Article

Biosorption of Chromium from Textile Wastewater Using *Mimosa pudica* Tannin Gel

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Abstract. The heavy metal content is very dangerous because it can pollute the environment. One of the heavy metals waste commonly found in the textile industry is chromium (Cr). *Mimosa pudica* is a weed plant and its availability is very abundant. However, it also contains tannin which can be developed into tannin gel biosorbent to adsorption heavy metal content in the wastewater. The purpose of this research is to study *Mimosa pudica* tannin as a Cr biosorbent from textile wastewater. In this research, the steps to synthesis tannin gel biosorbent are the tannin extraction from the leaves and stems of *Mimosa pudica* using water solvent and the condensation polymerization using formaldehyde to make it insoluble in water. The yield of *Mimosa pudica* tannin extract was 9.4% and the yield of *Mimosa pudica* tannin gel was 40%**.** The biosorption process of Cr from textile wastewater was done using *Mimosa pudica* tannin gel at the variations of biosorbent mass and contact time. The result showed that the biosorption process at a ratio of biosorbent and solvent (1:50 m/v) and contact time (60 minutes) can reduce the concentration of Cr (4 mg/L) to 0.7098 mg/L that was already below the threshold (1 mg/L).

Keywords: biosorption, condensation polymerization, extraction, *Mimosa pudica*, tannin gel

1. Introduction

Heavy metals are harmful to the environment. Several heavy metals are carcinogenic and if exposed to agricultural land will endanger life. Heavy metals can be accumulated in a cell of a plant which is animal and human food, also they can be accumulated in a living organism. The effluent of the textile industry can be a contributor to heavy metals [1]. The contamination of heavy metal from the waste textile industry to the environment based on the research has been studied shown in Table 1.

Table 1 The contamination of heavy metal in the environment

Location	Heavy Metal Content	Source of samples	Description	Ref
Jelegong village, Rancaekek, Bandung	LS-01: 0.9 mg/L Pb; 0.17 mg/L Cd; 174.7 mg/L Cr; 3.9 mg/L As; 92.2 mg/L Hg LS-02: 9.7 mg/L Pb; 0.13 mg/L Cd; 34.1 mg/L Cr; 3.7 mg/L As; 25.9 mg/L Hg, LS-03: 11.7 mg/L Pb; 0.15 mg/L Cd; 27.4 mg/L Cr; 4 mg/L As LS-04: 10.5 mg/L Pb; 0.08 mg/L Cd; 25.6 mg/L Cr; 4.2 mg/L As; 12.3 mg/L Hg	Rice fields	The Cr content exceeded the threshold of Regulation of the Environment Minister of Republic Indonesia, No.5 in 2014 (1 mg/L)	[1]
Langsur river, Sidoarjo	0.0213 mg/L Cr	River	The Cr content was under the threshold of Regulation of the Environment Minister of Republic Indonesia, No.5 in 2014 (1 mg/L).	[2]
	7.05 mg/kg Cr	Betok fish *Anabas testudinaus*	The Cr content exceeded the threshold of Dirjen POM, 1989 (2.5 mg/kg)	[2]
Citarum river, Bandung	point A3 : 0.075 mg/L Cr point A4 : 0.093 mg/L Cr	River	The Cr content exceeded the threshold of PP No. 82 in 2001 at water body class II (0.05 mg/L)	[3]
Ranaghat-Fulia, India	833.5 μg/g Cr 679.7μg/g Cr 79.3-241.6 μg/g Cr	Roots of aquatic weeds *Glossogobius giuris* fish Sediment soil on October	The Cr content was highly contaminated	[4]
Madhabdi, Bangladesh	2.15 mg/L Cr 0.44 mg/L Pb	The Effluent of 34 handloom-dyeing industries	The Cr content exceeded IEDS (The Industrial Effluent Discharge Standards) for inland surface water of Bangladesh i.e. 0.5 mg/L and IWGV (Irrigation Water Guideline Values) i.e. 0.011 mg/L	[5]

In areas of Surakarta, the Cr heavy metal from wastewater was also founded in the Pasar Kliwon textile industry. The Cr content of its wastewater was 4 mg/L that exceeds the threshold of the Republic Indonesia government regulation.

Adsorption processes are being widely used by researchers and it has been proved that adsorption is an effective method due to its advantages including stability, utility, low cost, ease of operation, and performance so it should be explored further to recover heavy metal from water. Many low-cost adsorbents have been used to remove heavy metals like industrial effluent (such as fly ash, blast furnace slag and sludge, black liquor lignin, red mud, and waste slurry, etc., agricultural waste (such as rice husk, eggshell, sawdust, rice husk, and lemon peel, microbial such as *Bacillus licheniformis* and algae such as *Cladophora glomerata* [6,7,8]. Many researchers consider biosorption as an adsorption process that utilizes adsorbents extracted from biological sources [9].

Biosorption has several benefits, including eco-friendly, cheap, high performance, reusable, and the possibility of metal recovery [10]. Biosorbents are commonly low-cost, however, the costs of preparation and pretreatment processes of these materials could not be disregard. Some of the living biomaterials, such as fungi, bacteria, and waste biomass need some cultural media and the implementation of modification procedures which increase the final cost [11]. However, for example on biosorption using brown algae increasing its surface area can reduce the cost of the economy due to increasing effective collisions, making available active sites for heavy metal ions, reducing reaction time, and reducing consumption of biosorbent doses [9].

Biowaste such as agricultural waste was often published in adsorption studies in recent years because of limited porosity, the chemical structure, and surface functional groups related to high adsorption capacity and its capability to adsorb chemically and ion exchange of metal ions from aqueous solutions. Resin tannin is also included in this subclassification of biosorbent [11]. The biosorption process can be done to adsorb Pb using *Persimmon* tannin gel with various contact times 10, 20, 30, 40, 50, and 60. The amount 250 mL Pb metal ion with a concentration of 200 mg/L mixed with 0.1-gram Persimmon tannin gel. The mixture was stirred at 120 rpm. Then it was analyzed using Atomic Absorption Spectrophotometer (AAS) to determine the concentration of Pb metal ions that were adsorbed [12].

Resin tannin can be made from the tannin of various plants e.g. *Acacia mangium Wild* [13], persimmon [14], mangrove [15] also *Mimosa pudica* which is a so-called touch-me-not or sensitive plant widely found as a tropical weed in a lot of countries [16]. The availability is very abundant as a weed plant. *Mimosa pudica* contains tannin which is useful in medical cases such as for bleeding disorders like menorrhagia, dysentery with blood, mucus, and piles [17]. Meanwhile, *Mimosa pudica* has not been studied as a biosorbent for removing heavy metals in wastewater. The purpose of this research is to study *Mimosa pudica* tannin as a Cr biosorbent from textile wastewater. There are two steps to synthesis tannin gel biosorbent. They are the tannin extraction and the condensation polymerization process. Tannin is easily soluble in water so the condensation polymerization process is needed to make it insoluble in water. The extraction of *Mimosa pudica* tannin was done using water solvent [18]. The condensation polymerization process was done by the reaction of tannin extract and formaldehyde [19].

2. Materials and Methods

Materials that were used in this study were the leaves and stems of *Mimosa pudica* plant, wastewater of the textile industry areas especially the screen printing industry located in Pasar Kliwon, Surakarta, nitric acid (HNO_3 65% Merck, Germany), sodium hydroxide (NaOH 99% Merck, Germany), formaldehyde (CH_2O 37,5%, Mallinckrodt chemicals, USA), potassium dichromate ($K_2Cr_2O_7$ 99,9% Merck, Germany).

2.1. Extraction of Tannin from *Mimosa pudica* plant

Mimosa pudica plant was obtained from the fields and bushes around the Sebelas Maret University, Surakarta. The leaves and stems are washed using clean water, dried in the oven, and crushed using a grinding miller to form a powder. Extraction was carried out by heating *Mimosa pudica* powder in water as a solvent with a ratio *Mimosa pudica* powder: water of 1:20 (m/v) at 100°C while stirring for 3 hours [18, 20, 21]. The extract of the extraction process was separated from its residue using filter paper. Then the evaporation process was carried out to remove the water content in the extract of tannin. The drying process was also done in the oven for 24 hours at 100°C to get tannin powder.

2.2. Synthesis of *Mimosa pudica* Tannin Gel

Five grams of tannin powder were dissolved in 32 mL of 0.125 mol/L NaOH then 30 mL of distilled water was added and heated at 80°C. After thoroughly stirring, 2.4 mL of formaldehyde was added to the mixture and maintained at 80°C for 8 hours, this process is called condensation polymerization. Then, it was dried in an oven at 65°C for 24 hours. After drying, the tannin gel was crushed into small particles and washed with distilled water and 0.01 mol/L HNO_3 to remove unreacted NaOH. After that, the washed tannin gel was dried again in the oven so that can be used as an adsorbent [19].

2.3. Biosorption Process of Cr Using *Mimosa pudica* Tanin Gel

Based on the Cr measurement of wastewater of the textile industry areas especially the screen printing industry located in Pasar Kliwon, Surakarta, one of the wastewater contained a Cr concentration of 4 mg/L. Biosorption experiments were conducted using *Mimosa pudica* tannin gel to wastewater that contained 4 mg/L Cr with a volume of 100 mL and stirred using a 120 rpm stirrer with variations of mass of biosorbent (0.5; 1; 1.5 and 2 grams or 1:200; 1:100; 1:67, 1:50 m/v) and variation of time (10, 20, 30, 40, 50 and 60 minutes).

After the adsorption process finished, the filtrate was separated from the residue with Whatman 40 filter paper and analyzed using AAS to measure the final concentration of Cr. The standard solution of Cr(VI) (1000 mg/L) was prepared by dissolving potassium dichromate into distilled water**.** The solution was diluted into various concentrations, i.e. 0, 1, 2, 3, and 4 mg/L Cr for the absorbance measurements using AAS.

3. Results and Discussion

3.1. Extraction Result of *Mimosa pudica* tannin

The total mass of extracted tannin obtained was 4.7 grams from the extraction of 50 grams of tannin powder. So, the yield of tannin extracted was 9.4%. The water was used as a solvent because it has high polarity with Synder index 9.0. The more polar the solvent the better it is used for extraction due to its solute [22]. In comparison with other research, the yield of tannin extracted from several plants can be seen in Table 2.

Table 2. The yield of tannin extraction from many plants using water solvent.

Plants	Extraction time	The size of the powder plant	Yield	References
Allepo pine	6 h	1 mm	26%	[23]
Eucalyptus globulus	2 h	-	14%	[24]
Areca catechu	2 h	0.250 mm	19.5%	[21]

The yield of tannin extraction from *Mimosa pudica* in this research was lower (9.4 %) than other plants. It may be happened to depend on their actual tannin content, time of extraction, and the size of the powder plant [21].

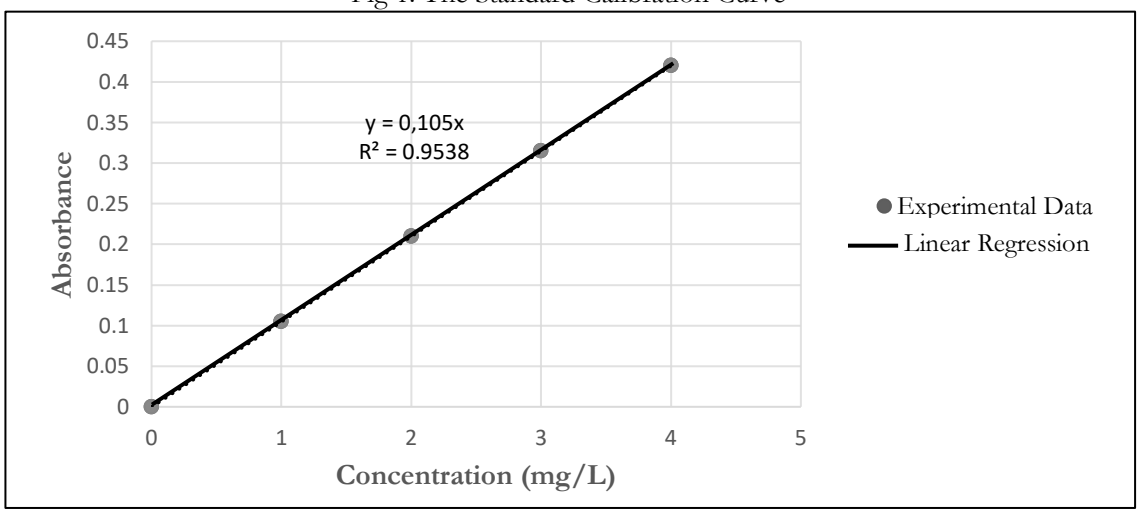
3.2. *Mimosa pudica* Tannin Gel

Tannin gel was made from tannin extract through condensation polymerization reaction with formaldehyde and sodium hydroxide as catalyst. The condensation polymerization reaction is the polymerization of monomer tannin to form a tannin polymer so that it has a stronger molecular structure and is not easily soluble in water. The total mass of tannin gel from this process was 2 grams from 5 grams of *Mimosa pudica* tannin. So, the yield of *Mimosa pudica* gel tannin was 40%.

3.3. Biosorption Process of Cr Using *Mimosa pudica* Tannin Gel

Atomic Absorption Spectrophotometer (AAS) analysis was carried out to determine the heavy metal Cr that could be adsorbed *Mimosa pudica* tannin gel. The calibration curve used was made from standard solutions 0, 1, 2, 3, and 4 mg/L Cr which their absorbance was measured using AAS. The absorbance obtained from each standard solution was shown in Figure 1 with linear regression of y (absorbance)= 0.105 x (concentration, mg/L) and a determination coefficient (R^2) of 0.9538. The greater R^2 value approaching the number 1 indicates the better calibration curve created by the standard solution.

Fig 1. The Standard Calibration Curve



The Cr concentration of wastewater was 4 mg/L due to its concentration in one of the textile industry areas in Pasar Kliwon, Surakarta. The results of the analysis of Cr heavy metal adsorption by *Mimosa pudica* tannin gel can be seen in Table 3 and Figure 2.

Table 3. Cr Analysis of Biosorption Result Using *Mimosa pudica* Tannin Gel

Biosorption Time (Minutes)	Concentration Cr Before Biosorption (mg/L)	Concentration Cr After Biosorption (mg/L)			
		1:200 (m/v)	1:100 (m/v)	1:67 (m/v)	1:50 (m/v)
10	4	3.9386	3.4740	3.2649	2.8115
20	4	3.9053	3.3304	3.0912	2.7469
30	4	3.8821	3.2893	2.7568	2.2090
40	4	3.8752	3.2414	2.3420	1.2583
50	4	3.8701	3.0840	2.0903	1.0890
60	4	3.8617	2.8031	1.7627	0.7098

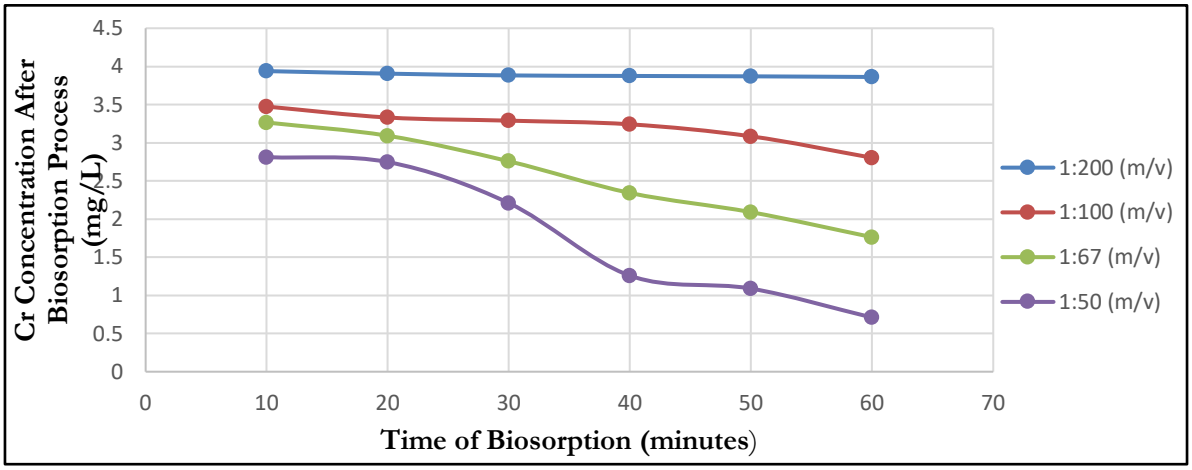


Fig 2. The correlation of Cr Concentration Result and Biosorption Time at Various the Ratio of Tannin Gel Mass and Volume of Solvent

Percent Cr adsorbed can be determined using equation (1).

$$\%\text{Cr Adsorbed} = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

C_0 is the initial concentration of Cr (mg/L), and C is the final concentration of Cr (mg/L) after the biosorption process. The results of percent Cr adsorbed can be seen in Table 4.

Table 4. Percent Cr Adsorbed using *Mimosa Pudica* Tannin Gel

Biosorption Time (Minutes)	Percent Cr Adsorbed (%)			
	1:200 (m/v)	1:100 (m/v)	1:67 (m/v)	1:50 (m/v)
10	1.54	13.15	18.38	29.71
20	2.37	16.74	22.72	31.33
30	2.95	17.77	31.08	44.78
40	3.12	18.97	41.45	68.54
50	3.25	22.90	47.74	72.78
60	3.46	29.92	55.93	82.26

The ratio of biosorbent and wastewater volume that was studied in this research were 1:200, 1:100, 1:67, and 1:50 at temperature 30°C. From Figure 1, Table 1, and Table 2, the highest Cr heavy metal adsorbed at 1:50 (m/v) with percent Cr adsorbed was 82.26%. It could be concluded that the greater mass of biosorbent, the greater mass of Cr metal adsorbed. This happened because the active surface of the adsorbent was greater so it could adsorb Cr heavy metal more. It was appropriate with the research of biosorption that has been studied before as on the table 5

Table 5. Biosorption process using many plant tannin gel

Tannin gel	Heavy metal	Dose of Biosorbent	The Cr adsorbed	References
Accacia mangium	Pb	1:25 (m/v)	70.81%	[13]
Persimmon	Cr	1:50 (m/v)	78%	[14]
Mangrove	Pb	1:25 (m/v)	79.94%	[15]
Mangrove	Cu	1:25 (m/v)	43.75%	[15]

The variation of time biosorption process was done at 10, 20, 30, 40, 50, and 60 minutes. From Figure 1, the high biosorption of Cr heavy metal was at 60 minutes. It can conclude the longer time of biosorption, the greater mass of Cr was adsorbed. The contact time was appropriate with the research of biosorption Pb heavy metal from *Accacia mangium* tannin gel with the result of high biosorption Pb heavy metal at 60 minutes [13]. The research biosorption of Cr using *Persimmon* tannin gel had resulted in high biosorption of Cr heavy metal at 60 minutes [14]. The research of biosorption Pb and Cu with *Mangrove*

tannin gel that had resulted in high biosorption of Pb were 60 minutes, and Cu was 120 minutes [15].

The optimal condition to adsorb Cr from wastewater with *Mimosa pudica* tannin gel is 1:50 (m/v) at a contact time of 60 minutes with concentrations Cr in the solution after adsorption was 0,7 mg/L. This concentration was under the threshold of Cr concentration in textile wastewater based on the regulation of the Environment Minister of Republic Indonesia No.5 in 2014 which was 1 mg/L.

4. Conclusions

Based on the results of research that has been done can be concluded as follows:

1. The condensation polymerization process aimed to strengthen the structure of tannin as a biosorbent so the biosorbent was not easily dissolved in water.
2. The yield of *Mimosa pudica* tannin extract was 9.4% and the yield of *Mimosa pudica* tannin gel was 40%.
3. Biosorption of Cr heavy metal using *Mimosa pudica* gel tannin can reduce the concentration of Cr to 0.7098 mg/L below the threshold of Cr concentration in textile wastewater based on the regulation the Environment Minister of Republic Indonesia No.5 in 2014 which was 1 mg/L.
4. The optimal condition to adsorb of Cr heavy metal of wastewater using *Mimosa pudica* tannin gel was 1:50 (m/v) with a contact time of 60 minutes.

5. Acknowledgment

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