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Research Article

Optimization of Chromium (VI) Adsorption using Microalgae Biomass (*Spirulina sp.*) and its Application in Leather Tannery Waste

Optimasi Adsorpsi Kromium (VI) menggunakan Biomassa Mikroalga (Spirulina sp.) dan Aplikasinya pada Limbah Cair Penyamakan Kulit

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Abstract

This study was conducted to examine the adsorption of Cr (VI) metal using Spirulina sp (inactive) biomass and its application in leather tannery wastewater. The treatment was carried out to determine the influence of independent variables on Cr (VI) adsorption with variations in pH, contact time, and metal solution concentration. The values of the solution pH, adsorption time, and concentration of the best metal solution were used to determine the center points of the optimization variables through Response Surface Methodology (RSM). The results showed that based on the FTIR test, macromolecules present in Spirulina sp biomass included amino, carboxylate, and hydroxy groups. The combination of factor variables that produced the optimum response was at pH 3.165, contact time of 66.58 minutes, and Cr (VI) metal ion solution concentration of 22.9 mg/L, resulting in a Cr (VI) adsorption efficiency of 69.66%. The adsorption pattern was included in the Freundlich adsorption isotherm, and the application of Spirulina sp biomass adsorbent to tannery waste reduced the concentration of Cr (VI) from 3.9 g/L to an undetectable level at <1.4 g/L.

Keywords: adsorption; chrome; microalgae; RSM; tanning

Abstrak

Penelitian ini bertujuan untuk mempelajari adsorpsi logam Cr (VI) menggunakan biomassa Spirulina sp. (inaktif) dan pengaplikasiannya pada limbah cair penyamakan kulit. Perlakuan penelitian dilakukan untuk mengetahui pengaruh variabel independen terhadap adsorpsi Cr (VI) dengan variasi pH, waktu kontak dan konsentrasi larutan logam. Hasil pH larutan, waktu adsorpsi dan konsentrasi larutan logam yang terbaik digunakan untuk penentuan titik-titik pusat variabel optimasi menggunakan Response Surface Methodology (RSM). Uji FTIR makromolekul penyusun biomassa Spirulina sp. mengandung gugus amino, karboksilat dan hidroksi. Kombinasi variabel faktor yang menghasilkan respon optimum berada pada pH 3,165, waktu kontak 66,58 menit, konsentrasi larutan ion logam Cr (VI) 22,9 mg/L dan menghasilkan respon efisiensi adsorpsi Cr (VI) sebesar 69,66%. Pola adsorpsi pada penelitian ini termasuk dalam isotherm adsorpsi Freundlich. Aplikasi adsorben biomassa Spirulina sp. pada limbah penyamakan kulit dapat menurunkan konsentrasi Cr (VI) dalam limbah yang awalnya sebesar 3,9 μg/L turun menjadi tidak terdeteksi (<1,4 μg/L).

***Kata kunci**: adsorpsi; krom; mikroalga; penyamakan; RSM*

1. Introduction

Liquid leather tannery waste is hazardous when directly disposed of into the environment due to its toxicity attributed to Cr (VI), sulfides, and ammonia content [1]. Cr (VI) is the most widely used tannery agent, accounting for approximately 85% of global leather tannery. The presence of heavy metals in water is absorbed and accumulated in the cells of organisms living in the environment [2].

Commonly used methods for waste treatment include precipitation, filtration, oxidation, ozonation, irradiation, ion exchange, or photodegradation. Adsorption is one highly efficient method for heavy metal removal from liquid waste [3].

Previous studies have used microalgae biomass in the absorption of heavy metal ions [4][5]. This study used *Spirulina sp.*, a type of microalgae, endemic to Indonesian waters and has a higher adsorption capacity compared to *Scenedesmus sp.* and *Oscillatoria sp.* in absorbing heavy metals from liquid waste [4][6].

Several microalgae species reportedly have the potential to absorb metal ions, either in the living (active) or dead (inactive) state [7]. Although *Spirulina sp.* has been used as an adsorbent for leather tannery waste through active culture for phytoremediation [8], the use of inactivated biomass remains unexplored. The use of inactive biomass is not dependent on the live cell metabolism, allowing for more flexibility in environmental conditions such as pH, light, and temperature. Optimization of the microalgae adsorption process for waste has also not been thoroughly examined. This step is necessary to obtain optimal variables in the adsorption process, and one method effective method is the Response Surface Methodology (RSM).

RSM is useful for optimizing processes, where the response obtained is influenced by independent variables [9]. This method is also used to establish a model depicting the relationship between independent variables and the response, showing the process conditions with the best response [10]. Therefore, this study aimed to determine the optimal pH, time, and concentration in the Cr (VI) adsorption process using *Spirulina sp.* biomass and its application to leather tannery waste.

2. Research Methods

2.1 Equipment and Materials

The materials used included *Spirulina platensis* biomass obtained from CV. Neoalgae (Sukoharjo, Central Java), chrome tannery process waste from a leather tannery industry in East Java, pure chromium standard solution with a concentration of 1000 mg/L from $K_2Cr_2O_7$ p.a 99.5% (Merck), HNO_3 (technical), and NH_4OH (technical).

The equipment used included a pH meter for pH control, a Fourier Transform Infrared (FTIR) Spectrophotometer for biomass functional group characterization, and an Ultraviolet-Visible (UV-Vis) Spectrophotometer for Cr (VI) concentration testing. The software used for Cr (VI) adsorption optimization was Statistica 10.

2.2 Adsorption Variable Influences

The independent variables were pH, time, and metal concentration, while biomass was mixed with Cr (VI) solution at specific concentrations and pH in Erlenmeyer flasks. This study used 0.1 M

HNO_3 and 0.1 M NH_4OH to adjust the solution pH. The metal solution concentrations were varied through dilution from a 1000 mg/L metal stock solution [11].

2.2.1 Influence of pH on adsorption

About 100 mL of Cr (VI) solution (20 mg/L) was prepared, and its pH was adjusted using 0.1 M HNO_3 and 0.1 M NH_4OH. The pH variations included 2, 3, 4, and 5, while 400 mg of biomass was added to each solution in a 250 ml Erlenmeyer flask. Stirring was carried out at room temperature using a magnetic stirrer for 60 minutes. The mixture was then filtered with Whatman 41 filter paper. The concentration of Cr (VI) ions after adsorption was determined with a UV-Vis spectrophotometer.

2.2.2 Influence of Contact Time on Adsorption

About 100 mL of Cr (VI) solution with a concentration of 20 mg/L at the optimum pH was mixed with 400 mg of biomass in a 250 mL Erlenmeyer flask and stirred at room temperature. Contact time was varied to 30, 60, 90, 120, 150, and 180 minutes, then the mixture was filtered with Whatman 41 filter paper, and the Cr (VI) concentration was determined using a UV-Vis spectrophotometer.

2.2.3 Influence of Solution Concentration on Adsorption

About 100 mL of metal solution with concentrations set at 10, 20, and 30 mg/L at optimum pH was mixed with 400 mg of biomass in a 250 mL Erlenmeyer flask at room temperature using the optimum time. Filtration was then performed, and the Cr (VI) concentration was determined with a UV-Vis spectrophotometer.

2.3 Determination of Adsorption Isotherms

Adsorption capacity and efficiency were calculated using Equations 1 and 2. The linear form of the Langmuir and Freundlich isotherm equations is shown in Equations 3 and 4.

$$q_e = \frac{(C_0 - C_e)V}{w} \quad \text{.......(1)}$$

$$\%E = \frac{(C_0 - C_e)}{C_0} x\ 100\ \% \quad \text{.......(2)}$$

$$\frac{C_e}{q_e} = \frac{1}{Q_0 k_L} + \frac{C_e}{Q_0} \quad \text{.......(3)}$$

$$log(x/m) = \log k_F + \frac{1}{n} \log C_e \quad \text{.......(4)}$$

where, q_e is the adsorbed metal ion (mg/g); C_0 is the metal ion concentration before adsorption (mg/L); C_e is the metal ion concentration after adsorption (mg/L); V is the volume of the metal ion solution (L); w is the amount of *Spirulina sp.* biomass adsorbent (g) and %E is the adsorption efficiency. Q_o is the amount of adsorbed substance, and k_L is the Langmuir constant [11]. x is the amount of solute adsorbed. Meanwhile, m is the weight of the adsorbent used (g). k_F and n are constants that combine factors affecting adsorption, such as the capacity and intensity of adsorption [12].

2.4 Optimization of Cr (VI) Adsorption

Optimization aims to develop an empirical model to find optimal parameters for maximum or minimum responses [13]. This step can be performed using the RSM method [14]. The optimal pH of the solution, adsorption time, and metal solution concentration were determined to establish the central points of the variables. RSM was used to examine the influence of pH treatment, adsorption time, and metal solution concentration on the response variable, namely the adsorption efficiency of Cr (VI) metal ions.

Central Composite Design (CCD), an experimental design in RSM was used to construct a polynomial model of a mathematical function from independent variables to the response (y). The independent variables were pH (x_1), contact time (x_2), and Cr (VI) (x_3). The CCD experimental design was tabulated using Statistica 10 software. Based on the design type, 16 experiments are required, as summarized in Table 1.

The software analyzed the model that best fits the response conditions to identify the optimal points for the given response [15]. The lower, upper, and center points of the design were encoded as -1, 1, 0, and α, where +1 shows the high level, -1 the low level, $\alpha = 2^{n/4}$ (n is the number of variables or factors) represents the star point, and 0 signifies the center point. Star points were added to the design to generate an estimate of the surface area in the model, and the optimization formulation was presented in Table 2.

2.5 Application of Adsorption to Leather Tannery Waste

As part of the characterization stage, the waste was analyzed to determine the initial Cr (VI) concentration. The final Cr (VI) concentration in the waste was determined by adding 1 g of *Spirulina sp.* biomass adsorbent to 100 mL of waste at the optimum pH. Stirring was carried out at room temperature for the optimum time, followed by filtration. The filtrate was analyzed for Cr (VI) concentration as the final concentration in the waste. FTIR analysis was conducted for biomass characterization before and after Cr (VI) adsorption [11].

Table 1. CCD optimization

Run	x_1	x_2 (minute)	x_3 (mg/L)
1	2.00	30.00	10.00
2	2.00	30.00	30.00
3	2.00	90.00	10.00
4	2.00	90.00	30.00
5	4.00	30.00	10.00
6	4.00	30.00	30.00
7	4.00	90.00	10.00
8	4.00	90.00	30.00
9	3.00	60.00	20.00
10	1.24	60.00	20.00
11	4.76	60.00	20.00
12	3.00	7.08	20.00
13	3.00	112.9	20.00
14	3.00	60.00	2.36
15	3.00	60.00	37.64
16	3.00	60.00	20.00

Table 2. Optimization formula factors

Factor	Unit	Star Point (Low)	Low Level (-1)	Center point (0)	High Level (+1)	Star Point (High)
pH (x_1)		1.24	2.00	3.00	4.00	4.76
Contact time (x_2)	minute	7.08	30.00	60.00	90.00	112.91
Initial concentration of Cr (VI) (x_3)	mg/L	2.36	10.00	20.00	30.00	37.64

3. Results and Discussion

3.1 Characterization of Biomass with FTIR

FTIR results were used to identify functional groups in *Spirulina sp.* biomass. Based on the spectrum in Figure 1, *Spirulina sp.* biomass before Cr (VI) adsorption showed absorption at the wavenumber of 2928.57 cm^{-1} representing a stretching vibration of -OH [16]. There was also absorption at the wavenumbers of 3306 cm^{-1} and 1453 cm-1 showing stretching vibrations of N-H and C-H bonds respectively. Additionally, stretching vibrations of C=O (carboxylate ester) and C-O were observed at wavenumbers of 1652 cm-1 [17] and 1153 cm^{-1} [18]. FTIR results after Cr (VI) adsorption showed a shift in wavenumbers. Functional groups that experienced a shift in wavenumbers were assumed to play a role in Cr (VI) adsorption.

Adsorption of Cr (VI) metal resulted in a shift in wavenumbers due to the positively charged surface of the biomass, attracting anionic species electrostatically, and leading to strong physiosorption [19]. Therefore, based on the FTIR spectrum in Figure 1, functional groups in Spirulina sp. biomass implicated in the adsorption process of Cr (VI) included hydroxyl (-OH) from polysaccharides, C=O peptide (-CONH-) originating from proteins, and amine groups [5].

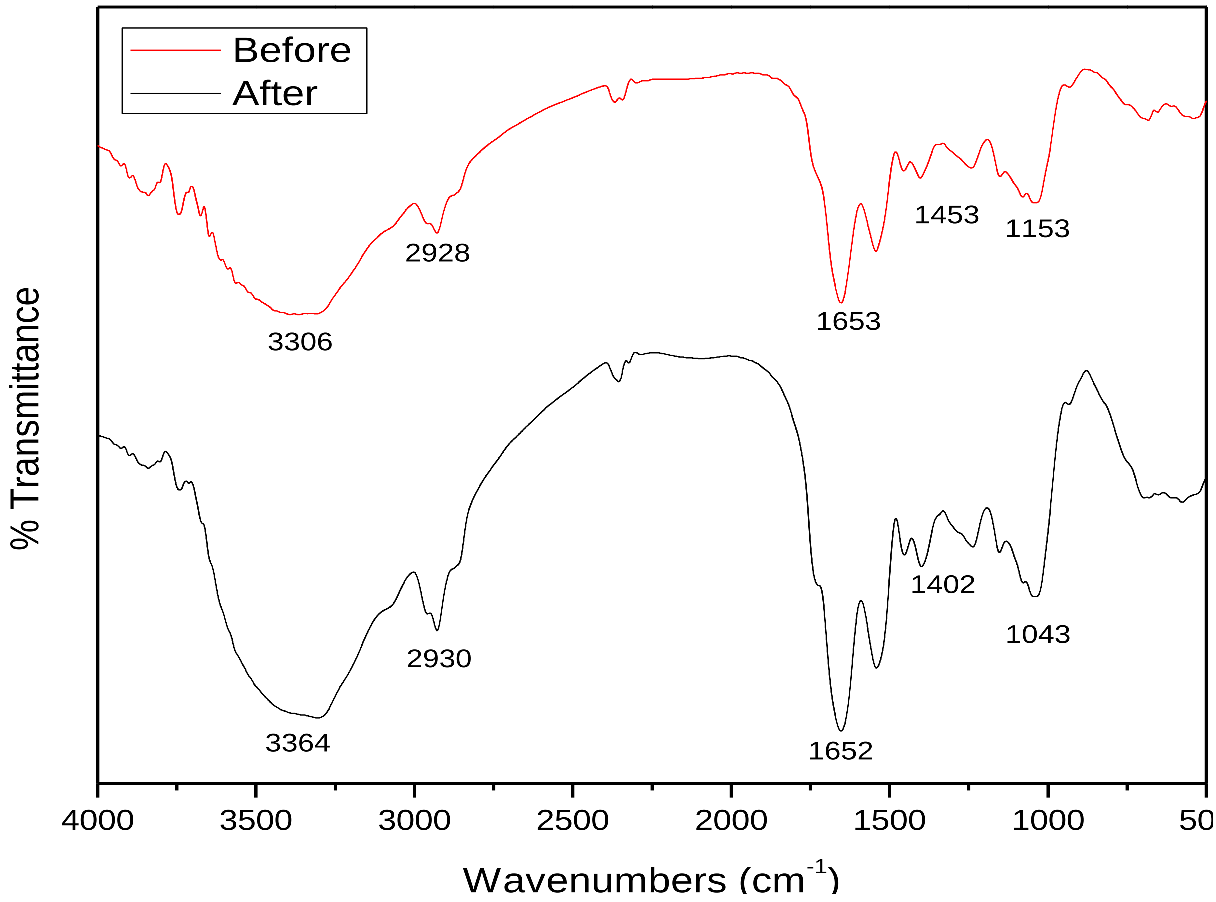

Figure 1. FTIR spectra of Spirulina biomass before and after Cr (VI) adsorption

3.2 Influence of pH on Adsorption

The initial pH of the solution is crucial for Cr (VI) adsorption because the protonation of the adsorbent configures active ion exchange sites and surface activity [20]. The results of Cr (VI) metal ion adsorption with pH variation are shown in Figure 2.

The highest adsorption capacity for Cr (VI) metal ions was achieved at an initial solution pH of 3. As discussed in the FTIR analysis, the biomass contains easily hydrolyzable groups including amines and aldehydes. Both of these groups are easily protonated, expanding more binding sites upon acidification of the biomass [4]. At low pH, the biomass surface containing anionic groups such as amines, carboxyls, and hydroxyls are protonated and become positively charged. Concurrently, through its free electron pairs, Cr (VI) metal ions in an acidic solution exist in the form of anionic species, such as $HCrO_4^-$, CrO_4^{2-}, and $Cr_2O_7^{2-}$, which easily interact with the adsorbent, resulting in a relatively high adsorbed amount.

3.3 Influence of Time on Adsorption

In the initial minutes (Figure 3), adsorption occurred rapidly due to the abundance of active sites in the adsorbent. However, after 60 minutes, Cr (VI) adsorption remained relatively constant. Extending the time up to 180 minutes did not significantly increase the adsorption capacity. Equilibrium was achieved at this point, where all active sites on the *Spirulina sp.* adsorbent were saturated. After reaching equilibrium, the significantly adsorbed amount of metal ions does not change with the additional contact time between Cr (VI) metal ions and the adsorbent [19].

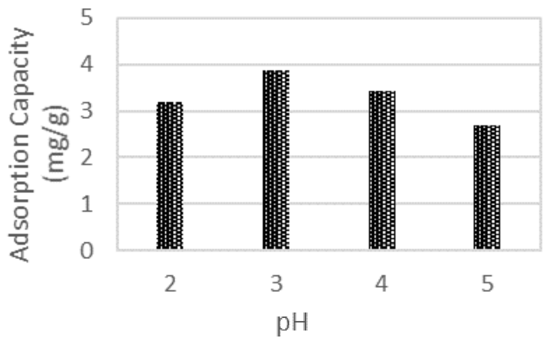

Figure 2. Influence of solution pH on Cr (VI) adsorption capacity

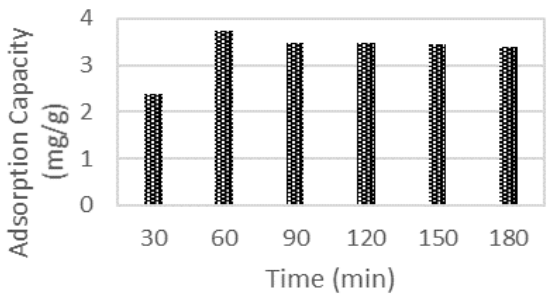

Figure 3. Influence of time on Cr (VI) adsorption capacity

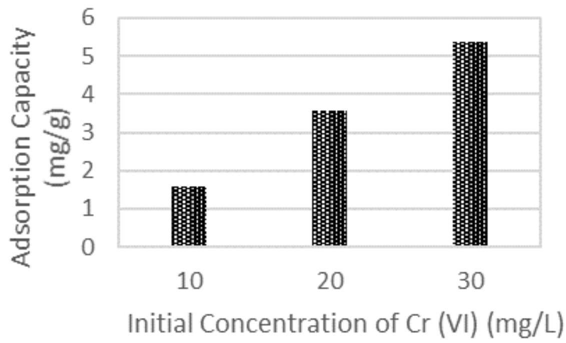

Figure 4. Influence of initial concentration of Cr (VI) on adsorption capacity

3.4 Influence of Cr (VI) Concentration on Adsorption

Based on Figure 4, the adsorption capacity of Cr (VI) was influenced by the metal concentration. In this case, increasing the concentration of the metal solution with a constant amount of adsorbent also improved the adsorption capacity. The number of active sites on the adsorbent surface is proportional to the surface area [20]. When the active sites are not yet saturated, the increase in Cr (VI) concentration in contact will be proportional to heightened Cr (VI) adsorption capacity. The biomass surface has limited binding sites, and after completing adsorption at those sites, further loading of Cr is not feasible [5].

3.5 Adsorption Isotherm Model

The relationship between the adsorbate, adsorbent, and surface properties is reflected in the adsorption isotherm [21]. Adsorption data at various Cr (VI) concentrations were used to determine the adsorption isotherm.

Based on the R^2 value in Table 3, the Freundlich isotherm could better interpret the adsorption data (R^2 = 0.97) compared to the Langmuir isotherm, implying the adsorbent surface was heterogeneous [5]. Additionally, the adsorption observed followed a physisorption mechanism, causing weak bonding between the adsorbent and adsorbate, which allowed for desorption to occur, and the adsorbent could be reused [19].

Table 3 shows the parameter values in the adsorption isotherm, including k_F and 1/n values showing the capacity of the adsorbent, while k_F and Q_0 represent the maximum amount of adsorbate absorbed by the adsorbent in mg. The larger the k_F and Q_0 values, the greater the adsorption capacity. Based on this data, it was observed that the *Spirulina sp.* biomass adsorbent had a maximum adsorption capacity of 0.389 mg/g. The magnitude of 1/n provides a measure of adsorption favorability, with values between 1 and 10 showing favorable adsorption. For this study, the 1/n value also presents similar results, representing favorable adsorption [22].

3.6 Optimization of Factor Combinations for Cr (VI) Ion Adsorption

The central variable points were determined from the data on the best pH, time, and Cr (VI) concentration (Figure 3-4). Optimization of adsorption in this study used three independent variables, namely pH, time, and Cr (VI) concentration, as well as one response variable, the percentage of Cr (VI) adsorption. Optimal conditions were determined using Statistica 10 software to generate mathematical equations and polynomial models that fit the results [23].

The program determines the model type based on the coefficient of determination R^2 and the significance of the F_{count}. The type of polynomial model can also be observed from the sum of squares in the model order (Sequential Model Sum of Squares), lack of fit test, R^2, and adjusted-R^2 [24]. A model is considered good when it has significant values for the response and insignificant values for the lack of fit test. An insignificant lack of fit test value shows that the model is suitable or sufficiently represents the data [13].

Table 3. Langmuir and Freundlich isotherm parameters

Adsorbent	Freundlich Isotherm			Langmuir Isotherm		
	k_f (mg/g)	1/n	R^2	Q_0 (mg/g)	k_L (L/mg)	R^2
Spirulina sp. Biomass	0.21	1.43	0.97	7.54	0.41	0.58

The results obtained from 16 experiments are presented in Table 4. To find the predicted adsorption efficiency values, calculations were carried out based on the model equation determined according to the recommendations provided by STATISTICA 10, applying the CCD experimental design [25]. The model is presented in Equation 5, and the predicted flux values are depicted in Table 4.

$$y_{\mathbf{prediction}} = 39.7290 + 18.1896x_1 + 0.9438x_2 + 4.1046x_3 - 2.2516x_1{}^2 - 0.0059x_2{}^2 - 0.0673x_3{}^2 - 0.1719x_1x_3 - 0.0072x_2x_3 \quad \text{.....................................(5)}$$

Description:
x_1 = pH of Cr (VI) metal ion solution
x_2 = contact time (minutes)
x_3 = concentration of Cr (VI) (mg/L)

Table 4 shows a difference between the observed and predicted values, as shown in the error column (% error). Therefore, a variance analysis was considered necessary to evaluate the suitability and accuracy of the experimental results obtained through an F-test. The accuracy test of the regression model was carried out by dividing the mean of squares of regression (MS_{reg}) and the mean of squares of residuals (MS_{res}). Both metrics were then compared with the table value of Fisher (F), where both M_{Sreg} and M_{Sres} represented the Sum of Squares divided by the Degree of Freedom [13]. The results of the subsequent variance analysis followed the hypotheses:

H_0 = all β_i values are zero
H_1= at least one β_i is not zero
H_0 is declared true if $F_{count}<F_{Table}$.

Another test was conducted to strengthen the assumption of model suitability through a lack of fit test [26], following the hypotheses:

H_0 = there is no lack of fit; the model created is suitable for the data
H_1 = there is a lack of fit; the model created does not represent the data

Table 4. Cr (VI) adsorption efficiency in 16 experiments

Run	pH	Time (minutes)	Concentration Cr (VI) (mg/L)	Adsorption Efficiency Cr (VI) (%)		
	x_1	x_2	x_3	$y_{observation}$	$y_{predictions}$	% error
1	2.00	30.00	10.00	40.78	39.41	3.33
2	2.00	30.00	30.00	56.31	56.49	0.32
3	2.00	90.00	10.00	48.78	49.60	1.66
4	2.00	90.00	30.00	56.03	58.06	3.62
5	4.00	30.00	10.00	47.72	45.34	4.99
6	4.00	30.00	30.00	56.71	55.54	2.04
7	4.00	90.00	10.00	56.06	55.52	0.94
8	4.00	90.00	30.00	56.10	57.11	1.80
9	3.00	60.00	20.00	68.67	66.38	3.32
10	1.24	60.00	20.00	58.30	57.18	1.92
11	4.76	60.00	20.00	60.01	61.58	2.62
12	3.00	7.08	20.00	42.31	44.81	5.91
13	3.00	112.91	20.00	57.23	55.17	3.58
14	3.00	60.00	2.36	35.43	37.22	5.05
15	3.00	60.00	37.64	55.02	53.68	2.43
16	3.00	60.00	20.00	64.05	66.38	3.64

H_0 was accepted when the p-value was more than the degree of significance, α = 0.05 [13]. The accuracy of this model was also reflected in the value of the coefficient of determination R^2. When the R^2 value exceeded 70%, it was considered accurate. This shows that the value estimated by the model is close to the experimental value. ANOVA calculations were obtained using STATISTICA Ver.10 Software as shown in Table 5.

Based on Table 5, the value of F_{Count} = 7.4775, while F_{Table} = 3.34. Given that F_{Count} was > F_{Table}, H0 was rejected and the alternative hypothesis H1 was accepted. In other words, the independent variables x_i had a significant influence on the model. Table 4 also shows that the p-value in the lack of fit test was 0.733, or greater than the α value. Therefore, H0 was accepted, signifying that the model was considered appropriate. The coefficient of determination, R^2, reached 0.96, hence, the model was considered suitable because it met the three test parameters [13].

The influences of each factor forming the equation were also analyzed based on the results of the ANOVA test. According to Equation 5, three effects influencing the value of Cr (VI) adsorption efficiency were observed, namely linear, quadratic, and interaction influences. An influence is considered statistically significant at $p \leq 0.05$. The impact of these three influences was determined by the coefficients, and the corresponding p-values were presented in Table 6.

Based on Table 6 and Equation 5, the variables pH, time, and the concentration of Cr (VI) metal ions, along with the quadratic influences, had a significant impact. All three variables showed a significant influence, both in terms of linear and quadratic. The quadratic factors of pH (x_1^2), adsorption time (x_2^2), and metal ion solution concentration (x_3^2) showed a negative impact on the response of adsorption efficiency. In contrast, the interaction between these factors had no significant influence on the adsorption efficiency of Cr (VI) because the p-values were greater than 0.05 [27]. Equation 5 was then simplified into Equation 6.

Table 6. Significance of each empirical model factor

Factor	p
x_1	0.020349
x_1^2	0.037510
x_2	0.001191
x_2^2	0.000795
x_3	0.000160
x_3^2	0.000211
$x_1.x_2$	0.999010
$x_1.x_3$	0.125761
$x_2.x_3$	0.067476

Table 5. Cr (VI) adsorption ANOVA

Source	Sum of squares	Degree of freedom	Mean square	F_{count}	$F_{0.05}$ (Table*)	p	R^2
SS regression	1330.368	9.00	147.8186	7.4775	3.34		0.9602
S.S. error	44.865	6.00	7.4775				
Lack of fit	34.193	5.00	6.8386			0.733	
S.S. total	1129.449						

*F_{Table} of F distribution percentages for 0.05% probability

$$y_{pred} = 39.7290 + 18.1896x_1 + 0.9438x_2 + 4.1046x_3 - 2.2516x_1^2 - 0.0059x_2^2 - 0.0673x_3^2 \quad \text{......(6)}$$

The optimum conditions were determined based on the stationary values for each model. Stationary values represent the highest response and serve as the best parameter for the performance of Cr (VI) metal ion adsorption. The position of the stationary point was identified mathematically using a matrix method assisted by STATISTICA Ver.10 software [28].

Optimization showed that the variables producing the optimum response for Cr (VI) adsorption efficiency at 69.66% were x_1=3.165, x_2=66.58 minutes, and x_3=22.90 mg/L. The RSM modeling results for Cr (VI) adsorption efficiency are illustrated in Figures 5 and 6 in the form of surface and contour plots. In this interaction, the initial concentration of Cr (VI) (x2) was set at 20 mg/L, which was the optimal initial concentration for Cr (VI) in the adsorption process.

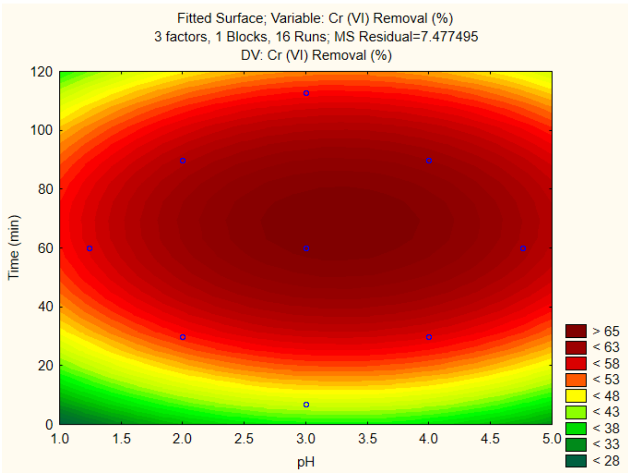

Figure 5. Contour plot of interaction of pH (x_1) with adsorption time (x_2) and initial concentration of Cr (VI) 20 mg/L (x_3) against percent adsorption of Cr (VI)

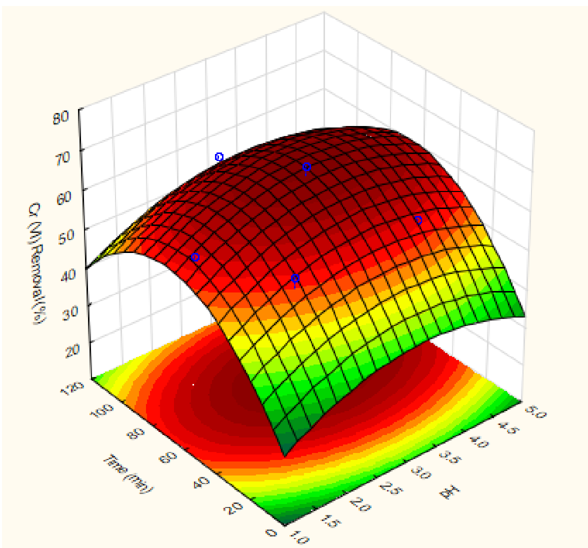

Figure 6. Surface plot 3D Interaction of pH (x_1) with adsorption time (x_2) and initial concentration of Cr (VI) 20 mg/L (x_3) on percent adsorption of Cr (VI)

The circular contour lines with a blue point at the center shown in Figure 5 depict the best response values, signifying an increase in the efficiency of Cr (VI) ion adsorption. The red-colored area represents the highest adsorption efficiency. The best response values were obtained by conditioning the factors at the central point, on the contour within the center of the circle. Figure 6 presents a three-dimensional representation of the adsorption efficiency response, showing that pH and time significantly influence the percentage removal of Cr (VI) with a maximum stationary region. The selection of codes representing data close to the optimum point (coded as 0) is crucial because a significant shift in prediction can result in the failure to find the optimum point [13].

Additional experiments under optimum conditions were conducted to confirm the predicted results. The optimization showed that the optimal adsorption conditions were x_1=3.165, x_2=66.58 minutes, and x_3 22.90 mg/L resulting in a Cr (VI) adsorption efficiency of 69.66%.

3.7 Application of Cr (VI) Adsorption on leather tannery waste

The initial concentration of Cr (VI) in tannery waste was 3.9 μg/L, and then adsorption was carried out using *Spirulina sp.* biomass adsorbent under known optimum conditions. Based on the test results, the Cr (VI) present in the wastewater sample after adsorption was undetectable (<1.4 μg/L). This shows that the use of *Spirulina sp*. biomass can reduce the Cr (VI) concentration in leather tanning wastewater. In another study that used Chlorella vulgaris microalgae biomass as an adsorbent for Cr (VI) in leather tanning wastewater, a reduction in Cr (VI) concentration reaching 30.01% was observed [29]. The decrease in efficiency observed was attributed to the significant interaction between the functional groups of microalgae biomass and other compounds (competitors) in wastewater during the chromium removal process [29].

4. Conclusion

In conclusion, *Spirulina sp.* biomass was identified as a suitable material for the adsorption of Cr (VI) from solutions. The functional groups detected in the composition included amino, carboxylate, and hydroxyl groups. Furthermore, the combination of factor variables that yielded the optimum response using the RSM method was at pH 3.165, contact time of 66.58 minutes, and concentration of Cr (VI) metal ion solution at 22.9 mg/L, resulting in an adsorption efficiency response of 69.66%. The application of *Spirulina sp.* biomass adsorbent in tannery wastewater effectively reduced the concentration of Cr (VI) from 3.9 μg/L to an undetectable level of <1.4 μg/L.

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