

Biosorption of nickel by ground fallen waste coffee plant leaves powder: Equilibrium, kinetics, Thermodynamics and Optimization (RSM)

M. Tukaram bai^{1*}, P. Venkateswrlu¹, Husam Talib Hamzah¹, V. Sridevi¹, Ch. A. I. Raju¹

¹Department of Chemical Engineering, Colleg of Engineering, Andhra University, Visakhapatnam, Andhra Pradesh, India.

Abstract. This study reports the biosorption of nickel using powdered fallen coffee leaves. BET, SEM, FTIR, and XRD characterize the biosorbents. We go over the findings from thermodynamic, kinetic, and equilibrium biosorption experiments. Here are some of the factors that were studied: agitation duration (t), biosorbent size, pH of the aqueous solution (ranging from 1 to 8), initial nickel concentration (C₀), pH (ranging from 5 to 150), temperature (ranging from 283 to 323), and so on. Coffee leaf powder is best when the pH is 4. This biosorbent pair works best when dosed at 18 g/L for nickel biosorption. Nitrogen absorption is 4.219 mg/g when coffee leaf powder is used. For nickel biosorption, CCD has optimized four parameters. The data on nickel biosorption are tightly matched to the biosorbent model of pseudo-second-order. The negative sign of the free energy change (ΔG) for coffee leaf powder (-1546 J/mol) reflects both the practicality and spontaneous nature of the biosorbent-material. Powdered coffee leaves are predicted to undergo enthalpy changes of 62.99 J/mol K and entropy changes of 51.08 J/mol K. When the value of ΔS is positive, it indicates that the randomness is increasing, and when the value of enthalpy change is positive, it indicates that the process is endothermic.

Keywords: coffee waste, Biosorption, Nickel, Coffee plant leaves, waste fallen plant, pollutant.

1 Introduction

Industries such as mining, electroplating, and others release large amounts of pollutants into the environment as a result of human activity. The most noticeable contaminants are heavy metals, which include cadmium, copper, lead, and zinc. Aside from not biodegrading in nature, heavy metals can readily accumulate in ecosystems and living things. Their increased concentration in the environment is partly due to this. This is extremely dangerous for the ecosystem and all forms of life on Earth. Although heavy metals are more commonly found

* Corresponding Author: dr.mtbai@andhrauniversity.edu.in,

in the ground and water, they are able to get into the air and mix with dust [1]. The advancement of industry in recent decades has brought about a level of material affluence and comfortable living that has not been seen before in the history of human development. The matching industrial growth rate, on the other hand, has resulted in ecological imbalances and excessive air, water, and land pollution. Nature has its own prevention and control mechanisms to save itself from deterioration and extinction. Nevertheless, our ecosystem has been significantly contaminated by discharging untreated solid, liquid, and gaseous effluents with different characteristics that cause serious health hazards. Also, environmental pollution is directly proportional to the population, per capita consumption of industrial goods, and pollutants per unit of industrial production [2,3]. The persistent pursuit of more effective technology to lessen environmental heavy metal contamination is an ongoing effort. Some of the technologies that can be used to reduce heavy metals in wastewater and aquatic environments include adsorption, chemical precipitation, flotation, ion exchange, coagulation, and membrane filtration. Those technologies can be expensive and produce unwanted side effects, which is a major bummer. To that end, adsorption on adsorbents has long been regarded as a flexible and economical strategy for heavy metal remediation [3]. This is an easy way to get rid of heavy metals in water by letting them adsorb on adsorbents and then collecting the adsorbents themselves. Because of this, the amount of heavy metals in the water environment that was being studied is reduced. When solids, liquids, vapors, or gases are absorbed from the outside, this process is known as adsorption. Adsorption occurs across the whole surface area of the adsorbent, dispersing the absorbed substance. Thanks to its many useful qualities, activated carbon has recently become the material of choice for adsorbents. Because of its enormous adsorption surface and abundance of functional groups and micropores, activated carbon is an effective heavy metal removal agent [1,4]. Activated carbons made from lignite or wood are expensive, thus scientists are looking for cheaper, more locally sourced materials that can be used to make adsorbents with the same desirable qualities [5]. Alternative, cost-effective adsorbents are always being sought after. To remove heavy metals from polluted water sources, Demirbas (2008) highlighted the potential for adsorbents made from agri-food sector by-products such as fruit waste (skins, husks), tea and coffee waste (spent beans, skin, pulp), and so on [6]. Processing coffee beans results in substantial quantities of by-products, and coffee is the world's second most popular agri-food product [7]. There is a lot of promise in the physicochemical studies and existing literature for the synthesis of valuable chemicals and materials from coffee bean manufacturing by-products [8]. The byproducts of roasting and grinding coffee beans, known as grounds, can be recycled into bioenergy and useful materials like polymers and composites in addition to biologically active chemicals [9]. Coffee processing produces many byproducts, but the most ubiquitous and consequential of these is spent coffee grounds. Powdered wasted coffee grounds are an organic waste product that is created after the extraction of coffee beans. These days, most people put their used coffee grinds to use in making bioenergy, extracting biological active ingredients, or making valuable polymers and composites. Used coffee grounds have obvious potential as an adsorbent for cleaning polluted areas of heavy metals, but little is known about their effectiveness in this regard. Used coffee grounds are great in adsorbing heavy metals via complexation due to their small size, porosity, and high specific surface area. They also contain lignin and tannin, which are polyhydroxy polyphenol functional groups [9]. Researchers Kim et al. (2020) looked at the feasibility of using used coffee grounds to remove cadmium (Cd) from water. Researchers in Seoul, Korea, used leftover coffee grounds collected from a nearby cafe for the experiment. Then, for two weeks, they let the extracted coffee grounds air dry. The dried grounds were placed in plastic bottles and subjected to a 0.5 mm sieve before being utilized in the investigation. It is important to note that the discarded coffee grounds were neither physically or chemically prepared before being used for assessment. Its adsorption effectiveness was measured in comparison to that

of zeolite, a well-studied adsorbent [1]. If left untreated, coffee grounds could be a viable, low-cost adsorbent for cadmium removal, as pointed out by Azouaou et al. (2010). In order to learn how various factors, such as adsorbent dosage, contact time, beginning pH, particle size, initial temperature, and initial cadmium content, affected the adsorption process using untreated coffee grounds, they performed kinetic and equilibrium studies. To examine the equilibrium data, the Langmuir, Freundlich, and Dubinin-Radushkevich adsorption isotherm models were employed. Coffee grounds show significant promise as a cost-effective and environmentally friendly raw material for cadmium adsorbents, according to the research. A comparison of the adsorption capacity of spent coffee grounds with different adsorbents was also reported by the paper's authors [10]; By analyzing the adsorption capabilities of activated carbons made from parchment and used coffee grounds, Figueroa et al. (2021) explored the potential for their production. The activated carbons were made by a co-calcination procedure with calcium carbonate. Thereafter, their ability to adsorb organic acids, phenolic compounds, and proteins was observed. This study's findings provide credence to the idea that used coffee grounds and parchment could be useful as inexpensive adsorbents for the extraction of organic molecules from water [11]. The aim of this work to investigate the biosorption of nickel using powdered fallen coffee leaves. Using BET, SEM, FTIR, and XRD analysis to characterize the biosorbents. We go over the findings from thermodynamic, kinetic, and equilibrium biosorption experiments.

2 Materials and Methods

2.1. Coffee leaf powder preparation

Chinthapalli, a rural part of Visakhapatnam, Andhra Pradesh, India, was the site of the coffee leaves collection. After being washed several times with distilled water, these leaves were free of dust and other contaminants. The next step was to let them dry in the sun until they were completely white and crisp. A mechanical grinder was used to reduce the dried leaves to a fine powder-like consistency. The several size fractions ranging from 45 to 300 μm were created when the powder was passed through a sieve. For their future usage as biosorbents, these powders were stored in individual airtight glass containers [12,13].

2.2. Time of agitation's impact on nickel biosorption

A 250-milliliter-capacity conical flask collected fifty milliliters of an aqueous solution with a concentration of twenty milligrams per liter. The biosorbent, which was 45 micrometers, was introduced to the aqueous solution in the flask at a rate of 10 grams per liter. After bringing the conical flask to room temperature, it was placed on an orbital shaker and allowed to remain there for one minute while it was shaken. Also, twenty-four additional samples were made in 250 mL conical flasks by adding 10 g/L of biosorbent to each flask and agitating them at varying periods: (2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 70, 80, 90, 100, 110, 120, 150, 180 and 210 min). After separating these samples using Whatman filter papers, the resulting filtrates were examined using AAS to determine the final concentrations of nickel [12-18].

2.3. The impact of biosorbent size on nickel biosorption

A conical flask with a capacity of 250 mL was filled with fifty milliliters of an aqueous solution. During the equilibrium agitation time, a 45 micrometer-sized biosorbent, with a concentration of 10 grams per liter, was added to the flask and shaken in an orbital shaker.

The final nickel concentration was determined by filtering the mixture and then subjecting the filtrate to AAS analysis. The same experimental approach was repeated with different sizes of biosorbent, precisely 75, 150, and 300 micrometers [2,3,12].

2.4. The impact of biosorbent dosage on nickel biosorption

A 250 mL conical flask was utilized, along with 50 mL of an aquatic solution that included 20 mg/L of cobalt. To achieve equilibrium agitation time, a biosorbent with a 45 μm size and a concentration of 2 g/L was subjected to agitation on an orbital shaker. A final concentration of nickel in the solution was strongminded by filtering the mixture and then analyzing the filtrate using an atomic absorption spectrometer (AAS). Using a variety of adsorbent dosages ranging from 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, and 24 g/L, eleven more samples were generated, and the experimental method was repeated seven times.

2.5. The impact of solution pH on nickel biosorption

Forty milliliters of a water solution was introduced to each of the twelve conical flasks to investigate the impact of pH on nickel biosorption. Aqueous solutions were placed in separate conical flasks of 250 milliliters each, and their pH levels were adjusted to 1, 2, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, and 8. Each conical flask introduced 18 grams per liter of biosorbent with a 45 μm size. During the equilibrium agitation time, the samples were shaken at room temperature on an orbital shaker. Separate filtering of the samples followed. AAS is used to determine the final nickel concentrations of the filtrates.

2.6. Consequence of initial concentration of nickel in aqueous solution

The following is a determination of the influence that original concentration has on the biosorption of nickel: Within eleven conical flasks with a capacity of 250 milliliters, fifty milliliters of aqueous solutions were collected, each of which contained a different concentration of nickel: five, ten, twenty, thirty, forty, fifty, sixty, seventy-five, one hundred, one hundred and fifty-five milliliters per liter, and one hundred and fifty milliliters per liter. In each conical flask, 18 grams per liter of biosorbent with a size of 45 micrometers was applied. Using an orbital shaker, the flasks were mixed at room temperature until the agitation time was equalized. After the samples had settled, a different filtering procedure was carried out. The final nickel contents in aqueous solutions were determined by analyzing the collected samples using AAS [18,19].

2.7. Methodology for biosorption experiments

We used four independent variables—pH, Co, w, and T—to achieve the maximum achievable nickel biosorption %. Under the RSM of STATISTICA 6.0, CCD was used to determine the correlation between the factors and the result, which was displayed as a percentage of nickel biosorption. An equal number of eight axial points ($\alpha = \sqrt{4}$) and six investigations at the center points ($\text{no}=(6)$) were included in each of the thirty experiments that utilized the CCD. Blood samples were tested using an AAS once the specified incubation time had passed. We used the STATISTICA-6.0 tool to run graphical, regression, and analyses of variance (ANOVA) experiments. We utilized the student's t-test in conjunction with the p-values to ascertain the coefficient's statistical significance. Lots of coefficients of determination were able to explain the model's variance.

2.8. Investigations on kinetics plus thermodynamics

Each of the twenty-five conical flasks was filled with fifty milliliters of an aqueous solution that contained twenty milligrams per liter of nickel. Each flask introduced 10 grams of biosorbent per liter, weighing 45 micrometers. An orbital shaker was used to shake the conical flasks for a variety of time intervals, including 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 70, 80, 90, 100, 110, 120, 150, 180, and 210 minutes. After that, they were permitted to settle and filter independently, and the resulting filtrates were subjected to AAS analysis to determine the ultimate amounts of nickel. With the use of these data, the order of biosorption was established. We determined how temperature influences the biosorption rate through the following process: Each of the five conical flasks was filled with fifty milliliters of an aqueous solution containing twenty milligrams per liter of cobalt. These flasks were each given 18 grams per liter of biosorbent with a size of 45 micrometers. An orbital shaker was used to shake the conical flasks; the temperatures used were as follows: 283, 293, 303, 313, and 323 degrees Kelvin. After being separated, these samples were settled and filtered. Applying AAS allowed for the determination of the final nickel concentrations of the filtrates. These data were used to estimate the changes in enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) during adsorption.

3 Results and Discussion

3.1. Evaluation of coffee leaf powder for nickel biosorption in an equilibrium setting

3.1.1. Impact of duration of agitation

The percentage of nickel biosorption varies from 1 to 210 minutes of agitation duration. Figure 1 displays the outcomes. After 120 minutes, the coffee leaf powder reaches its maximum biosorption percentage of nickel, 85.05% and 1.701 mg/g. To examine the additional parameters, a 120-minute equilibrium agitation time is employed.

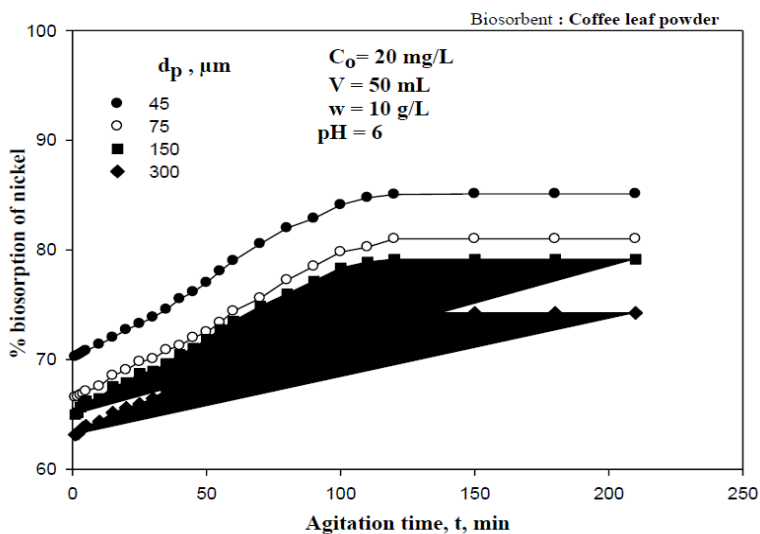


Fig. 1. Biosorption percentage of nickel as a function of agitation duration

3.1.2. Biosorbent size effect

This study uses biosorbents with 45, 75, 150, and 300 μm diameters. Figure 2 shows the percentage of nickel biosorption versus the biosorbent size. The percentage of nickel biosorption decreases from 85.1% (1.702 mg/g) to 74.25% (1.485 mg/g) as the biosorbent size goes up from 45 to 300 μm . As the biosorbent shrinks in size, its surface area increases, allowing more active areas to be reached.

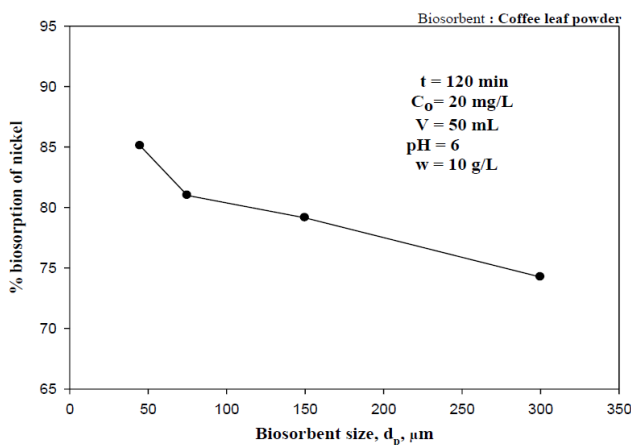


Fig. 2. Biosorption of nickel as a function of biosorbent size.

3.1.3. Biosorbent dose effect

Adjusting the adsorbent concentration from 2 to 24 g/L while maintaining constant all other variables allows us to study the correlation between biosorbent loading and nickel ion biosorption. To see how the biosorbent's percentage of nickel absorption changes with dosage, see Figure 3. From 80.5% to 90.9% more metal ions are biosorbed when the biosorbent dose is increased from 2 to 18 g/L. The biosorption of metal ions, however, stays somewhat consistent even after increasing the dosage to 18 g/L. Consequently, for the upcoming studies, a dosage of 18 grams per liter of biosorbent has been selected.

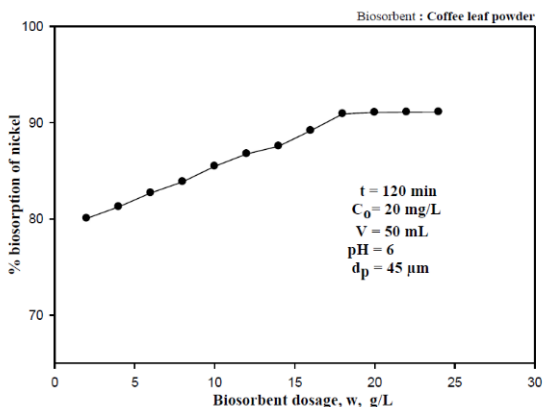


Fig. 3. Correlation between biosorbent dosage and nickel biosorption percentage

3.1.4. Consequence of pH of the aqueous solution

The consequence of the initial pH of aqueous solution on the % biosorption of nickel is investigated between pH of 1 to 8 and presented in Figure 4. biosorption % of nickel is increased in the lower pH range of 1 to 3.5 (82.52 % to 92.28%) and decreased at a higher pH range of 4.5 to 8. The low-slung level of nickel uptake (0.916 mg/g at pH of 1) at lower pH values could be attributed to the increased concentration of hydrogen (H⁺) competing for nickel (II) – binding sites on the biosorbent. Because metal ion soluble hydroxylated complexes compete for active sites, the percentage of biosorption decreases as pH increases. Because of their role in ion exchange during biosorption, ester sulphonate groups'-SO₃ stretching is very noticeable. The main functional groups of biosorbents responsible for the biosorption of nickel are hydroxyl, carbonyl, and carboxyl [18]. In the present study, the maximum % biosorption of 93.09% is obtained at pH = 4. The exact optimum value of pH = 4 was stated by Vijayaraghavan et al. [19] for the biosorption of nickel.

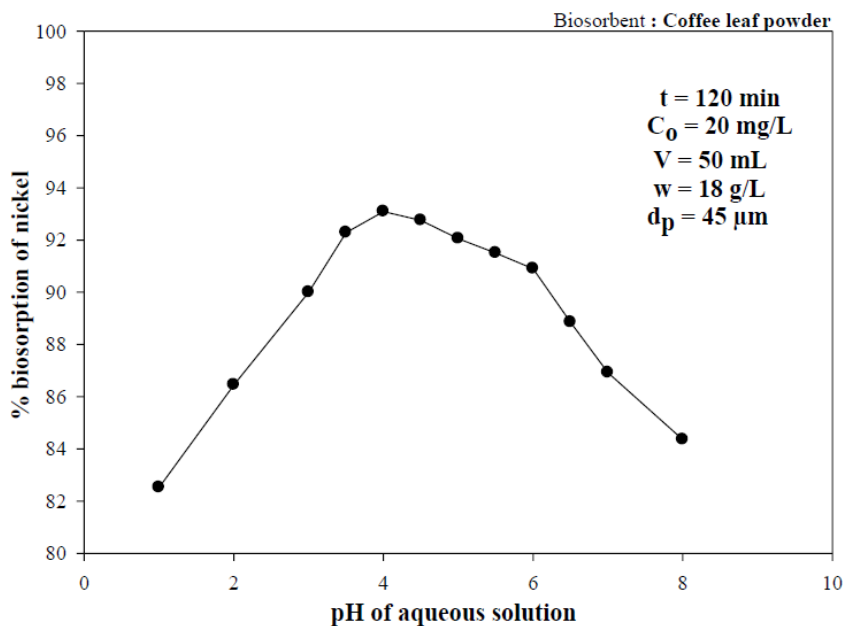


Fig. 4. Aqueous solution pH and nickel biosorption percentage.

3.1.5. Consequence of initial concentration of nickel in the aqueous solution

The starting concentration of nickel in biosorption tests ranges from 5 to 150 mg/L. From 5 to 150 mg/L, the percentage of nickel biosorption changes from 94.5% to 46.52%. according to the Figure 5. In the C₀ range of 5–20 mg/L, there is only a slight drop in nickel biosorption percentage, from 94.5% (0.261 mg/g) to 93.9% (1.034 mg/g). There is a steep decline in biosorption rate beyond the initial concentration of 20 mg/L of nickel. From 5 to 150 mg/L, the metal absorption rose from 0.261 mg/g to 3.989 mg/g, respectively, as the nickel content increased.

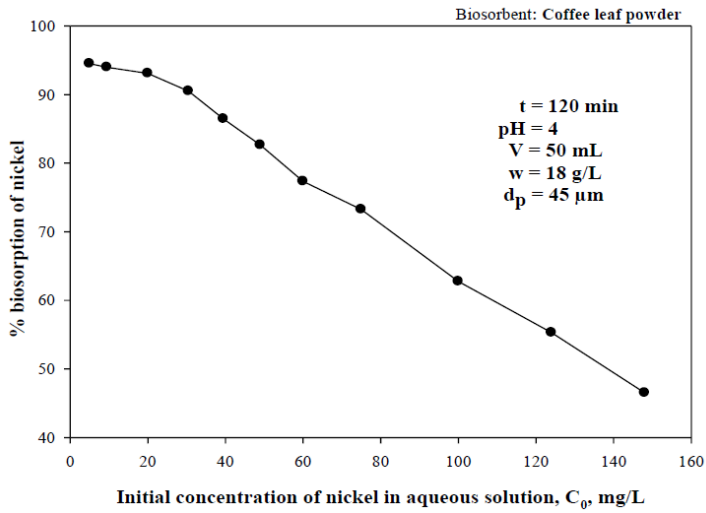


Fig. 5. Nickel biosorption rate as a function of starting nickel concentration.

3.1.6. The impact of temperature

This investigation looks at the effect of temperature on the biosorption % of nickel at 283, 293, 303, 313, and 323 degrees Celsius. The plots are shown in **Figure 6**. % biosorption increased with increased temperature.

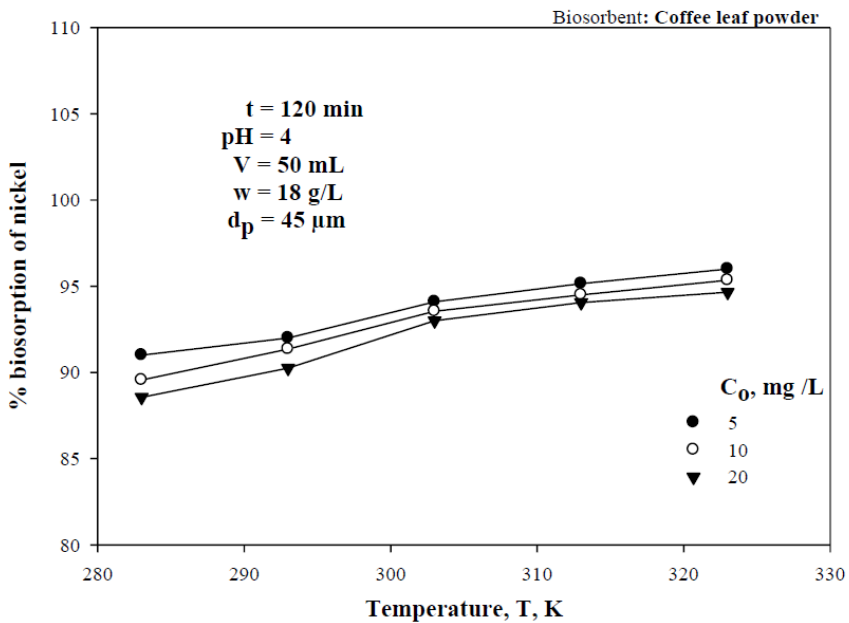


Fig. 6. Impact of temperature on nickel biosorption.

3.2. Optimization of the chosen parameters through CCD

The Box-Behken design model has been developed to perfect the biosorption process. Using the quadratic model, the relationship between the four independent variables found in this study and the percentage of nickel biosorption has been clearly outlined. For optimizing medium ingredients, the regression equation was as follows:

The quantity of nickel that is biosorption is determined by calculating the following variables: pH of the aqueous solution (X1), starting concentration of nickel (X2), dose of the biosorbent (X3), and temperature (X4). **Table 1** shows the CCD results for nickel biosorption by coffee leaf powder, while **Table 2** shows the values of several process variables in coded and uncoded form [12-15]. Analyzing the experimental data using multiple regression is:

$$Y = -443.688 + 7.864 X_1 - 0.009 X_2 + 3.289 X_3 + 3.292 X_4 - 0.403 X^2 - 0.093 X^1 - 0.066 X^2 - 0.005 X_4^2 - 0.079 X_1X_2 - 0.028 X_1X_3 - 0.010 X_1X_4 - 0.028 X_2X_3 + 0.005 X_2X_4 - 0.005 X_3X_4$$

Table 1. The biosorption of nickel by coffee leaf powder as determined by CCD.

Run no.	X1, pH	X2, Co	X3 , w	X4,, T	% biosorption of nickel	
					Experimental	Predicted
1	-1	-1	-1	-1	91.25	91.28
2	-1	-1	-1	1	92.16	92.14
3	-1	-1	1	-1	92.09	92.10
4	-1	-1	1	1	92.32	92.26
5	-1	1	-1	-1	91.75	91.62
6	-1	1	-1	1	92.71	92.82
7	-1	1	1	-1	91.50	91.58
8	-1	1	1	1	92.10	92.07
9	1	-1	-1	-1	92.35	92.29
10	1	-1	-1	1	92.85	92.77
11	1	-1	1	-1	92.82	92.72
12	1	-1	1	1	92.46	92.49
13	1	1	-1	-1	92.00	92.07
14	1	1	-1	1	93.00	92.88
15	1	1	1	-1	91.70	91.62
16	1	1	1	1	91.75	91.73
17	-2	0	0	0	92.65	92.61
18	2	0	0	0	93.15	93.28
19	0	-2	0	0	93.22	93.30
20	0	2	0	0	92.88	92.89
21	0	0	-2	0	90.65	90.70
22	0	0	2	0	90.34	90.38
23	0	0	0	-2	91.50	91.54
24	0	0	0	2	92.45	92.50
25	0	0	0	0	94.10	94.11
26	0	0	0	0	94.10	94.11
27	0	0	0	0	94.11	94.11
28	0	0	0	0	94.10	94.11
29	0	0	0	0	94.11	94.11
30	0	0	0	0	94.12	94.11

Table 2. The percentage of nickel biosorption by coffee leaf powder as a function of several process factors, both coded and uncoded.

Variable	Name	Range and levels				
		-2	-1	0	1	2
X1	pH of aqueous solution	2	3	4	5	6
X2	The initial concentration of nickel in aqueous solution, Co, mg/L	10	15	20	25	30
X3	Biosorbent dosage, w, g/L	14	16	18	20	22
X4	Temperature, T, K	283	293	303	313	323

Observed response values and experimental conditions (coded values) were presented in a mixed-factorial layout with twenty-four runs, six centers, and eight axes. R2 equals 0.996, and R2 (adj) equals 0.9923. The agitation time is fifty minutes, and the biosorbent size is forty-five micrometers.

3.3. Regression analysis interpretation

Table 3 compiles the outcomes of the regression model described above, derived from equation. The regression model is generally highly significant, as indicated by Fischer's 'F-statistics' value (=MSmodel/MSerror), accompanied by a low probability 'P' value. According to Fisher's F-test, the regression model is extremely significant (Fmodel = 97.75), while the probability value is very small (Pmodel > F=0.000000). That is proven by the model's analysis of variance (ANOVA). It is important to note that at the 5% level, the estimated F-value (F0.05 (14.15) = MSmodel/MSerror = 97.75) is higher than the tabular F-value (F0.05 (14.15) tabular = 2.42), suggesting that there are considerable variances in treatment.

Table 3. Analysis of variance (ANOVA) for the full quadratic model of nickel biosorption.

variation Source	SS	df	Mean square(MS)	F-value	P > F
Model	31.1079	14	2.2219	269.97	0.000000
Error	0.1235	15	0.00823		
Total	31.2314	29			

df- degree of freedom; SS- sum of squares; F- factor F; P, probability. R²= 0.9960; R² (adj):0.9923

For a given set of coefficients, a lower P value and a larger t value indicate statistical significance. By examining the 't' and 'P' values in **Table 4**, we find that the following terms are highly significant in explaining the specific and combined effects of adsorption parameters on nickel biosorption and response prediction. The terms in question are X1, X2, X3, X4, X12, X22, X2, X42, X1X2, X1X3, X2X3, X2X4, and X3X1.

Table 4. The predicted coefficients of determination for the biosorption of nickel onto powdered coffee leaves.

Terms	Regression coefficient	Standard error of the coefficient	t-value	P-value
Constant	-535.74	17.8566	-30.003	0.00000
X1	6.83	0.7362	9.279	0.00000
X1* X1	-0.29	0.0173	-16.733	0.00000
X2	0.39	0.1472	2.628	0.01903
X2* X2	-0.01	0.0007	-14.568	0.00000
X3	11.31	0.3830	29.530	0.00000
X3* X3	-0.22	0.0043	-51.431	0.00000
X4	3.35	0.1078	31.063	0.00000
X4* X4	-0.01	0.0002	-30.078	0.00000
X1* X2	-0.03	0.0045	-6.270	0.00002
X1* X3	-0.05	0.0113	-4.424	0.00049
X1* X4	-0.01	0.0023	-4.176	0.00081
X2* X3	-0.02	0.0023	-9.598	0.00000
X2* X4	0.00	0.0005	3.653	0.00236
X3* X4	-0.01	0.0011	-7.835	0.00000

Insignificant: $P \leq 0.05$

The optimal sets of conditions for % biosorption of nickel onto coffee leaf powder are:

pH of aqueous solution = 4.32, Biosorbent dosage, $w = 17.89$ g/L Initial nickel concentration, $C_0 = 18.79$ mg/L and Temperature, $T, K = 304.9$ K

Ninety-four point seven percent is the extent of nickel biosorption under the conditions described above. Figure 7 shows a comparison between the rate anticipated by equation and the percentage of biosorption obtained during testing. The experimental values are consistent with the anticipated values, with an error margin of less than 0.0182%.

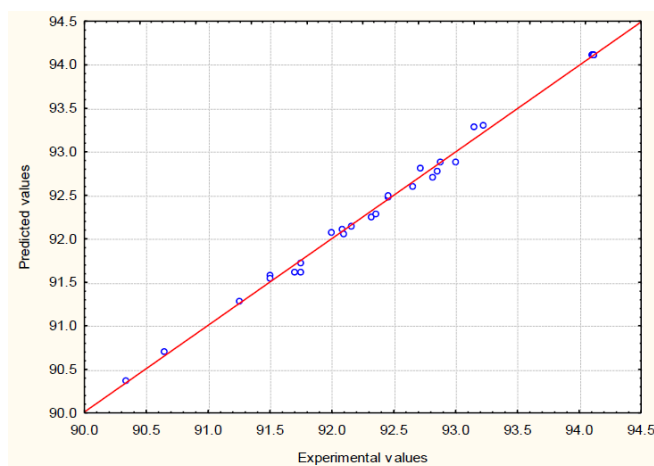


Fig. 7. Chart comparing the results from the experiments with the predictions.

The results of this study show that the model does not adequately account for 1.092% of the total variances, as indicated by a subsequent value of the regression coefficient ($R^2 = 0.9891$) for equation. Applying the analysis of variance (ANOVA), one may examine the statistical significance of the ratio of the mean square owing to regression and the mean square due to residual error. According to the data in the table, the overall model has a higher F-statistic. This number is so large that it suggests the model equation can adequately explain the biosorption %. The model is generally considered statistically significant at the 95% confidence level when the P value is less than 0.05. The model's estimated percentage of biosorption is shown in Table 4. It is known that the linear terms of the variables X_1 ($P=0.000000$), X_2 ($P=0.000000$), X_3 ($P=0.000000$), X_4 ($P=0.000000$) are significant ($P < 0.05$). Among the interaction terms, all the interactions between X_1-X_2 ($P = 0.000002$), X_1-X_3 ($P = 0.00049$), X_1-X_4 ($P = 0.00081$), X_2-X_3 ($P = 0.000000$), X_2-X_4 ($P = 0.000236$) and X_3-X_4 ($P = 0.000000$) all the terms ($P < 0.05$) are highly significant on the biosorption capacity. And the squared terms X_1^2 ($P = 0.000000$), X_2^2 ($P = 0.000000$), X_3^2 ($P = 0.000000$) and X_4^2 ($P = 240.000000$) are also highly significant on adsorption.

3.4. The mutual effect of biosorption variables

The response surface plots Figures 8(a) to 8(f) are used to help visualize the percentage of biosorption that occurs across a variety of different combinations of independent factors. Biosorption percentages are higher for low and high variables, respectively, as can be seen from all of the response surface plots. It has come to light that there is a certain area where the biosorption percentage is not showing any growth or decrease trend. As a result, we know that the biosorption parameters are fine-tuned to achieve maximum biosorption. You can see from the graphs in Figures 8(a), 8(b), and 8(c) that PH plays a significant impact in the nickel % biosorption. There has been a relatively high interaction between pH and C_0 , w, and T, as shown by the corresponding $P = 0.00002$, $P = 0.00049$, and $P = 0.00081$, separately. It is deduced from the curvature of the contour. C_0 has an appreciable amount of interaction effect with w, ($P = 0.000000$) and T ($P = 0.000236$) Figures 8 (d) and Figures 8 (e). The biosorbent dosage has played an important role in % biosorption of nickel in interaction with temperature Figure 8 (f) with a P value of 0.000000. In Table 5, we can see the projected ideal values compared to the experimental ones. The results from the experiment closely match the ones from the CCD.

Table 5. Evaluation of the best possible CCD values in relation to their experimental counterparts.

Biosorbent	Variable studied	CCD	Experimental
<i>Sargassum tentorium</i> powder	aqueous solution (pH)	4.32	4.5
	The initial concentration of nickel, C_0 , mg/L	18.79	20
	Biosorbent dosage, w, g/L	17.89	18
	Temperature, T, K	304.91	303
	% biosorption of nickel	94.17	93

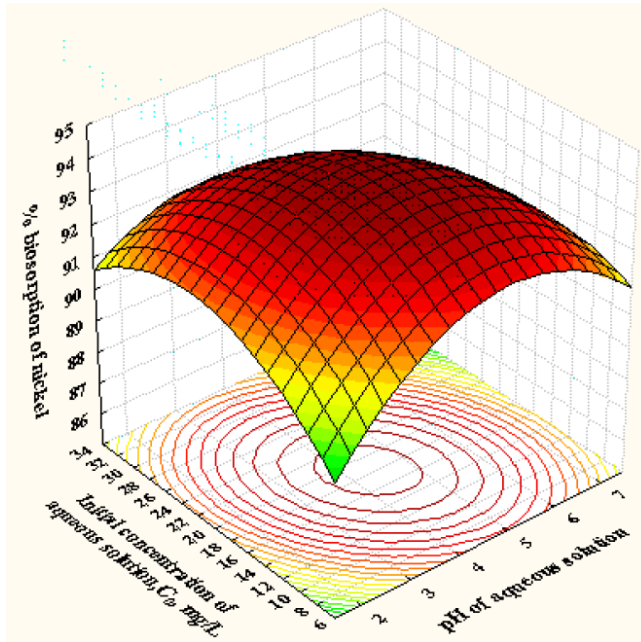


Fig. 8. (a). Impacts of pH and C_o at $w= 12$ g/L and $T=303$ K as an interactive surface map in three dimensions.

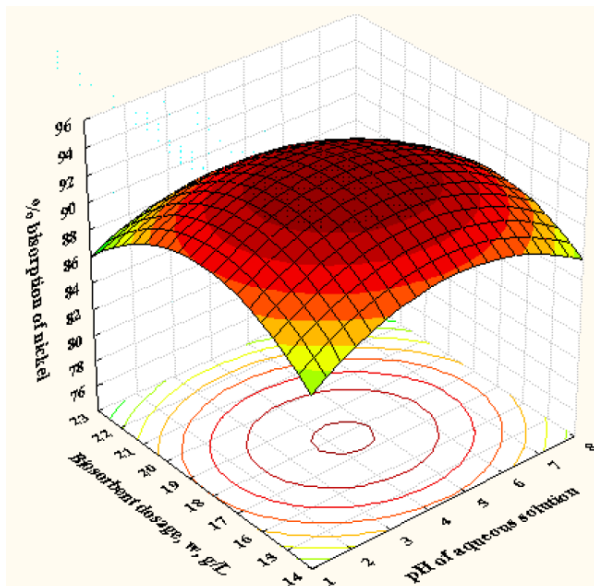


Fig. 8. (b). Surface reaction in three dimensions: pH and water's interactive effects at 5 mg/L CO_2 and 303 °C.

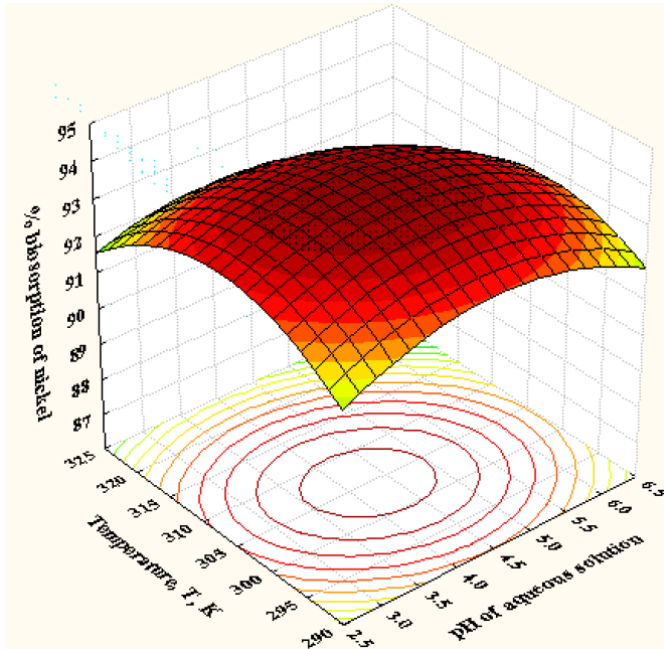


Fig. 8. (c). Three-dimensional response surface: Phosphorus and temperature interact when $w = 12$ g/L and $C_0 = 5$ mg/L.

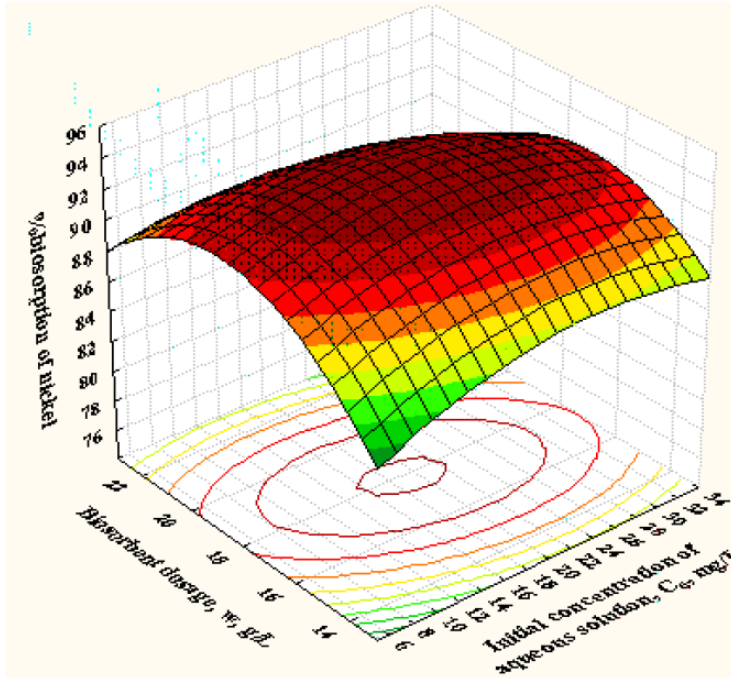


Fig. 8. (d). Interactions between C_0 and w at pH 5 and $T = 303$ K, as shown in a three-dimensional response surface map.

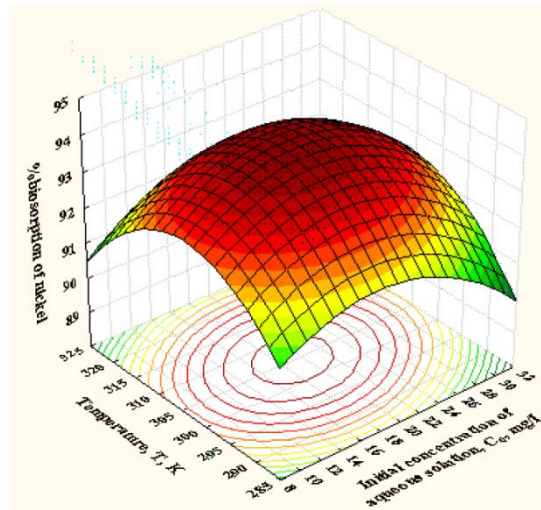


Fig. 8. (e). Interactions between C0 and T at pH 5 and w= 12 g/L are shown in a three-dimensional response surface plot.

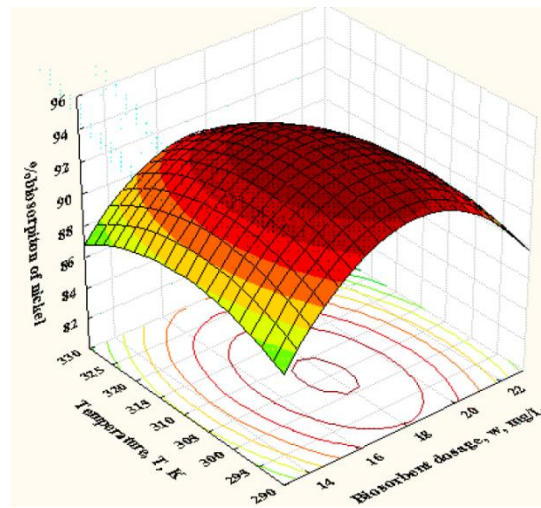


Fig. 8. (f). At a pH of 5 and a concentration of 5 mg/L, the 3D response surface plot shows the interactive effects of water and temperature.

3.5. The Freundlich isotherm

In Figure 9, the Freundlich isotherm is depicted as the curve connecting $\log q_e$ and $\log C_e$. The resulting equation is:

$$\log q_e = 0.329 \log C_e + 0.021$$

The correlation coefficient of the resultant equation is 0.93. With a value of 0.329, which falls somewhere between 0 and 1, the Freundlich isotherm was able to fit the experimental data in this investigation.

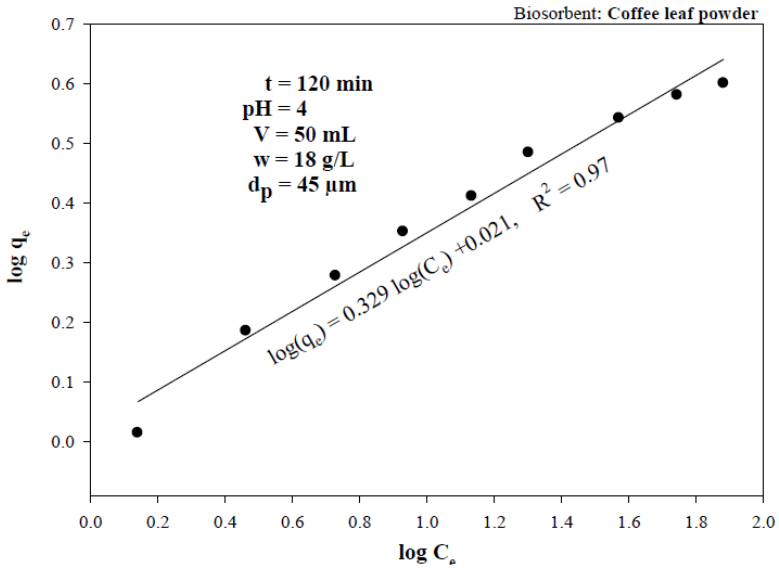


Fig. 9. Nickel biosorption Freundlich isotherm.

3.6. The Langmuir isotherm

Figure 10 shows the results of the Langmuir isotherm drawn from the current data. The resulting equation is:

$$(C_e/q_e) = 0.237 C_e + 1.430$$

Results show that the nickel ions bind strongly to the surface of coffee leaf powder, with linearity (correlation coefficient, $R^2 = 0.99$) and q_m and b values of 4.219 and 0.165, respectively. A positive RL value of 0.507 indicates that nickel is biosorbent on coffee leaf powder.

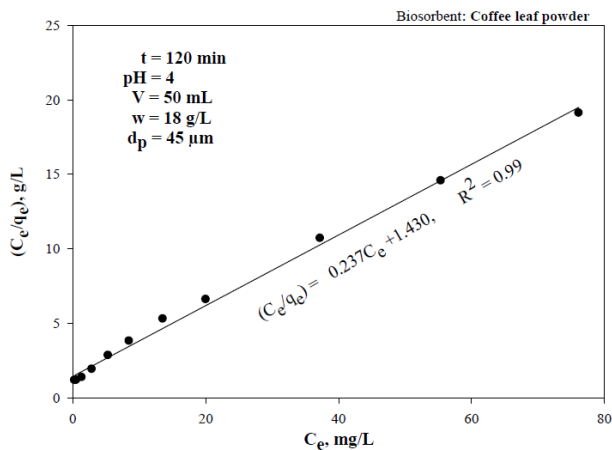


Fig. 10. Nickel biosorption using the Langmuir isotherm.

3.7. Temkin isotherm

Figure 11. shows the linear plot obtained by applying the linear version of the Temkin isotherm to the current data. The biosorption equation for nickel is as follows:

$$q_e = 0.7010 \ln C_e + 0.877$$

From the above equation, bT is 3593, and AT is 493.

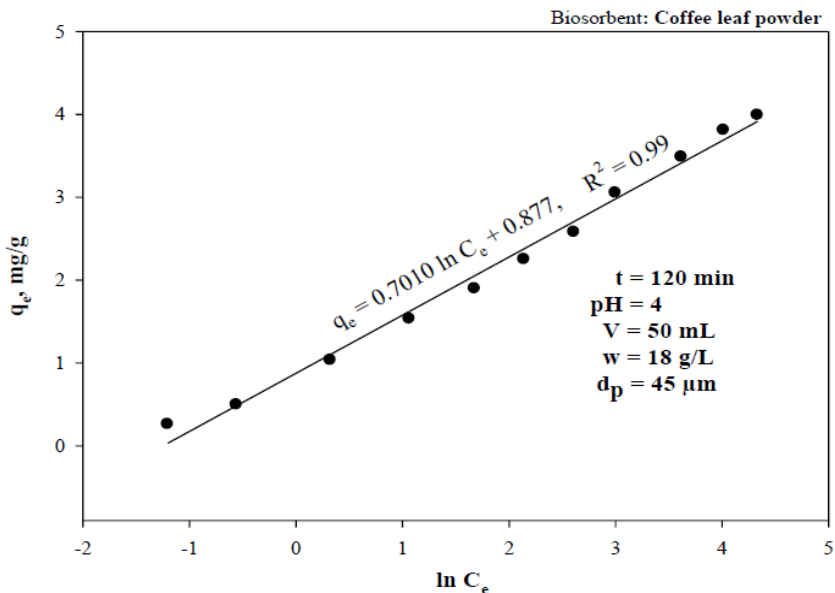


Fig. 11. Nickel biosorption using the Temkin isotherm.

3.8. The Redlich- Peterson isotherm

With the given experimental results, the equation is shown in Figure 12 with the following parameters: A = 1L/mg (assumed), V = 50 mL, T = 303 K, and dp = 45 μm:

$$\ln ((C_e/q_e)-1) = 1.043 \ln C_e - 1.401$$

A constant of 0.246 L/mg and an exponent of 1.043 are given by the Redlich-Peterson isotherm, respectively. An outstanding option for characterizing nickel biosorption, the Redlich-Peterson isotherm model has a correlation coefficient of 0.99.

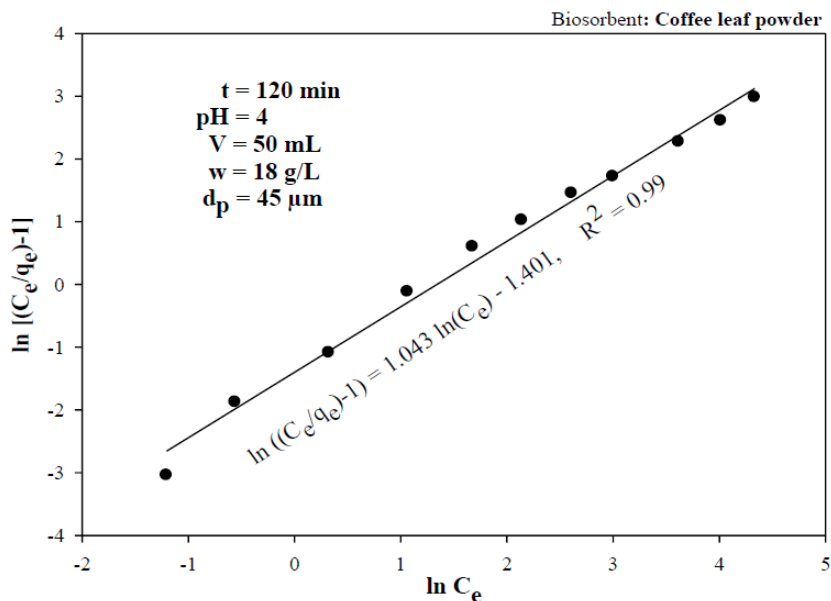


Fig. 12. Nickel biosorption using the Redlich-Petersson isotherm.

Table 6 compiles the isotherm constants calculated for each of the four isotherms. With a correlation coefficient of 0.99, the Langmuir, Temkin, and Redlich-Peterson isotherms satisfactorily explain the equilibrium data in the present study. The Freundlich isotherm comes in second place.

Table 6. Isotherm parameters for several isotherm models using coffee leaf powder.

Isotherm	Constants
Freundlich	Kf = 0.021 mg/g
	R ² = 0.93
Langmuir	q _m = 4.219 mg/g
	b = 0.165 L/mg
Temkin	R ² = 0.99
	AT = 3.493 L/mg
	bT = 3593.6
Redlich- Peterson	R ² = 0.99
	B = 0.246 L/mg
	R ² = 0.99

3.10. The Kinetics of biosorption

The method for studying kinetics involves mixing 50 mL of an aqueous solution (with a concentration of 20 mg/L) with a 45μm biosorbent and keeping the mixture at 303 K. Figures 13 and 14 show the pseudo-second-order kinetic, or (t/qt) versus 't' plot, and the Lagergren, or log (q_e-qt) versus 't' plot, similarly. All of the rate constants and kinetic equations that came out of it are in Table 7. When comparing the first-order and pseudo-second-order kinetics, the latter offers a more precise account of the mechanism of the interactions between nickel and coffee leaf powder (R² = 0.99 vs. 0.85, respectively).

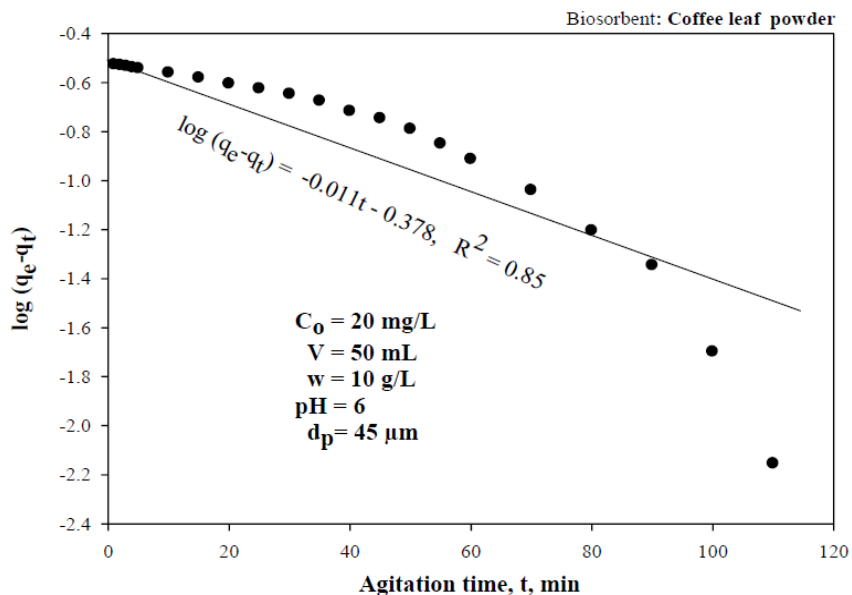


Fig. 13. Nickel biosorption following first-order kinetics.

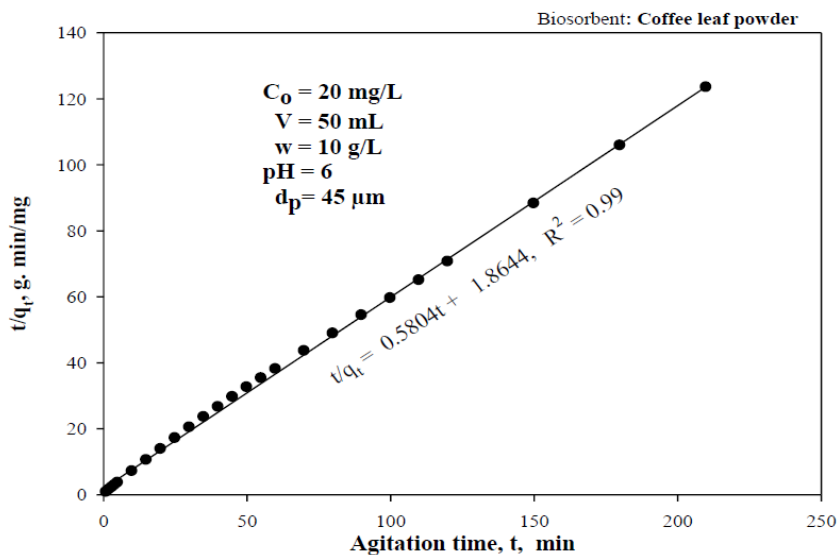


Fig. 14. Nickel biosorption using second-order kinetics.

Table 7. Rate constants and kinetic equations.

Order	Kinetic equation	Rate constant	R ²
Pseudo-first order	$\log(q_e - q_t) = -0.011t - 0.378$	$K_1 = 0.025 \text{ min}^{-1}$	0.85
Pseudo-second order	$t/q_t = 0.5804t + 1.8649$	$K_2 = 0.180 \text{ g/mg-min}$	0.99

3.11 Biosorption thermodynamics

We study the temperature dependence of biosorption behavior by conducting experiments between 283 and 323 K. In Figure 15, you can see the biosorption data plotted using the Van't Hoff method. A positive enthalpy change, as shown in this study, implies that the biosorption process is endothermic. Considering that the value of ΔS is positive, it may be concluded that the process is irreversible. Additionally, it is suggested that the randomness at the interface between the solid and solution rises when the biosorption of nickel onto coffee leaf powder occurs. There is a strong affinity for nickel in coffee leaf powder, and the value of ΔG is negative, suggesting that the procedure is feasible and that the sorption occurs spontaneously [16-18].

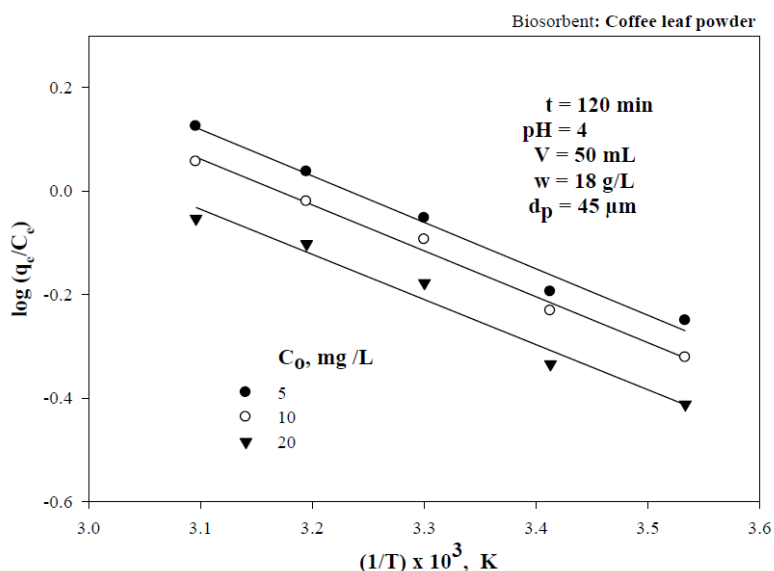


Fig. 15. Biosorption of nickel: the Van't Hoff plot.

In the current experiment, the values of ΔS , ΔH , and ΔG were found for various starting concentrations of nickel. These values are displayed in **Table 8**.

Table 8. Coffee leaf powder's thermodynamic characteristics for nickel biosorption.

C ₀ , mg/L	ΔS, J/mol-K	ΔH, J/mol	-ΔG, kJ/mol				
			283 K	293 K	303 K	313 K	323 K
5	55.52	17.17	15.69	16.25	16.80	17.36	17.91
10	53.80	16.983	15.20	15.74	16.28	16.82	17.36
20	51.08	16.67	14.43	14.94	15.46	15.97	16.48

4 Conclusion

Heavy metals pose a threat to human health in aquatic environments, therefore scientists are working to find ways to filter them out of water and wastewater. Most of the time, optimizing the purification technique to get the best value of each of the process factors is required to

get the best effectiveness of removal and sorption capacities of the pollutants on the sorbent materials. Nickel biosorption onto powdered coffee leaves that has been crushed up. In the case of nickel biosorption, the equilibrium agitation duration will be 120 minutes. The pH level of 4 is just right. 18 grams per liter is the ideal dosage. The uptake capacity of 4.219 mg/g is the highest that can be achieved at 303 K. Using CCD, the parameters are adjusted as follows: pH = 4.32, w = 17.89 g/L, Co = 18.79 mg/L, and T = 304.9 K. This results in the highest possible biosorption of nickel onto coffee leaf powder, which is 94.17%. Using pseudo second order kinetics ($K_2 = 0.180 \text{ g / (mg-min)}$), the kinetic studies demonstrate that the biosorption of nickel is more accurately characterized by this method. Endothermic biosorption occurs when the value of ΔH is positive. Because the value of ΔS is positive, the biosorption process cannot be reversed. It is a spontaneous biosorption, and the ΔG value is negative.

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