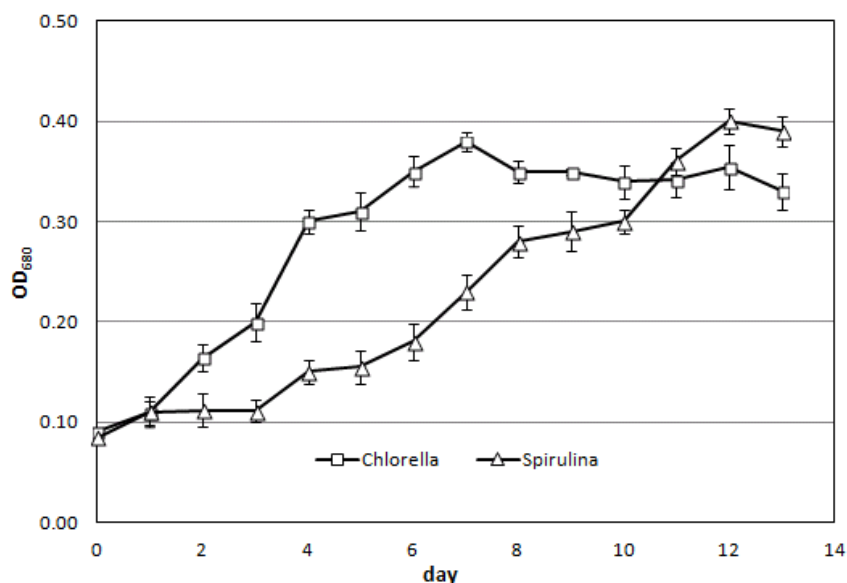


Fig. 1: Cultivation of *Chlorella vulgaris* and *Spirulina platensis* in 25% diluted textile wastewater

Table 2: Growth rate microalgae in textile wastewater

Microalgae	Wastewater dilution (%)	OD _{max}	μ (1/day)
<i>Chlorella vulgaris</i>	15	0.36	0.057
	20	0.38	0.082
	25	0.43	0.295
	30	0.30	0.075
<i>Spirulina platensis</i>	15	0.35	0.029
	20	0.36	0.057
	30	0.27	0.080

the growth of *Chlorella vulgaris* and *Spirulina platensis* in textile with 15% dilution wastewater during 13 days of cultivation. Microalgae *Chlorella* were able to utilize the nutrients i.e., Nitrogen and Phosphorous in the waste better than *Spirulina*. In the first three days, *Spirulina* grow slowly in lag phase prior to its rapid growth in the exponential phase which means that *Chlorella* were able to adapt easily to the waste than *Spirulina*. From Fig. 1, the calculated growth rate are 0.21/day and 0.14/day for *Chlorella* and *Spirulina*, respectively.

The effect of initial concentration of heavy metals was conducted by variation of dilution of textile waste water with 15-30% volume. Table 2 shows that there is an increase of growth rate of *Chlorella vulgaris* and *Spirulina platensis* by increasing concentrations of textile wastewater. At a concentration of 30% vol., the growth rate of *Chlorella vulgaris* and *Spirulina sp* decrease due to the heavy metals levels causing toxic effects to the growth. The heavy metals have degree of toxicity based on this sequences: Cd>Co>Cr>Cu>Pb>Ni>Zn>Al>Fe (Lukavsky *et al.*, 2003). Furthermore Banerjee *et al.* (2004) explained the growth of microalgae is limited at 20 ppm of Cr ions in the solution.

Heavy metals removals by using microalgae: The experiment of heavy metals removal was conducted by using free and immobilized algae cell. The capacity of algae biomass can be described by an equilibrium sorption isotherm, which is characterized by certain constants whose values express the surface properties and affinity of the biomass (Horváthová *et al.*, 2009). The biosorption isotherms were investigated by using Langmuir isotherm model. The Langmuir sorption isotherm has been successfully applied to many pollutant biosorption processes and has been the most widely used for the biosorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the sorbent.

When non-immobilized biomass was used for biosorption process is very fast in the first day of biosorption. In this experiments, kinetics of biosorption Cu and Cr using immobilized and free cells of algae *Chlorella* and *Spirulina* were studied. In both cases when free-algae cell was used, the equilibrium was reached within one day. But the immobilized biomass reached the equilibrium mostly after 5 day. Algae *Spirulina* shows a better in absorption of heavy metals both for free or immobilized algae as compared to *Chlorella*.

The variation of bead: waste ratio is presented in Table 3. It is observed that free-cell immobilization give lower performance than immobilized algae. The free-cell immobilization is fast in the beginning period before the cells already reached the loading capacity. The immobilized algae require much longer time for its sorption of heavy metals. Increasing bead volume in the solution leads to an increase of the heavy metals removal (Fig. 2).

Table 3: Final concentration and removal efficiency at final day of adsorption

Type	Concentration at final day			
	Cu (ppm)	% Cu removal	Cr (ppm)	% Cr removal
C free	1.1	72	8.6	52
C 1:1	0.3	84	2.0	86
C 1:2	0.3	84	1.9	87
C 1:3	0.2	89	1.6	89
S free	1.0	74	7.6	69
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

Table 4: A comparison of langmuir adsorption isotherm for both species of microalgae for different initial concentration

	Concentration	Cu		Cr	
		q_{max} (mg/g)	k_b (mg/L)	q_{max} (mg/g)	k_b (mg/L)
<i>Spirulina</i>	15	1.64	0.052	12.3	0.34
	20	1.75	0.043	14.6	0.26
	25	1.93	0.031	16.2	0.15
	30	1.94	0.030	16.8	0.13
<i>Chlorella</i>	15	1.14	0.054	10.2	0.45
	20	1.28	0.047	11.4	0.35
	25	1.45	0.035	13.6	0.23
	30	1.47	0.033	13.7	0.22

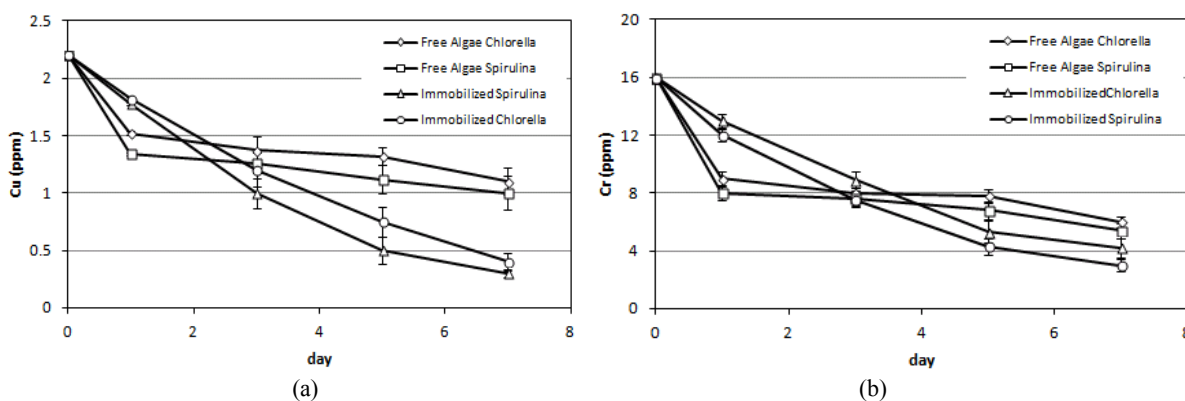


Fig. 2: The concentration of Cu (a) and Cr (b) as function of adsorption time for microalgae *Chlorella* and *Spirulina*

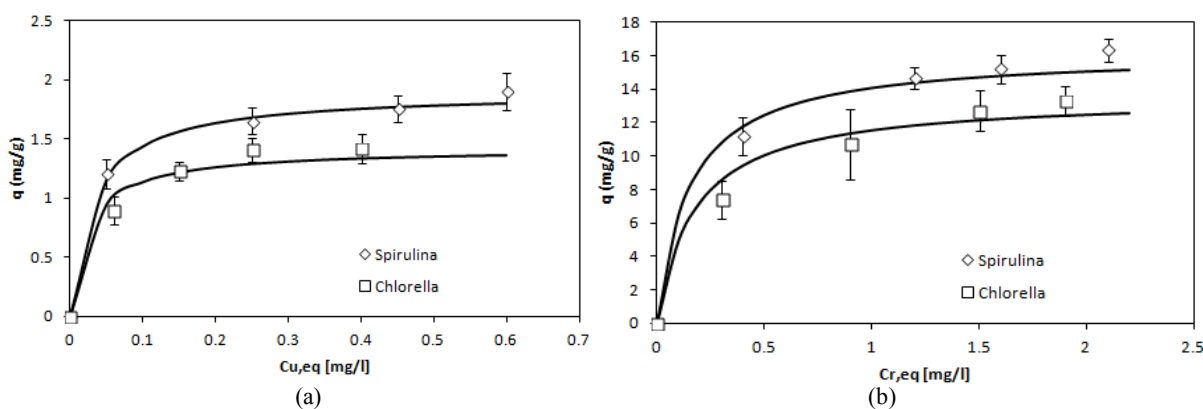


Fig. 3: Sorption isotherm model of Cu (a) and Cr (b) adsorption by using *Chlorella* and *Spirulina*

Biosorption isotherm model for immobilized microalgae: In the current study, both *Spirulina* and *Chlorella* species demonstrated their capacity in absorbing heavy metals of Cu and Cr. Figure 3 shows the biosorption isotherm by using Langmuir model which is best to the experimental data. Algae *Spirulina*

show higher loading capacity in absorbing heavy metals of Cu and Cr, 16.2 and 1.93 mg/g, respectively (Table 4). This may be due to the cell size of *Spirulina* which is greater than *Chlorella* sp., *Spirulina* has size more than 200 μm , lead for larger bonding sites as compared to *Chlorella* sp., Chojnacka *et al.* (2005)

reported that metals ion bind the cell surface by forming multiple bonds. When cells are surrounded by large number of metal ions, each ion tends to bind and consequently increasing the loading capacity. De-Bashan and Bashan (2010) concluded that the cell density will have linear correlation with metal uptake rates.

The experiment with variation of dilution of textile waste was conducted to evaluate the effect of initial heavy metals concentration. Table 4 shows the variation of diluted waste and its affect to maximum loading capacity and kb values. The Cu uptake ability for *Chlorella vulgaris* with initial concentration of 15, 20, 25 and 30% give q_{max} at 1.14, 1.28, 1.45, dan 1.47 mg/g, respectively. While Cu uptake at same concentration variation by using *Spirulina platensis* are 1.64, 1.75, 1.93, dan 1.94 mg/g, respectively. The Cr uptake by *Chlorella vulgaris* in the initial concentration of 15-30% was achieved at 10.2-13.7 mg/g which is lesser than *Spirulina* at 12.3-16.8 g/g. The uptake rate of Cr is greater than Cu ion which may because of size of Cu (0.96 Å) is greater than Cr ion (0.63 Å). The greater size eventually leads to unproblematic absorption.

The different output was showed by Michalak *et al.* (2007). In their research, *Spirulina* was shown to have less efficiency than *Chlorella*. This is perhaps due to influence of pH during sorption. Where a sat 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.

CONCLUSION

The algae *Chlorella* and *Spirulina* have important potential for the removal of Cu and Cr ions from textile waste water. The results concluded that both immobilized algae in alginate and free-cell algae can be used as effective biosorbents for removal of these ions. The biosorption capacity of *Chlorella* algae immobilized into alginate for Cu and Cr is lower than capacity of *Spirulina* sp. The effects of initial concentration to the absorption capacity and ions removal have been successfully shown by both algae species. At the dilution of 30%, the growth of algae cell was retarded due to the toxicity of waste water. The maximum of ions removal was achieved by algae *Spirulina* at 90%.

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