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Optimization of Pb (II) Ion Removal from Synthetic Wastewater Using Dead (*Chlorophyta*) Macroalgae: Prediction by RSM Method

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Abstract

The Pb^{2+} ions biosorption removal onto dead biomass of *Chlorophyta* algae is optimized by employing response surface methodology (RSM). Central composite design (CCD)-based experiments were carried out, and RSM was used to evaluate the results. The effects of contact time (15-120min), with pH solution (2-7), initial lead concentration (25-100 mg/L), biomass dose (0.01-1 g/100 mL), agitation speed (100-300 rpm) on the biosorption process were investigated. The optimal conditions of the experimental, data were pH (5), metal concentration (50mg/L), dosage (0.2g/100mL), agitation speed (200 rpm), and contact time of 120 min with constant particle size (63 μm), which gave 98.88% removal efficiency. All the variables and reactions in the biosorption experiments were evaluated using the desirability function to determine the optimal point at which the desired parameters may be attained. The promising results obtained indicate the potential use of *Chlorphyta* green macroalgae to treat industrial wastewater polluted with toxic metals.

Keywords: *Adsorption; Chlorophyta Algae; Pb (II) ions removal; Algae characteristics; Response surface methodology.*

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1- Introduction

Water contamination is a major issue that affects millions of people worldwide and poses a threat to the entire ecosystem. It not only ranks among the top global risk factors for a variety of illnesses, diseases, and fatalities, but it also plays a role in the ongoing global decline in the sources of potable water. Some of the most dangerous and pervasive contaminants that have negative impacts on the environment are heavy metal ions [1, 2]. Lead (II), a non-biodegradable and highly poisonous heavy metal, is one of the heavy metals discharged to water sources from industrial wastes such as vehicle manufacture, fuel cells, batteries, plastics, pulp industries, and so on [3, 4]. Since heavy metals cannot dissolve and are dangerous by nature, they pose substantial environmental dangers [5]. Pb(II) ions removal has received a lot of attention from researchers because it is regularly used in the battery manufacturing, gasoline combustion, mining, and electroplating industries [6, 7] and is thought to be a carcinogenic heavy metal that is particularly deadly at low concentrations [8, 9]. As a result, environmental engineers face significant difficulty in removing lead from water sources [10]. Several methods, such as ion exchange, electrochemistry, chemical precipitation, solvent extraction, membrane processes, flotation, and sorptive flotation method, are historically used to eliminate pollutants from wastewater [11]. A study by Abdulkareem and Alwared [12] found that the biosorption process is superior to other techniques for eliminating heavy metals from aqueous environments. High removal efficiency, low cost, ease of handling, and application across a broad pH range are a few of them.

Activated carbon is the most frequently used adsorbent material, but its cost is still high, according to Romero-Cano et al. [13], hence the technique is expected to have few uses. For that specific purpose, various researches have been carried out aiming to explore natural adsorbents, due to the large range of biological materials available and their propensity to improve metals uptake. Microorganisms, algae, and lignocellulosic materials are examples of biological materials that have the capacity to link with metal ions. These materials may have evolved naturally, without human interference, may have been generated for commercial purposes, or may have been

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*Corresponding Author: Email: d.dawood1011@coeng.uobaghdad.edu.iq designated as residue from agricultural and fermentative operations [14]. These biological materials mostly consist of cellulose and hemicellulose, but they also contain smaller amounts of organic and inorganic chemicals. Algae are regarded as efficient biosorbents due to their abundance of functional groups that can easily interact with particular pollutants in water, such as heavy metals [15]. Macroalgae have significant advantages over other biosorbents since they are abundant, can be grown in freshwater and saltwater under a variety of climatic settings, are inexpensive to prepare as a biosorbent and have a high heavy metal removal efficiency [16, 17]. Biosorption can occur passively or through the metabolic processes of living organisms. The ability to store at room temperature, the capacity to be used as a biosorbent for an extended period of time without losing its biosorption properties, the invulnerability to the toxicity of the effluent in which they are considered for treatment, the higher removal capacities in comparison to living microalgae are just a few of the advantages dry biomass has over living organisms [18, 19]. Metal biosorption capability in algae has already been evaluated. Solisio et al. [20] investigated the biosorption of mercury by dry biomass of Chlorella vulgaris. Abdelkareem et al. [21] evaluated the removal of Lead and Copper ions, using the Chlorophyceae algae and a mix of Chlorophyceae; Cyanophyceae, and Bacillariophyceae algae.

The focus of this research was to analyze and evaluate the lead biosorption removal employing dried biomass of *Chlorophyta* algae as a biosorbent, as well as to optimize the parameters involved for optimal lead removal efficiency. Response surface methodology (RSM) was used to investigate the effects of metal concentration, biosorbent dose, solution pH, and contact time on the biosorption mechanism using a central composite design (CCD).

2- Experimental Work

2.1. Materials

2.1.1. Algae preparation

The harvested algae were found on the water's surface in the Al-Yousfya irrigation canal in Baghdad/ Iraq. Fig. 1 depicted their microscopic pictures. Analysis of algal samples reveals that Bacillariophyta makes up 4% of the remaining 96% Chlorophyta. The dead algae were properly cleaned with tap water and then with distilled water to remove salt and impurities. After being washed, it was dried by air for a few days before being dried for 24 hours at 60°C in an oven, Fig. 2. The dried algae were then milled, sieved to get the required particle size (63 μm), and then kept at room temperature in a dry condition for subsequent use.

2.1.2. Stock Solution Preparation

A quantity of 1.6 gm of Pb $(NO_3)_2$ was dissolved in distilled water to prepare the stock solution of Pb (II) ions. A concentration of (25–100) mg/L was then obtained through dilution, and NaoH and HCl were utilized to obtain the required pH within range (2-7).

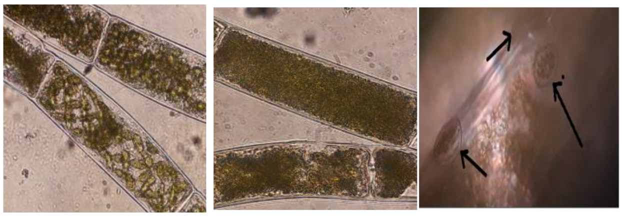

(a) (b) (c)

Fig. 1. Microscopic Images of Chlorophyta Macroalgae, (a) *Spirogyra subsalsa, (b) Mougeotia robusta, (c) Cocconeis pseudomarginata*


(a) (b)

Fig. 2. Raw and Powdered Algae, (a) Raw algae, (b) Powdered Algae

2.2. Batch adsorption runs

To conduct batch sorption tests, 250 mL conical flasks were loaded with 100 mL of the desired concentration of lead ions and macroalgae dosage. Experiments were carried out at room temperature by altering the initial pH value (2–7), a bio-sorbent dose (0.01–1) g/100 mL, an initial Pb(II) ions concentration (25–100) mg/L, agitation speed (100-300) rpm and 120 minutes contact time. At the end of the shaking time of (15-120) min with 15 min intervals, 10 mL of each sample was withdrawn and examined by using a flame atomic absorption spectrophotometer. Then, the removal percentage and equilibrium mass of Pb(II) ions were subsequently calculated using Eqs. 1 and 2, respectively.

$$\text{percentage of lead removal} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

$$q_e = (C_o - C_e) \times \frac{V}{m} \quad (2)$$

Where V represents lead solution volume (L), Co and Ce are the starting and equilibrium concentrations (mg/L) of metal ions, and m is algae mass (g).

Studying the adsorption isotherms and kinetics was conducted while maintaining other parameters constant, at concentrations ranging from 5 to 125 mg/L and contact times ranging from 0 to 180 min.

2.3. Experimental design

In order to improve and optimize processes as well as figure out the effects of numerous influencing parameters even in complicated interactions, response surface methodology (RSM) integrates statistical and mathematical tools [22]. The use of experimental design methodologies in the adsorption runs improves the efficiency of the adsorption process, more validation of the response to desired values, and overall cost savings [23]. In this investigation, five independent variables were used to maximize lead biosorption removal: metal concentration (A), algae dose (B), agitation speed (C), pH (D), and contact time (E). The Design Expert (version 13) was utilized for analyzing the experimental results, analysis of variance (ANOVA), and regression analysis of the generated data, as shown in Table 1. The lead biosorption removal (Y) was chosen as the experimental design's output response. To predict the best condition, the regression analysis technique based on the quadratic equation model (Eq. 3) was applied. Whereas Y stands for a predicted response, xi and xj represent coded variables, Bo; offset term, Bi, Bj, and Bij represent first-order, quadratic, and interaction effects, and i and j for factor index numbers.

$$Y = B_0 + B_1X_1 + B_2X_2 + B_3X_3 + B_{11}X_{12} + B_{22}X_{22} + B_{33}X_{32} + B_{12}X_1X_2 + B_{23}X_2X_3 + B_{13}X_1X_3 \quad (3)$$

Both the regression equation and the response surface graphs were utilized to decide the optimal values for the variables [24]. The fitted level of the quadratic equation model was explained using the determination coefficient (R^2), degree of freedom (DF), F-value, P-value, coefficient of variation (C.V.), and sufficient precision value.

Table 1. Range and Levels of Independent Parameters in the Experiment

Factor	Parameters	Units	Low level	High level
A	Lead concentration	mg/L	25	100
B	Algae dosage	g/100mL	0.01	1
C	Agitation speed	rpm	100	300
D	pH	-	2	7
E	Contact time	min	15	120

3- Results and Discussion

3.1. Adsorbent characterization

3.1.1. Fourier Transform Infrared (FTIR)

The functional groups involved in algae before and after the adsorption of lead ions are depicted in Fig. 3 and Fig. 4, respectively. The typical algal cell wall is made up of an amorphous matrix and a fibril skeleton in many Chlorophyta algae. Algal cell walls are composed of polysaccharides called alginic acid, chitin, and xylan, which are recognized to serve as metal-binding sites. The algal surface has chemical compounds such as carboxyl, hydroxyl, sulfhydryl, phosphate, sulfate, imidazole, and amine that can bind metal ions. Lead ions bind to the surface of algae as part of their mechanism for adsorbing metals, and subsequently, absorption occurs. Algal biosorption must occur via one of the two mechanisms: (1) an ion-exchange technique using the ions Ca, Mg, Na, and K ions on the surface of algae to displace them; (2) complexing of lead ion and functional groups [5, 25].

Fig. 3 represents free algae FTIR analysis before adsorption which shows numerous functional groups the 1st functional group was the O−H bond (hydroxyl group) represented by 3287.04, the 2nd functional group was the anti-symmetrical stretching vibration of C–H bond (alkanes group) represented by 2920.3 and 2855.47, the 3rd functional group was C≡C bond (Alkynes group) represented by peaks at 2262.59, 2167.54, 2132.86, 2058.1 cm^{-1}, the 4th functional group was C=C bond (alkenes group) represented by 1648 cm^{-1}, the 5th functional group was C=O bond (Carbonyl group) depicted by peaks at 1992.23,1941.4,1804.43, and 1541.02 cm^{-1}, the 6th functional group was at peak 1417.86 cm^{-1} which is attributed to C−O environment found in algae, the 7th functional group was C–N bond (amine group) represented by 1018.94 cm^{-1}, the 8th functional group was C−X bond (Organohalogen compound group) represented by 1150.86, 872.57, 760.2, 705.3, 664.83, 604.69, 569.09, and 519.92 cm^{-1} [26]. Table 2 compares the functional group's bonds in terms of number before and after adsorption (single, double, and triple). In accordance with this, Table 2 displays the peak at 1648.14 cm^{-1} shifting to 1603.07 cm^{-1} after biosorption, demonstrating site-specific interactions. This might be a result of the free carboxyl group undergoing the normal transformation into a carboxylate group that takes place when Pb (II) ions and the carboxyl group interact. O-H stretching vibrations are what caused the strong peak at about 3278.04 cm^{-1} to shift to 3323.05 cm^{-1}. Moreover, FTIR spectra (Fig. 4) show that after Pb (II) ions treatment, the peaks at 2352.3, 2305.91, and 2127.93 cm^{-1} indicated slight variations that emerged in triple bond areas. Yet some peaks in the fingerprint region (from 1417.86 to 1415.27 cm^{-1} region, 1018.94 to 1030.91 cm^{-1}, 872.57 to 884.91 cm^{-1}, and 604.69 to 601.54 cm^{-1} region) exhibited a noticeable shift, indicating that hydroxyl, amino, and carboxyl groups were involved in Pb (II) adsorption [27]. Another researcher, Elgarahy et al. who used various types of algae as bio-sorbents for heavy metals removal, supports these findings [28].

3.1.2. Scanning Electron Microscopy -Energy Dispersive X-Ray Analyzer

The SEM micrographs of dead algae in Fig. 5 show considerable changes in the morphology of the investigated alga. Fig. 5 a and b show the morphological variations between algal biomass before and after lead biosorption. A meshwork structure deteriorated considerably in *Chlorophyta algae* enriched with Pb^{+2} ions. SEM images revealed a reduction of filament thickness, as well as a significant prevalence of reproductive structures. Furthermore, Pb^{+2} ion-enriched biomass displayed obvious cell wall deformation [29]. To elucidate dead algae components in greater detail, Fig. 6 illustrates the EDS spectrum. It lists the amounts of calcium, oxygen, and carbon, which are the three elements that make up most algae. The results revealed that carbon accounted for 68.5 percent of the material composition, with oxygen accounting for 26.4 percent and calcium accounting for 5.1 percent. When dry, macro-algae can include 20% lipids, 45% protein, and 20% carbs [30], which explains the major carbon content identified in the studied sample.

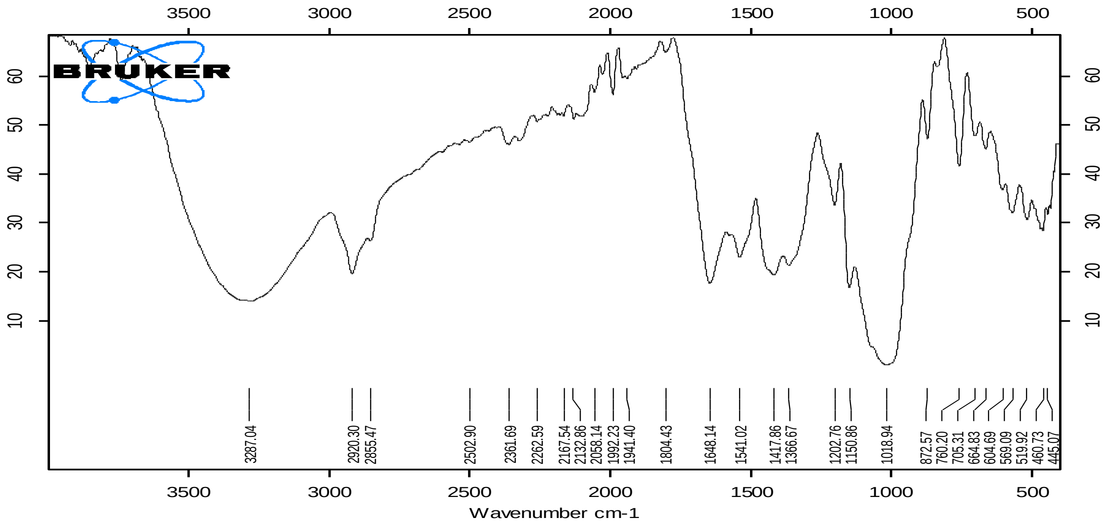


Fig. 3. FTIR of Algae Before Lead Adsorption

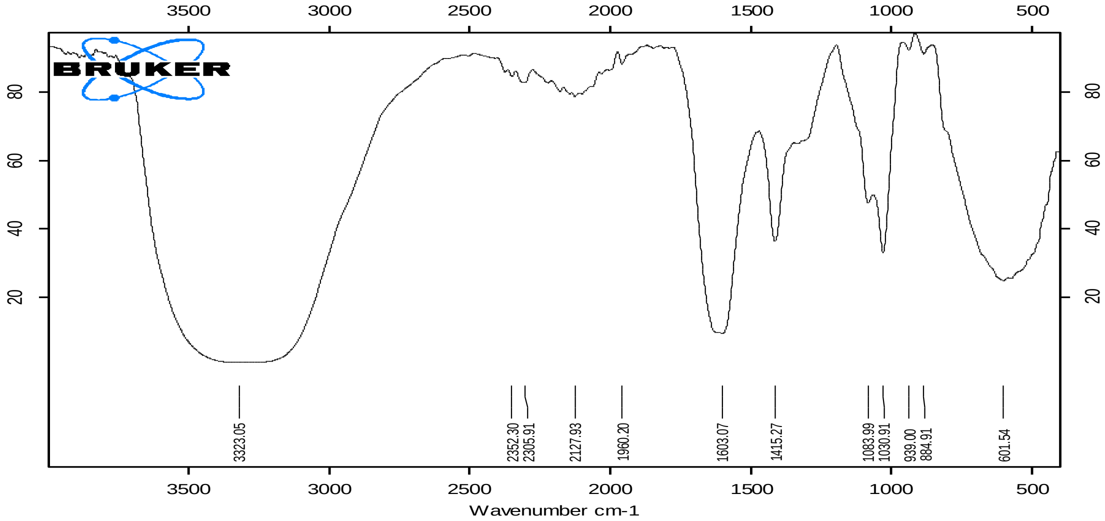
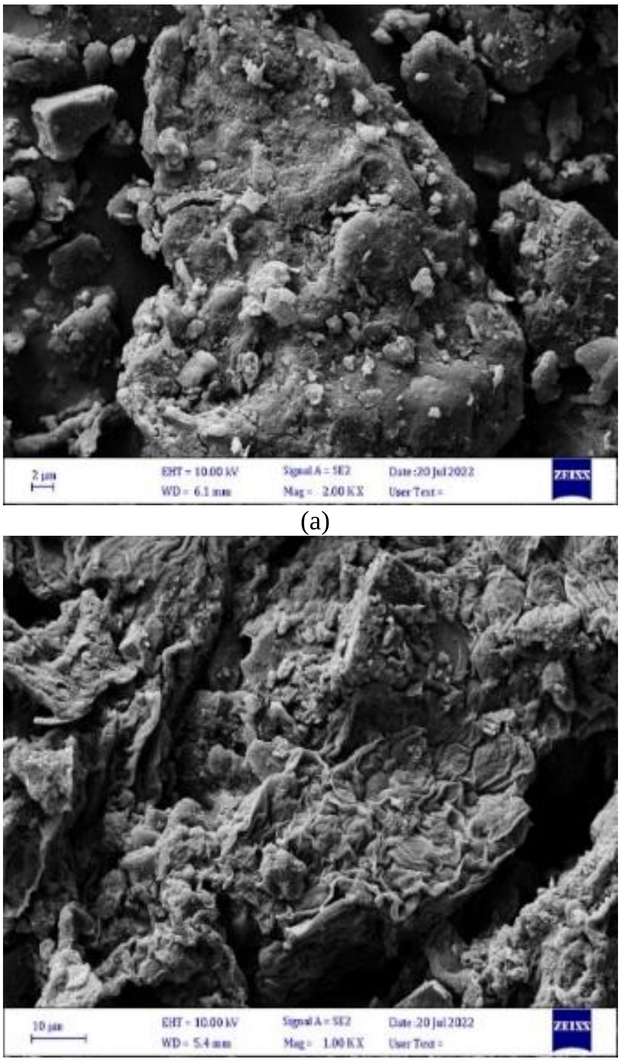


Fig. 4. FTIR of Algae After Lead Adsorption

Table 2. FTIR Absorption Bands of Algae

	Single bond (O-H, N-H, C-H)	Triple bond (C≡C , C≡N)	Double bond (C=C , C=N , C=O)	Fingerprint
Before treatment	3278.04	2361.69	1992.23	1417.86
	2920.3	2262.59	1941.4	1366.67
	2855.47	2167.54	1804.43	1202.76
	2502.9	2132.86	1648.14	1150.86
		2058.14	1541.02	1018.94
				872.57
				760.2
				705.31
				664.83
				604.69
				569.09
				519.92
After treatment	3323.05	2352.3	1960.2	1415.27
		2305.91	1603.07	1083.99
		2127.93		1030.91
				939
				884.91
				601.54



(a)

(b)

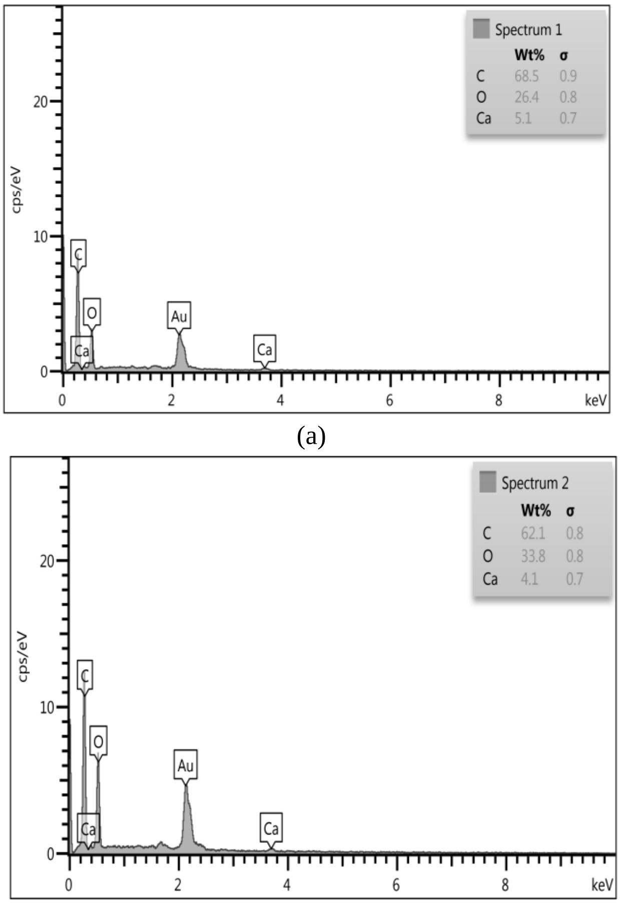
Fig. 5. SEM Micrograph of Algae: (a) Before Lead Adsorption, (b) After Lead Adsorption

3.2. Central composite design (CCD) analysis

Table 3 displays the levels of variables and experimental outcomes obtained using CCD. Eq. 4 gives the quadratic model for lead biosorption removal in terms of coded variables:

$$\text{Removal efficiency} = 53.11 + 0.3677B - 2.9C - 6.16D + 33.41E - 3.06CE - 5.85DE - 12.35B^2 - 4.9C^2 - 8.94D^2 \quad (4)$$

ANOVA was used to determine the model's significance, and the outcomes are shown in Table 4. For each model coefficient, the F and P values were utilized to confirm their applicability. The F-value of 175.54 for the model suggests that it is significant, F-value this high is due to noise. A statistically significant coefficient is one with a P-value less than 0.05, and a significant coefficient in the model's equation is one with a higher F-value [31]. Significant model terms have P-values less than 0.05, as indicated in Table 4, and the linear terms agitation speed (C), solution pH (D), and contact duration (E) are significant model terms. Values greater than 0.05 indicate that the model terms are unimportant, and the initial concentration (A) effect is unimportant because it is absent from Eq. 4. In addition, the algae dosage (B) effect was insignificant (P = 0.7401). The effects of squared terms of dosage^2 (B^2), agitation speed^2 (C^2), and pH^2 (D^2) and the interaction between pH solution and contact time (DE) were significant; however, the effects of interaction between agitation speed and contact time (CE) was insignificant (P>0.05) and were not required to explain the adsorption.



(a)

(b)

Fig. 6. EDS Spectra of Algae: (a)Before, (b) After adsorption

The amount of variation in response that the model is able to effectively explain is measured by the determination coefficient (R^2) [32]. As indicated in Table 4, the difference between the Expected R^2 of 0.9432 and the Adjusted R^2 of 0.9475 is less than 0.2. Nonetheless, the model equation showed a significant relationship between the response to lead biosorption removal and the independent variables. The lack-of-fit P-value of 1 demonstrated insignificance as was predicted, however, the model P-value of less than 0.05 indicated significance. If the P-value is more than 0.05, the predicted model is likely to be accurate [33].

As indicated by the Lack of Fit F-value of 0.22, the Lack of Fit is not significant when compared to the pure error. A big Lack of Fit F-value has a 100% probability of being the result of noise. By comparing the anticipated values at the design points to the average prediction error, a precision of 45.4559 is considered to be satisfactory. The plot of actual vs projected values in Fig. 7 shows the data distribution that is near the fitted line, demonstrating the model's adequacy to explain the experimental data. In this instance, the model's low probability value supported the rejection of the null hypothesis, and it was determined that the data had a normal distribution [34].

Table 3. The Central Composite Design and Experimental Lead Biosorption Removal Values

Time	lead conc.	Algae dosage	Agitation speed	pH	Actual Pb removal%	Predicted Pb removal %
15	25	0.2	200	5	10.25	14.37
30	25	0.2	200	5	18.64	23.58
45	25	0.2	200	5	29.85	32.79
60	25	0.2	200	5	38.45	42.00
75	25	0.2	200	5	50.12	51.21
90	25	0.2	200	5	62.34	60.42
105	25	0.2	200	5	70.65	69.63
120	25	0.2	200	5	74.23	78.85
15	50	0.2	200	5	15.32	14.37
30	50	0.2	200	5	21.64	23.58
45	50	0.2	200	5	35.32	32.79
60	50	0.2	200	5	48.65	42.00
75	50	0.2	200	5	58.65	51.21
90	50	0.2	200	5	70.45	60.42
105	50	0.2	200	5	85.36	69.63
120	50	0.2	200	5	98.88	78.85
15	100	0.2	200	5	9.23	14.37
30	100	0.2	200	5	15.32	23.58
45	100	0.2	200	5	25.34	32.79
60	100	0.2	200	5	34.65	42.00
75	100	0.2	200	5	44.32	51.21
90	100	0.2	200	5	57.62	60.42
105	100	0.2	200	5	67.32	69.63
120	100	0.2	200	5	70.23	78.85
15	50	0.01	200	5	11.68	6.56
30	50	0.01	200	5	19.26	15.77
45	50	0.01	200	5	27.84	24.99
60	50	0.01	200	5	35.65	34.20
75	50	0.01	200	5	43.71	43.41
90	50	0.01	200	5	51.24	52.62
105	50	0.01	200	5	55.74	61.83
120	50	0.01	200	5	60.18	71.04
15	50	0.1	200	5	13.54	10.71
30	50	0.1	200	5	21.32	19.93
45	50	0.1	200	5	29.95	29.14
60	50	0.1	200	5	41.76	38.35
75	50	0.1	200	5	49.25	47.56
90	50	0.1	200	5	54.47	56.77
105	50	0.1	200	5	65.78	65.98
120	50	0.1	200	5	78.28	75.19
15	50	0.5	200	5	14.23	19.28
30	50	0.5	200	5	24.35	28.49
45	50	0.5	200	5	33.77	37.70
60	50	0.5	200	5	46.88	46.91
75	50	0.5	200	5	63.45	56.12
90	50	0.5	200	5	69.41	65.34
105	50	0.5	200	5	76.52	74.55
120	50	0.5	200	5	83.56	83.76
15	50	1	200	5	9.71	7.30
30	50	1	200	5	18.23	16.51
45	50	1	200	5	26.37	25.72
60	50	1	200	5	35.78	34.93
75	50	1	200	5	43.65	44.14
90	50	1	200	5	52.78	53.35
105	50	1	200	5	61.48	62.57
120	50	1	200	5	68.42	71.78
15	50	0.2	100	5	11.25	9.30
30	50	0.2	100	5	18.65	19.39
45	50	0.2	100	5	28.34	29.47
60	50	0.2	100	5	36.81	39.56
75	50	0.2	100	5	41.35	49.65
90	50	0.2	100	5	65.52	59.73
105	50	0.2	100	5	74.67	69.82
120	50	0.2	100	5	80.23	79.90
15	50	0.2	300	5	10.11	9.63
30	50	0.2	300	5	17.85	17.97
45	50	0.2	300	5	25.64	26.30
60	50	0.2	300	5	33.45	34.64
75	50	0.2	300	5	39.48	42.98
90	50	0.2	300	5	50.17	51.31
105	50	0.2	300	5	61.92	59.65
120	50	0.2	300	5	71.85	67.99
15	50	0.2	200	2	12.35	6.16
30	50	0.2	200	2	19.81	17.38
45	50	0.2	200	2	27.84	28.59
60	50	0.2	200	2	36.71	39.81
75	50	0.2	200	2	52.34	51.03
90	50	0.2	200	2	61.76	62.24
105	50	0.2	200	2	72.31	73.46
120	50	0.2	200	2	80.23	84.68
15	50	0.2	200	7	7.68	5.54
30	50	0.2	200	7	17.32	13.41
45	50	0.2	200	7	25.46	21.28
60	50	0.2	200	7	33.74	29.16
75	50	0.2	200	7	37.25	37.03
90	50	0.2	200	7	41.62	44.91
105	50	0.2	200	7	46.37	52.78
120	50	0.2	200	7	55.32	60.65

Table 4. ANOVA Results for Lead Biosorption Removal

Source	**Sum of Squares**	**Df**	**Mean Square**	**F-value**	**p-value**	
Model	42143.19	9	4682.58	175.54	< 0.0001	significant
B-Alage dosage	2.96	1	2.96	0.1108	0.7401	
C-Agitation speed	134.27	1	134.27	5.03	0.0277	
D-pH range	607.50	1	607.50	22.77	< 0.0001	
E-Time	36839.78	1	36839.78	1381.08	< 0.0001	
CE	64.22	1	64.22	2.41	0.1248	
DE	242.29	1	242.29	9.08	0.0035	
B^2	968.36	1	968.36	36.30	< 0.0001	
C^2	278.66	1	278.66	10.45	0.0018	
D^2	830.30	1	830.30	31.13	< 0.0001	
Residual	2080.61	78	26.67			
Lack of Fit	1088.54	65	16.75	0.2194	1.0000	not significant
Pure Error	992.07	13	76.31			
Cor Total	44223.81	87				
Std. Dev.	Mean	C.V.%	R^2	R^2adj.	R^2pred.	Adeq. Precision
5.16	43.14	11.97	0.9530	0.9475	0.9432	45.4559

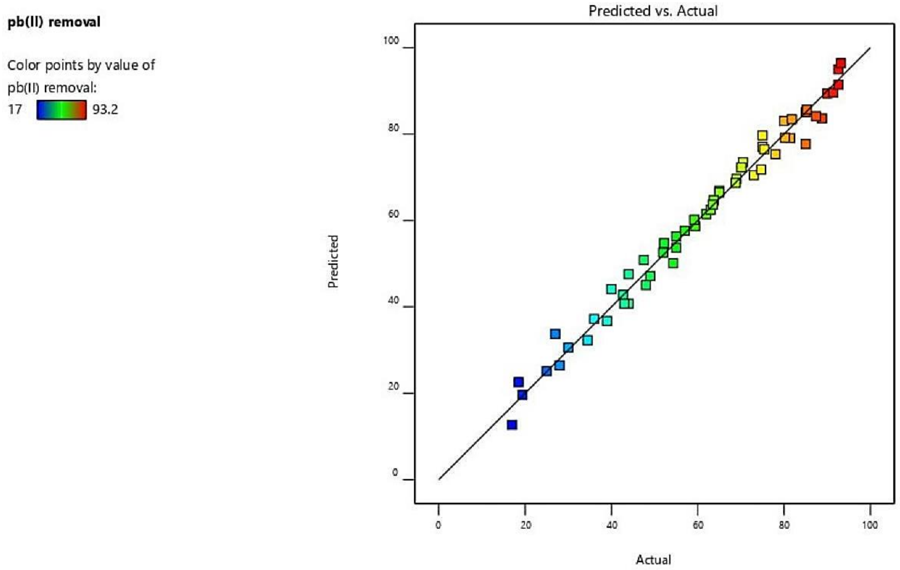


Fig. 7. Lead Biosorption Removal: A Comparison of Theoretical and Experimental Values

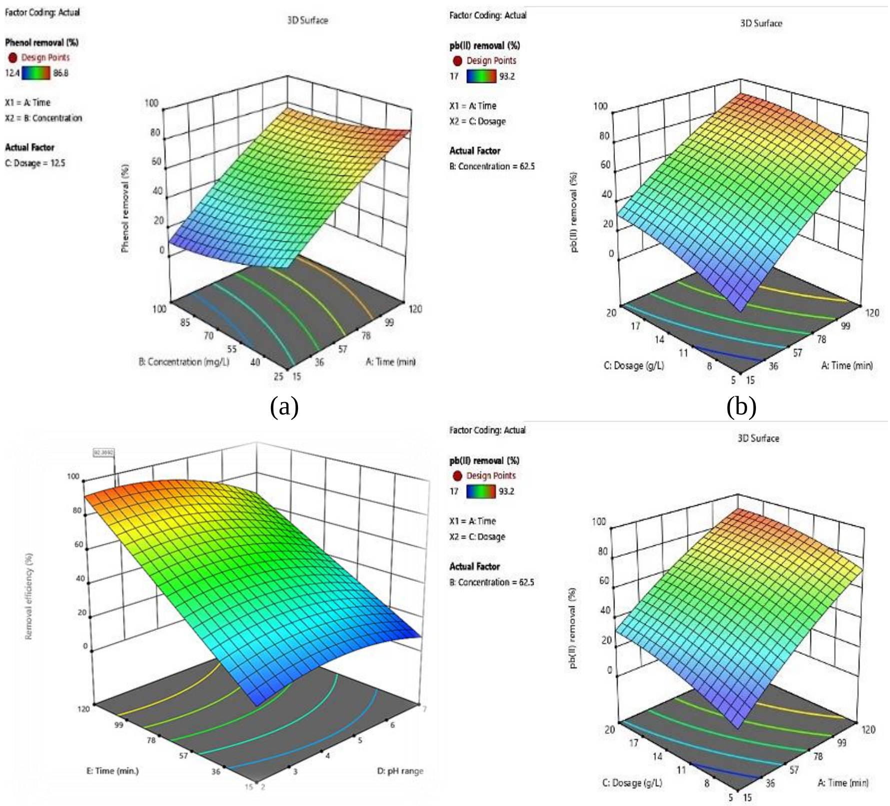
3.3. Batch experimental results

The graphs of the three-dimensional model for the percentage of lead removal from dead algae related to initial concentration, the dosage of algae, pH, shaking speed, and time are shown in Fig. 8. Figure Lead biosorption removal improved with time and eventually achieved equilibrium, as shown in Fig. 8 a, with a small but noticeable impact on the metal concentration. The efficiency of the Pb (II) ions removal improved along with the metal concentration. Fig. 8b demonstrates the interaction between adsorbent dosage and contact time on the removal efficiency. The proportion of lead removed improved as the adsorbent dosage was elevated to roughly 0.5g/100mL. Increasing the adsorbent dosage, in fact, gives enough active sites for heavy metal adsorption employing dead macroalgae.

As shown in Fig. 8 b, increasing the dosage of the biosorbent did not increase the removal of lead because, despite an increase in the amount of algal adsorbent used, the active sites on the adsorbent remained unsaturated throughout the adsorption process [35].

Fig. 8 c depicts the effect of initial solution pH on lead biosorption removal percent in the aqueous system. Pb(II) elimination was shown to be extremely sensitive to changes in solution pH. When the pH of the solution increased from 2 to 7, the efficacy of algae removal dropped. The results showed that the highest removal of lead ions occurred at pH 5, whereas minimal biosorption occurred under very acidic and moderately basic solutions. The overall surface charge on the active sites became positive at strongly acidic pH, and metal cations and protons “fight” for binding sites on the cell wall, resulting in decreased metal uptake [36].

As shown by Fig. 8 d, the optimum agitation speed was around 150 rpm, with an adsorption removal effectiveness of 92.36. The adsorbent accumulated at a lower agitation speed, resulting in inefficient adsorption. The adsorption removal effectiveness of algae was then steadily reduced until equilibrium was reached at an agitation rate of more than 150 rpm. Because of its poor affinity for the active site, Pb(II) may be considered to have bonded with it [37]. In terms of the impact of contact time, lead adsorption rose as contact time increased from 15 minutes to 120 minutes; however, as shown in Fig. 8, lead biosorption removal increased significantly from 60 minutes to 120 minutes.



(a) (b)

(c) (d)

Fig. 8. Response Surface Graphs for the Impact of Different Parameters

3.4. Optimization through the use of the desirability function

The desired target for each factor and the response were selected from a menu during numerical optimization. Several goals can be determined, including maximize, minimize, target, within range, none (for responses only), and set to a standard value (factors only). There must be a minimum and maximum limit for each variable that is used. To alter the shape of each objective's own desirability function, each objective can be assigned a weight. Combining the goals results in an overall desirability function. Desirability is an objective function that has a value of zero outside of the boundaries and one at the objective [34].

A point that improves the desirability function was discovered using numerical optimization. Initial concentration levels between 25 and 100 mg/l, biomass doses close to the maximum level of 1 g per 100 mL, agitation speeds near to the minimum level of 100 rpm, initial pH solutions between 2 and 7, and contact times at the maximum level of 120 min, which were set for maximum desirability. Each goal's relative importance to the others was altered. A ramp desirability is depicted in Fig. 9. The initial solution pH of 2.8, the initial metal concentration of 62.5 mg/l, algae dosage of 0.5 g/100 mL, lead removal of 92.36 percent, and desirability of 0.929 were found to be the best independent maximums. The calculated function may accurately reflect the experimental model and desired conditions, as evidenced by the obtained desirability value (0.929).

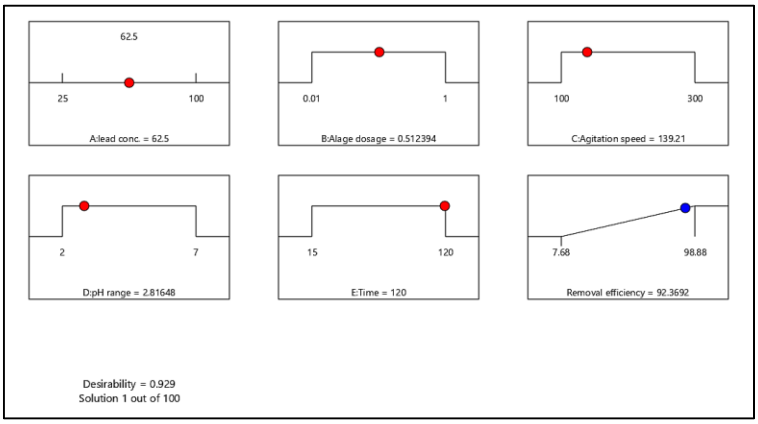


Fig. 9. Desirability Ramp for Numerical Optimization

4- Conclusions

The research presented here demonstrated that the dead biomass of *Chlorophyta* macroalgae served as an effective biosorbent of lead ions from synthetic wastewater. Experiments were conducted with a constant particle size of 63 micrometers and varied values of solution pH, metal ion concentration, algal dose, agitation speed, and contact time. The data demonstrated that the used algae is an effective adsorbing medium for lead ions and had a high adsorption efficiency for the treatment of lead-ion-contaminated wastewater. However, compared to the non-optimized condition, lead was removed by 98.88 percent when biosorption from aqueous solution was optimized using response surface methods. Maximum lead ion removal was achieved at the following values for the five independent variables: initial solution pH of 2.8; initial ion concentration of 62.5 mg/l; algae dosage of 0.512 g/mL; agitation speed of 139.21 rpm; contact time = 120 min. The surface structure of biosorbent, as seen by scanning electron microscopy (SEM) of algae, was more regular and porous before adsorption, but this regularity was lost and the surface became amorphous after adsorption. These findings suggest that dead *chlorophyte* algae biomass can be used as a biosorbent for purifying lead (II) from industrial wastewater.

References

[1] J. Bastos-Arrieta and C. Palet, “Sustainable Processes for the Removal of Heavy Metals from Aquatic Systems”, *Water*, Vol. 15, 2023, pp.761, https://doi.org/10.3390/w15040761

[2] M. Anbia, K. Kargosha, and S. Khoshbooei, “Heavy metal ions removal from aqueous media by modified magnetic mesoporous silica MCM-48”, *Chemical Engineering Research and Design*, Vol.93, 2015, pp.779-788, https://doi.org/10.1016/j.cherd.2014.07.018

[3] K. Li, Z. Zheng, and Y. Li, “Characterization and lead adsorption properties of activated carbons prepared from cotton stalk by one-step H3PO4 activation”, *Journal of hazardous materials*, Vol. 181, 2010, pp.440-447, https://doi.org/10.1016/j.jhazmat.2010.05.030

[4] A. Sarı, and M.Tuzen, “Kinetic and equilibrium studies of biosorption of Pb (II) and Cd (II) from aqueous solution by macrofungus (Amanita rubescens) biomass”, *Journal of hazardous materials*, Vol.164, 2009, pp.1004-1011, https://doi.org/10.1016/j.jhazmat.2008.09.002

[5] A. Kwarciak-Kozłowska, and L. Sławik-Dembiczak, “Biosorption of lead from municipal wastewater by alginate beads, free and alginate-immobilized Chlorella vulgaris”, *Desalination and Water Treatment*, Vol. 218, 2021, pp.303-308, https://doi.org/10.5004/dwt.2021.26969

[6] K. H. Kim, A. A. Keller, and J. K. Yang, “Removal of heavy metals from aqueous solution using a novel composite of recycled materialsm,” *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 425, 2013, pp.6-14, https://doi.org/10.1016/j.colsurfa.2013.02.044

[7] I. Ali, C. Peng, D. Lin, D. P. Saroj, I. Naz, Z. M. Khan, M. Sultan, and M. Ali, “Encapsulated green magnetic nanoparticles for the removal of toxic Pb^{2+} and Cd^{2+} from water: Development, characterization, and application”, *Journal of environmental management*, Vol. 234, 2019, pp.273-289, https://doi.org/10.1016/j.jenvman.2018.12.112

[8] A. soenmezay, M. S. Öncel, and N. bektaş, “Adsorption of lead and cadmium ions from aqueous solutions using manganoxide minerals”, *Transactions of Nonferrous Metals Society of China*, Vol. 22, 2012, pp.3131-3139, https://doi.org/10.1016/S1003-6326(12)61765-8

[9] N. Yin, K. Wang, L. Wang, and Z. Li, “Amino-functionalized MOFs combining ceramic membrane ultrafiltration for Pb (II) removal”, *Chemical Engineering Journal*, Vol. 306, 2016, pp.619-628, https://doi.org/10.1016/j.cej.2016.07.064

[10] Y. Y. Azila, M. D. Mashitah, and S. Bhatia, “Process optimization studies of lead (Pb (II)) biosorption onto immobilized cells of Pycnoporus sanguineus using response surface methodology”, *Bioresource technology*, Vol. 99, 2008, pp.8549-8552, https://doi.org/10.1016/j.biortech.2008.03.056

[11] A. M. Ridha, “Removal of lead (II) from aqueous solution using chitosan impregnated granular activated carbon”, *Journal of Engineering*, Vol. 23, 2017, pp.46-60, https://doi.org/10.31026/j.eng.2017.03.04

[12] H. N. Abdulkareem, and A. I. Alwared, "Performance of Immobilized Chlorella algae for removing Pb (II) ions from aqueous solution", *Iraqi Journal of Chemical and Petroleum Engineering*, Vol. 20, No. 3, 2019, pp.1-6, https://doi.org/10.31699/IJCPE.2019.3.1

[13] L. A. Romero-Cano, H. García-Rosero, L. V. Gonzalez-Gutierrez, L. A. Baldenegro-Pérez, and F. Carrasco-Marín, “Functionalized adsorbents prepared from fruit peels: Equilibrium, kinetic and thermodynamic studies for copper adsorption in aqueous solution”, *Journal of cleaner production*, Vol. 162, 2017, pp.195-204, https://doi.org/10.1016/j.jclepro.2017.06.032

[14] K. C. Sekhar, C. T. Kamala, N. S. Chary, and Y. Anjaneyulu, “Removal of heavy metals using a plant biomass with reference to environmental control”, *International Journal of Mineral Processing*, Vol. 68, No. (1-4), 2003, pp.37-45, https://doi.org/10.1016/S0301-7516(02)00047-9

[15] C. B. Vidal, D. Q. Melo, G. S. Raulino, A. D. da Luz, C. da Luz, and R. F. Nascimento," Multielement adsorption of metal ions using Tururi fibers (Manicaria Saccifera): experiments, mathematical modeling, and numerical simulation", *Desalination and Water Treatment*, Vol. 57, No. 19, 2016, pp.9001-9008, https://doi.org/10.1080/19443994.2015.1025441

[16] D. Inthorn, N. Sidtitoon, S. Silapanuntakul, and A. Incharoensakdi, "Sorption of mercury, cadmium, and lead by microalgae", *Sci Asia*, Vol. 28 No.3, 2002, pp.253-261, https://doi.org/10.2306/scienceasia1513-1874.2002.28.253

[17] R. Muñoz, M. T. Alvarez, A. Muñoz, E. Terrazas, B. Guieysse, and B. Mattiasson," Sequential removal of heavy metals ions and organic pollutants using an algal-bacterial consortium", *Chemosphere*, Vol.63 No.6, 2006, pp.903-911, https://doi.org/10.1016/j.chemosphere.2005.09.062

[18] R. K. Gautam, A. Mudhoo, G. Lofrano, and M. C. Chattopadhyaya, "Biomass-derived biosorbents for metal ions sequestration: Adsorbent modification and activation methods and adsorbent regeneration", *Journal of environmental chemical engineering*, Vol. 2 No. 1, 2014, pp.239-259, https://doi.org/10.1016/j.jece.2013.12.019

[19] J. C. M. Pires, "Handbook of Marine Microalgae", 2015.

[20] C. Solisio, S. Al Arni, and A. Converti, "Adsorption of inorganic mercury from aqueous solutions onto dry biomass of Chlorella vulgaris: kinetic and isotherm study", *Environmental Technology*, Vol. 40, No. 5, 2019, pp.664-672, https://doi.org/10.1080/09593330.2017.1400114

[21] H. Abdelkareem, A. Alwared, T. J. Al-Musawi, and F. Brouers, "A comparative study for the identification of superior biomass facilitating biosorption of copper and lead ions: a single alga or a mixture of algae", *International Journal of Environmental Research*, Vol. 13, 2019, pp.533-546, https://doi.org/10.1007/s41742-019-00194-9

[22] R. H. Myers, D. C. Montgomery, and C. M. Anderson-Cook, "Response surface methodology: process and product optimization using designed experiments", John Wiley and Sons, 2016.

[23] S. Al-Asheh, F. Banat, and F. Mohai, "Sorption of copper and nickel by spent animal bones", *Chemosphere*, Vol. 39, No. 12, 1999, pp.2087-2096, https://doi.org/10.1016/S0045-6535(99)00098-3

[24] D. C. Montgomery," Design and analysis of experiments", John Wiley and sons, 2017.

[25] R. Ahmad, and A. Mirza, "Facile one-pot green synthesis of Chitosan-Iron oxide (CS-Fe2O3) nanocomposite: Removal of Pb (II) and Cd (II) from synthetic and industrial wastewater", *Journal of Cleaner Production*, Vol. 186, 2018, pp.342-352, https://doi.org/10.1016/j.jclepro.2018.03.075

[26] J. Coates, "Interpretation of infrared spectra, a practical approach", 2000.

[27] J. Feng, J. Zhang, W. Song, J. Liu, Z. Hu, and B. Bao, "An environmental-friendly magnetic bio-adsorbent for high-efficiency Pb (II) removal: Preparation, characterization and its adsorption performance", *Ecotoxicology and Environmental Safety*, Vol. 203, 2020, p.111002, https://doi.org/10.1016/j.ecoenv.2020.111002

[28] A. M. Elgarahy, K. Z. Elwakeel, S. H. Mohammad, and G. A. Elshoubaky, "Multifunctional eco-friendly sorbent based on marine brown algae and bivalve shells for subsequent uptake of Congo red dye and copper (II) ions", *Journal of Environmental Chemical Engineering*, Vol. 8, No.4, 2020, p.103915, https://doi.org/10.1016/j.jece.2020.103915

[29] I. Michalak, K. Marycz, K. Basińska, and K. Chojnacka, "Using SEM-EDX and ICP-OES to investigate the elemental composition of green macroalga Vaucheria sessilis", *The Scientific World Journal*, 2014, Article ID 891928, pp.1-8, https://doi.org/10.1155/2014/891928

[30] V. R. Moreira, Y. A. R. Lebron, S. J. Freire, L. V. S. Santos, F. Palladino, and R. S. Jacob, "Biosorption of copper ions from aqueous solution using Chlorella pyrenoidosa: Optimization, equilibrium and kinetics studies", *Microchemical Journal*, Vol. 145, 2019, pp.119-129, https://doi.org/10.1016/j.microc.2018.10.027

[31] M. Sarkar, and P. Majumdar, "Application of response surface methodology for optimization of heavy metal biosorption using surfactant modified chitosan bead', *Chemical Engineering Journal*, Vol. 175, 2011, pp.376-387, https://doi.org/10.1016/j.cej.2011.09.125

[32] K. Yetilmezsoy, S. Demirel, and R.J. Vanderbei, "Response surface modeling of Pb (II) removal from aqueous solution by Pistacia vera L.: Box–Behnken experimental design", *Journal of hazardous materials*, Vol. 171, No. (1-3), 2009, pp.551-562, https://doi.org/10.1016/j.jhazmat.2009.06.035

[33] D.R. Hamsaveni, S.G. Prapulla, and S. Divakar, "Response surface methodological approach for the synthesis of isobutyl isobutyrate", *Process Biochemistry*, Vol. 36, No. 11, 2001, pp.1103-1109, https://doi.org/10.1016/S0032-9592(01)00142-X

[34] V. Afraz, H. Younesi, M. Bolandi, and M. R. Hadiani, "Optimization of lead and cadmium biosorption by Lactobacillus acidophilus using response surface methodology", *Biocatalysis and Agricultural Biotechnology*, Vol. 29, 2020, p.101828, https://doi.org/10.1016/j.bcab.2020.101828

[35] S. Abbasizadeh, A. R. Keshtkar, M. A. and Mousavian, "Preparation of a novel electrospun polyvinyl alcohol/titanium oxide nanofiber adsorbent modified with mercapto groups for uranium (VI) and thorium (IV) removal from aqueous solution", *Chemical Engineering Journal*, Vol. 220, 2013, pp.161-17, https://doi.org/10.1016/j.cej.2013.01.029

[36] M. Amini, H. Younesi, N. Bahramifar, A. A. Z. Lorestani, F. Ghorbani, A. Daneshi, and M. Sharifzadeh, "Application of response surface methodology for optimization of lead biosorption in an aqueous solution by Aspergillus niger", *Journal of hazardous materials*, Vol. 154, No. (1-3), 2008, pp.694-702, https://doi.org/10.1016/j.jhazmat.2007.10.114

[37] S. Fauzia, H. Aziz, D. Dahlan, and R. Zein, " Study of equilibrium, kinetic and thermodynamics for removal of Pb (II) in aqueous solution using Sago bark (Metroxylon sago)", *In AIP Conference Proceedings*, Vol. 2023, No. 1, 2018, p. 020081, https://doi.org/10.1063/1.5064078

تحسين إزالة ايونات الرصاص من مياه الصرف المصنع بأستخدام طحالب الكلورفيتا الميتة: تخمين بطريقة RSM

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الخلاصة

لقد تم استخدام طريقة منهجية استجابة السطح (RSM) في تحسين أداء كتلة الطحالب الميتة الكلورفيتا في إزالة ايونات الرصاص، تم اعتماد طريقة تصميم المركب المركزي (CCD) ومنهجية استجابة السطح في تحليل نتائج التجارب. تم دراسة تأثير كل من المتغيرات الاتية: زمن الامتزاز (١٥–١٢٠ دقيقة)، الاس الهيدروجيني للمحلول (٢–٧)، تركيز الرصاص الابتدائي (٢٥–١٠٠ مغم/لتر)، كمية المادة المازة (٠,٠١–١ غم لكل ١٠٠ مل)، سرعة الرج (١٠٠–٣٠٠ دورة في دقيقة) على عملية الامتزاز. كانت الظروف المثلى في البيانات التجريبية هي الرقم الهيدروجيني (٥)، وتركيز المعدن (٥٠ ملغم / لتر ، والجرعة (٠,٢غم / ١٠٠ مل)، وسرعة الرج (٢٠٠ دورة في الدقيقة)، والزمن ١٢٠ دقيقة مع ابقاء حجم الجسيمات للمادة المازة ثابت، مما أعطى ٩٨,٨٨ ٪ كفاءة الإزالة. تم تقييم جميع المتغيرات والتفاعلات في تجارب الامتزاز باستخدام دالة الرغبة لتحديد النقطة المثلى التي يمكن عندها الوصول إلى المتغيرات المرغوبة. وتشير النتائج التي تم الحصول عليها إلى إمكانية استخدام طحالب الكلورفيتا الميتة الخضراء في معالجة مياه الصرف الصناعي الملوثة بالمعادن سامة.

الكلمات الدالة: الامتزاز، طحالب الكلوروفيتا، محلول أيونات الرصاص الثنائي، خصائص الطحالب، RSM.