STUDIES FOR THE REMOVAL OF INDIGO CARAMINE DYE USING *QUISQUALIS INDICA* POWDER AND OPTIMIZATION USING CENTRAL COMPOSITE DESIGN

Dr. P. Brahmaji Rao[1] and Khaja Moyunuddin Mohammad[2]

[1]Associate Professor, Dept of Environmental Sciences, Acharya Nagarjuna University, Nagarjuna Nagar, Guntur- 522510, Andhra Pradesh, INDIA
[2]Research Scholar, Dept of Environmental Sciences, Acharya Nagarjuna University, Nagarjuna Nagar, Guntur- 522510, Andhra Pradesh, INDIA
Corresponding Author: Khaja Moyunuddin Mohammad
Email: chemkhaja@gmail.com

Abstract
Adding colors or dyes to water sources could make them inadmissible to purchasers however it may not be poisonous in a similar way. The wellspring of such contamination lies in the fast expansion in the utilization of manufactured colors or dyes. These squanders ruin the regular living space of the amphibian species, the best practice for the expulsion of colors and weighty metals is considered for the current examination is Biosorption Quisquails indica leaf powder is utilized for the expulsion of Indigo caramine dye from watery arrangement. The operating parameters involved are agitation time, biosorbent size and pH of the solution, initial concentration of solution, dosage of biosorbent and temperature of the solution. The kinetics and isotherm studies are also studied along with thermodynamic study. The optimization was also incorporated using Central Composite Design (CCD).
Keywords: RSM, temperature, pH, dye, dosage, biosorbent, Optimization, Kinetics.
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Introduction

Environmental protection has drawn more and more attention from society in recent years. Strict discharge regulations are in place for the release of colored wastewater into the environment as the presence of color in wastewater has grown to be a significant environmental problem. Wastewaters containing dyes are quite troublesome because they impair visual appeal and hinder photosynthesis and light penetration. Furthermore, the majority of dyes are harmful, carcinogenic, and mutagenic to people and other living things.
The continual degradation of the environment is mostly caused by the dye wastewater released from the textile and dyestuff industries. Dye-containing wastewater can be poisonous or even carcinogenic, which puts aquatic life at considerable risk. Due to the difficulties of treating dye-bearing wastewaters using traditional treatment techniques, one of the main issues is the removal of color from these wastewaters. Wastewater containing dyes has been treated using a variety of physical, chemical, and biological techniques, including solvent extraction, chemical oxidation, membrane filtration, coagulation, biosorption, and precipitation.
In the textile, rubber, paper, plastic, leather, cosmetics, pharmaceutical, and food sectors, among others, synthetic dyes are extensively utilized. Approximately 60% of all dyes

generated are utilized by the textile industry alone to paint different garments, while only 10-15% of these colors are released into the wastewater.

It has been demonstrated that biosorption has a strong chance of taking the place of traditional treatment techniques for the removal of metals and/or dyes. It is the process of sequestering either organic or inorganic substances by living or dead biomass or its derivatives; the biomass can include waste products from industry or agriculture as well as bacteria, fungus, yeasts, algae, and seaweeds. When compared to other existing technologies like ion exchange, reverse osmosis, precipitation, and adsorption, biosorption offers similar performance and is less expensive. As a result, it may be utilized to eliminate contaminants from wastewater, particularly those that are difficult for the environment to break down naturally, like dyes.

Several physico-chemical parameters, including temperature, pH, and ionic concentration or strength, as well as the kind of biomass and sorbate, the presence of other competing ions, and the circumstances of biomass processing, all affect the biosorption capability. Because sorption is unaffected by the toxicity of ions or contaminants and because maintaining a suitable growing environment or using nutrients is not necessary, using dead biomass seems more appealing than using living biomass.

Experimental Procedure

Materials

Without any additional purification, analytical grade reagents, including the color, were used. A stock solution with a mass of 1000 mg L–1 was made by dissolving an accurately weighed quantity of the dye in distilled water. To get the working solutions at the proper concentrations, the dye stock solution was further diluted with distilled water. The liquids' original pH was adjusted using 0.1 M HCl and 0.1 M NaOH solutions.

Biosorbent

Upon harvesting a Quisqualis indica leaf, the biomass was thoroughly cleansed with distilled water until all dirt was eliminated, and it was subsequently dried at 60º C for 3 days. The dried biomass was crushed, sieved, and stored for use in the experiments later on.

Analytical measurements

The concentration of alizarine cyanine dye was measured using a UV-vis spectrophotometer at a wavelength equivalent to the dye's maximum absorption in nanometers. The concentration and absorbance of the dye solution were shown as calibration curves.

Biosorption Studies

Batch biosorption investigations were conducted in 250 mL conical flasks holding 50 mL of the entire working volume. The beginning indigo caramine dye concentrations ranged from 20 to 200 mg L–1 at pH 2–8, while the concentrations of almond shell residues were 0.5–4 g L–1. Following that, the flasks were agitated for five to eighty minutes at room temperature (°C). A portion of the samples were collected and centrifuged on a regular basis. With the use of a UV–vis spectrophotometer, the dye's equilibrium concentration was determined at 460 nanometers.

Results and Discussion:

Characterization of Quisqualis indica leaf powder

FTIR spectrum

Figure 1(a) displays the FTIR values for powdered untreated Quisqualis indica leaf. Figure

1(a) and (b) displays the FTIR spectra of biomass loaded with Indigo Caramine dye in Quisqualis indica. Due to a little amount of C-O-C stretching overlap caused by the loading of the Indigo Caramine dye, the band at 1033.85 cm-1 is also displaced to 1035.77 cm-1. After treatment, the band peaks at 1155.36 and 1246.02 cm-1 are moved to 1157.29 and 1244.09 cm-1, respectively, as a result of symmetric -SO3 stretching and bending of the CH3 group. **[5]**.

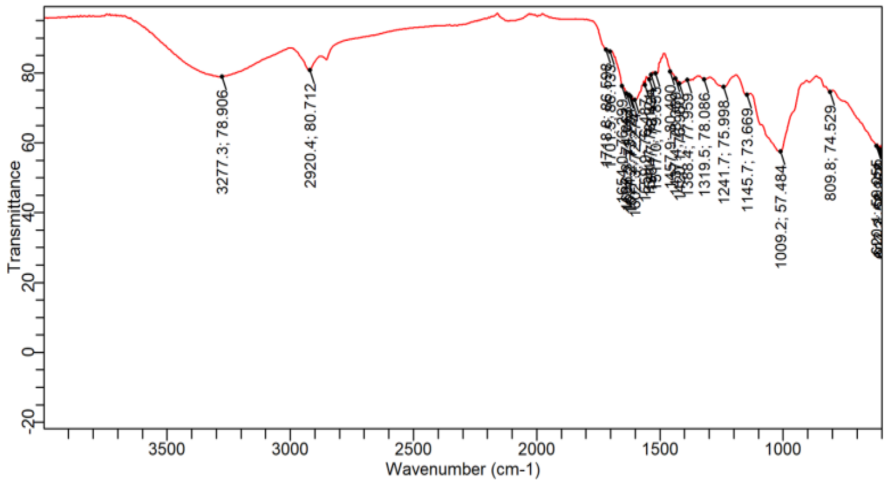

Figure 1(a): FTIR spectrum of Indigo Caramine dye treated Quisqualis indica leaf powder

Moreover, the Indigo Caramine dye loaded biomass does not exhibit the peaks at 2875.86 and 3012.81 cm-1, which are related to C-H stretching of the CH2 group/aliphatic stretching and = C-H of alkene or arene. The absence of the bounded -OH and -NH groups at peaks 3288.63 and 3334.92 cm-1 during biosorption may be caused by the dye indigo caramine's direct and primary participation in biosorption.

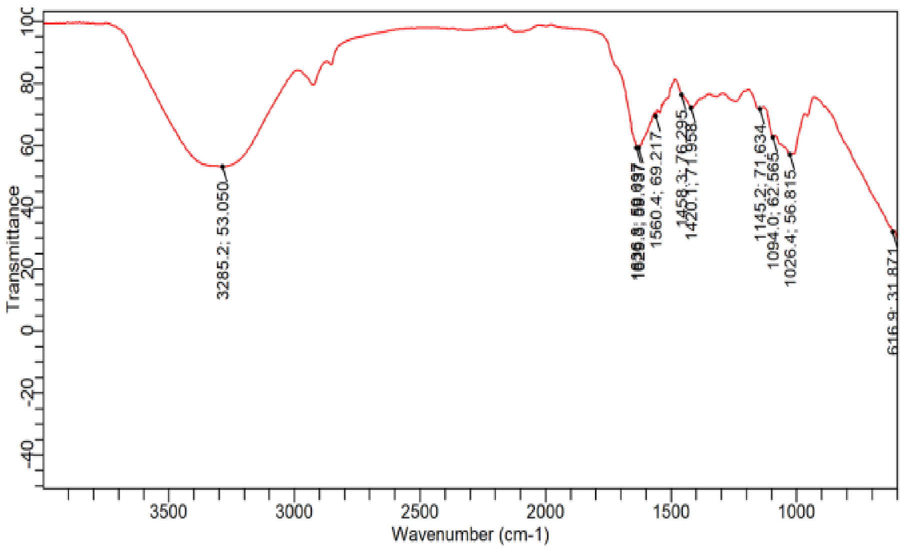

Figure 1(b): FTIR spectrum of Indigo Caramine dye treated Quisqualis indica leaf powder

Table – 1 Shift of FTIR peaks for untreated and treated Quisqualis indica leaf powder with Indigo Caramine dye

S. No.	Untreated powder, cm-1	Treated powder, cm-1	Description
1	-----	616.9	C-Cl stretching
2	809.8	----	C=C bending
3	----	1026.4	C=C bending
4	1094.0	----	CO-O-CO stretching
5	1153.6	-----	CO-O-CO stretching
6	----	1420.1	C-O stretching
7	----	1458.3	C-O stretching
8	1559.9	----	C-O stretching
9	----	1560.4	C-O stretching
10	----	1620.5	C-N stretching
11	1636.8	----	S=O stretching
12	2922.2	----	O-H bending
13	-----	3285.2	O-H bending
14	3292.6	----	N-O stretching

X-Ray Diffraction:

The XRD patterns for the untreated powder, which are displayed in figures. 2(a) and (b), are more or less amorphous and lack particularly sharp, identifiable peaks. Figures 2(a) and (b) depict the processed Indigo Caramine dye's XRD patterns, which are more or less amorphous in form and lack highly clear, identifiable peaks. The existence of CoCr2CoCr2O4, Co0.8Cr0.2, and Co7Cr8 is confirmed by the peaks at 2θ values of 0.625, 0.234, and 0324 (ICDD files). The equivalent d-values for them are 2.9472, 1.9124, and 4.8127. **[6]**.

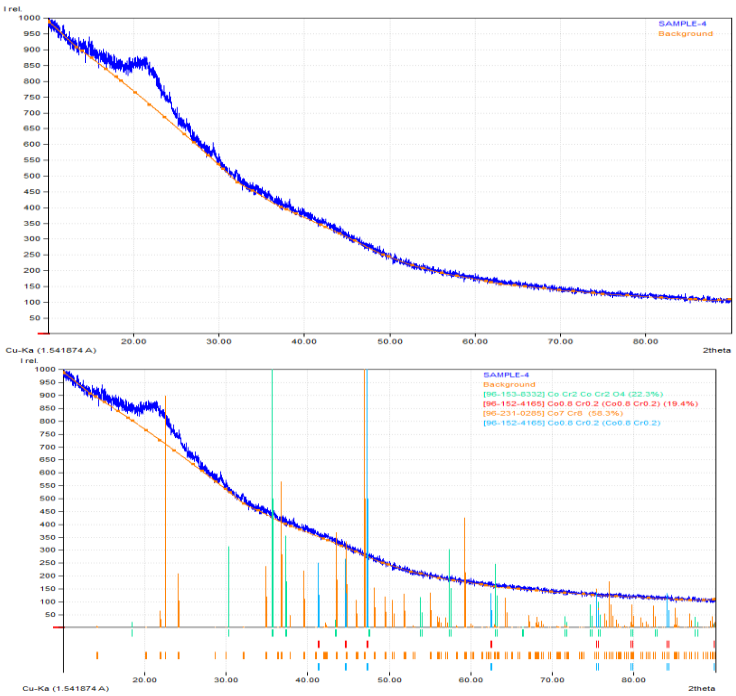

Figure 2(a): XRD pattern of Indigo Caramine dye untreated Quisqualis indica leaf powder

The XRD patterns for the untreated powder in Figures 2(b) are mostly amorphous and lack extremely sharp, identifiable peaks.AgBa0.26Sr0.74Sr0.74Ba0.26Ag, AgAl0.45F6Fe0.55RbRbAgFe55Al45F6, AgAlCsF6CsAgAlF6, AgAs2CuH3O8 Copper silver tri hydrogenbis (arsenate), AgBaH8O13P3 barium Silver Cyclo-Tri phosphate Tetra hydrate, and Ag Silver – 3C are all confirmed by the peaks at 2θ values of 0.180, 0.250, 0.035, 0.633, and 0.26. The d-values that correspond to these are 4.1620, 3.8702, 3.5094, 3.5009, and 5.1102.

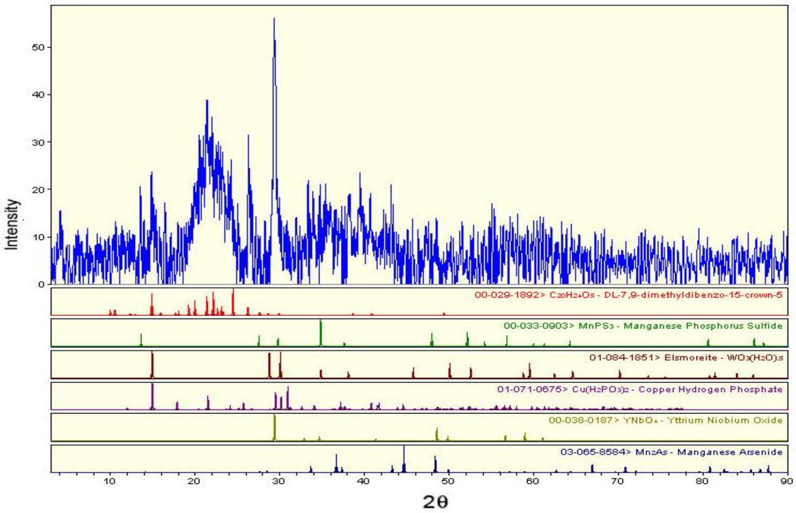

Figure 2 (b): XRD pattern of Indigo Caramine dyetreated Quisqualis indica leaf powder

Scanning Electron microscope (SEM):

Quisqualis indica leaf powder SEM micrographs taken both before and after biosorption are examined. The particles exhibit a granular, complex, uneven, and porous surface structure after biosorption, as shown in figures. 3(a) and (b), which is not present in the original Quisqualis indica leaf powder. **[8]**.

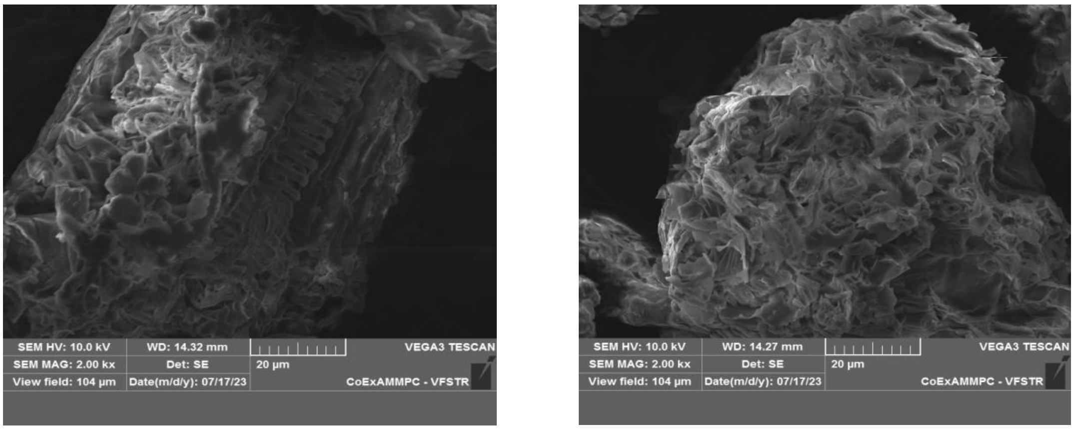

Figure 3(a): SEM pattern of treated Quisqualis indica leaf powder

Quisqualis indica leaf powder SEM micrographs taken both before and after biosorption are examined. The leaf powder seems less uneven and porous in the previous figures 3.a and (b)

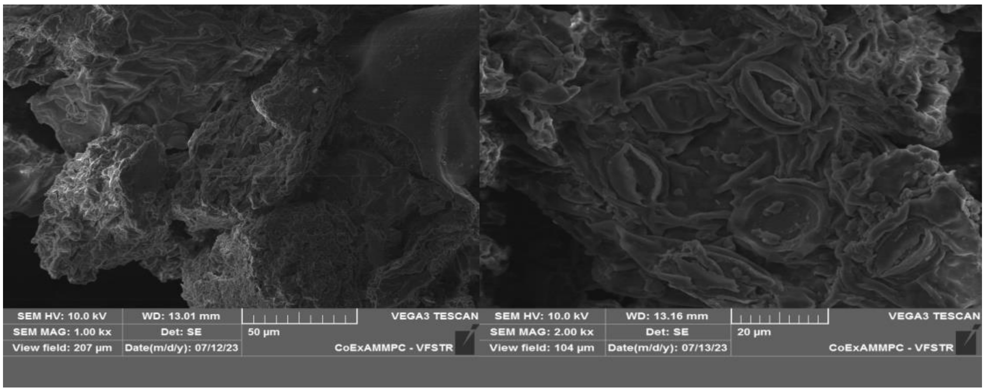

Figure 3(b) SEM pattern of treated Quisqualis indica leaf powder

Effect of agitation time:

The next section discusses how different factors affect the biosorption of indigo caramine dye. Figure 4 displays the % biosorption vs agitation time. Up to 25 minutes are observed to boost the 70% biosorption rate. After 25 minutes of agitation, the maximum percentage of biosorption is reached, and after 25 minutes, it remains constant, indicating that the equilibrium has been reached. **[9]**.

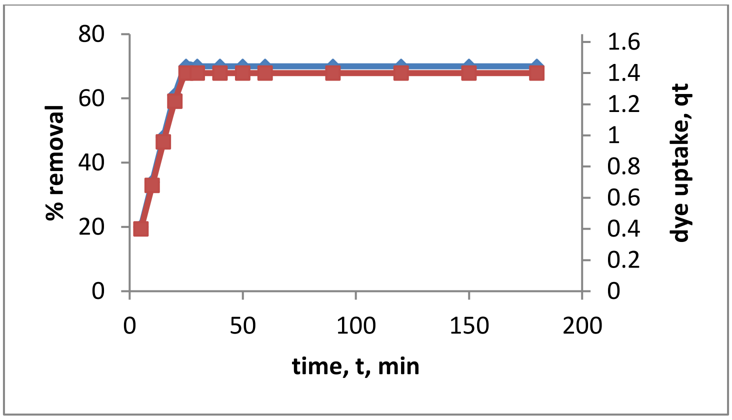

Figure 4: Effect of agitation time on % biosorption of Indigo Caramine dye

Effect of biosorbent size:

The percentage of dye indigo caramine that is bioabsorbed as a function of particle size is shown in Figure 5. As the size of the biosorbent increases from 53 to 152 µm, the proportion of biosorption decreases from 70% to 50%. More active areas on the biosorbent are exposed to the biosorbate as a result of the particle's decreasing size and increasing surface area. **[10]**.

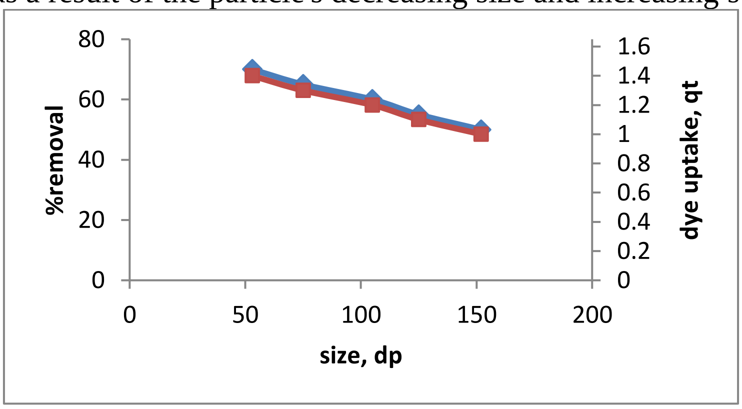

Figure 5: Effect of size on % biosorption of Indigo Caramine dye

Effect of pH:

Figure 6 illustrates how the pH of the aqueous solution affects the amount of dye that is bioabsorbed. When pH rises from 2 to 7 the proportion of biosorption increases from 45% to 70%. When pH rises from 7 to 8 the proportion of biosorption decreases from 70% to 80%. The electrostatic interaction between the biosorbent and the biosorbate is what propels dye ion biosorption. **[11].**

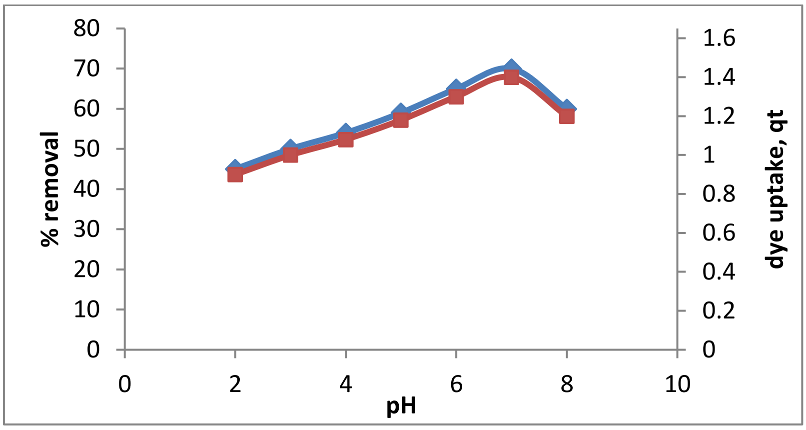

Figure 6: Effect of agitation time on % biosorption of Indigo Caramine dye

Effect of initial concentration of Indigo Caramine dye:

Figure 7 shows a graph showing the percentage of indigo caramine dye biosorption as a function of the dye's starting concentration. When the initial concentration of Indigo Caramine dye in the aqueous solution increases from 20 mg/L to 200 mg/L the percentage biosorption decreases from 70% to 50%. The rise in biosorbate and the constant number of accessible active sites on the biosorbent are responsible for this phenomenon. **[12]**.

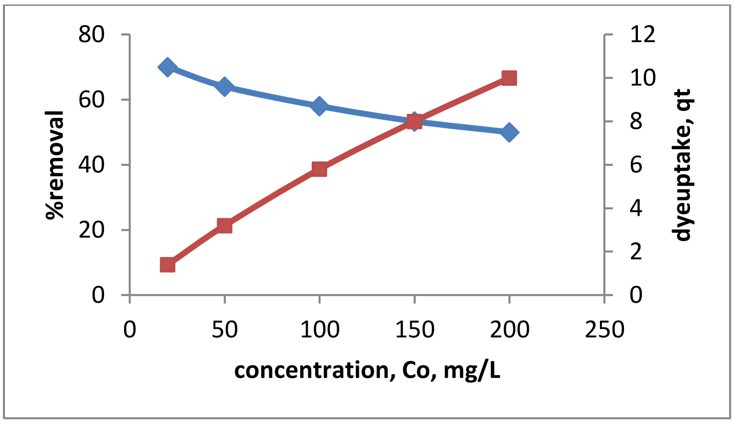

Figure 7: Effect of agitation time on % biosorption of Indigo Caramine dye

Effect of biosorbent dosage:

Figure 8 plots the % biosorption of the color indigo caramine vs the dose of the biosorbent. As the dosage of biosorbent is increased, the percentage of biosorption rises as well. As the dose is raised from 10 to 40 g/L, the percentage biosorption improves from 70% to 92% for a biosorbent size of 53 µm. Because there would be more active sites available for dye removal as the amount of biosorbent increased, this pattern is evident. **[13]**.

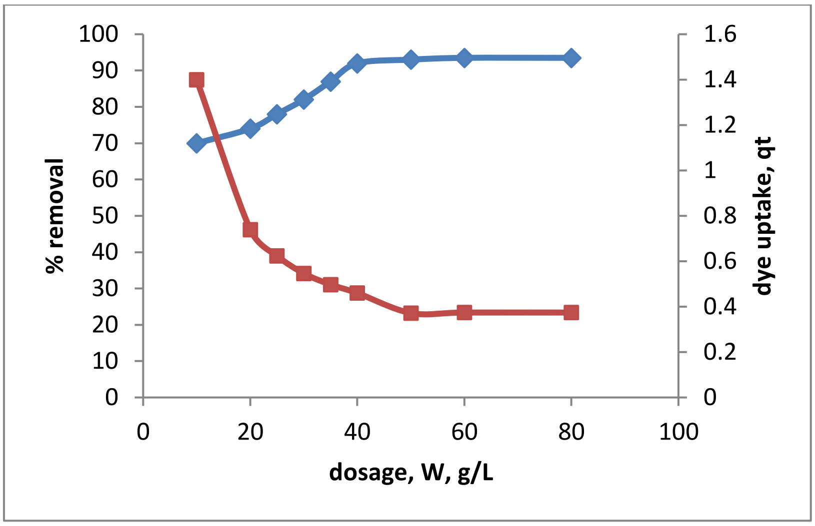

Figure 8: Effect of agitation time on % biosorption of Indigo Caramine dye

Effect of biosorbent temperature:

The biosorption rate of the green Indigo Caramine is displayed in the figure versus the biosorbent's temperature. Figure 9 Temperature increases from 283 to 323 K result in a rise in biosorption from 77% (0.5133 mg/g) to 94% (0.6266 mg/g). This behavior is clear as a higher dose would allow for the biosorption of more active sites for the color indigo caramine. **[14]**.

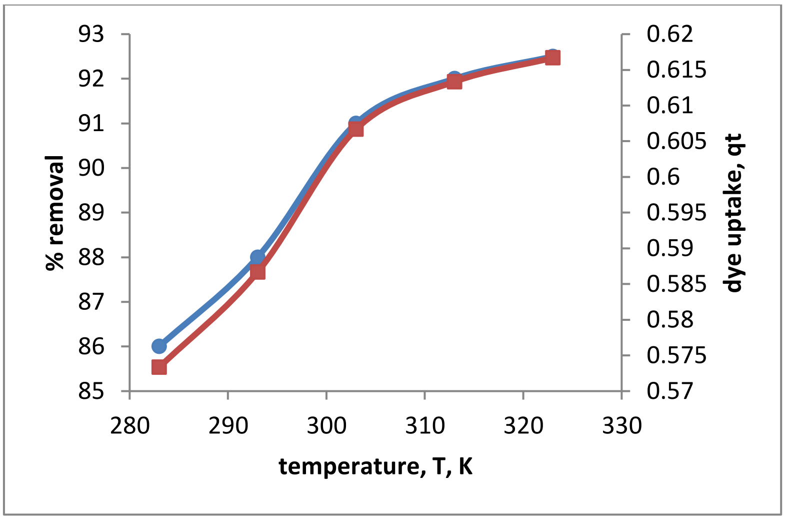

Figure 9: Dependence of % biosorption of Indigo Caramine dye on biosorbent temperature

Optimization using Response Surface Methodology (RSM):

Table 2 in the current investigation displays the amounts of four process input factors for the percentage of biosorption **[15]**. To determine the ideal conditions for dye biosorption, the factors that have the biggest impact on the reaction must be found. Regression analysis for medium constituent optimization shows that % biosorption of Indigo Caramine dye (Y) depends on pH (X1), Co (X2), w (X3), and T (X4).

Table – 2 Levels of different process variables in coded and un-coded form for % biosorption of Indigo Caramine dye using Quisqualis indica leaf powder

Variable	Name	Range and levels				
		-2	**-1**	**0**	**1**	**+2**
X_1	Biosorbent dosage, w, g/L	20	30	40	50	60
X_2	Initial concentration, C_o, mg/L	10	15	20	25	30
X_3	pH of aqueous solution	3	4	5	6	7
X_4	Temperature, K	283	293	303	313	323

The following equation represents multiple regression analysis of the experimental data:
Y = –2124.89+35.47 X1+3.72 X2 + 1.63 X3 + 13.27 X4 – 2.82 X12 –0.10 X22 –0.02 X32 – 0.02 X42 - 0.04 X1X2 – 0.02 X1X3 + 0.02 X1X4 - 0.01 X2X3 + 0.00 X2X4 + 0.00 X3X4 ----- (1)

Table- 3 ANOVA of Indigo Caramine dye biosorption for entire quadratic model

Source of variation	**SS**	**df**	**Mean square(MS)**	**F-value**	**P > F**
Model	505.6603	14	36.1185	257989.2	0.00000
Error	0.0021	15	0.00014		
Total	505.6624				

The model is reduced to the following form by removing insignificant term (X2).
Y = –2124.89+35.47 X1+3.72 X2 + 1.63 X3 + 13.27 X4 – 2.82 X12 –0.10 X22 –0.02 X32 – 0.02 X42 - 0.04 X1X2 – 0.02 X1X3 + 0.02 X1X4 - 0.01 X2X3 + 0.00 X2X4 + 0.00 X3X4 ---- (2)

Interpretation of residual graphs:

Fig.10 shows normal probability plot of residual values. The experimental values are in good agreement with predicted values with minimum error.

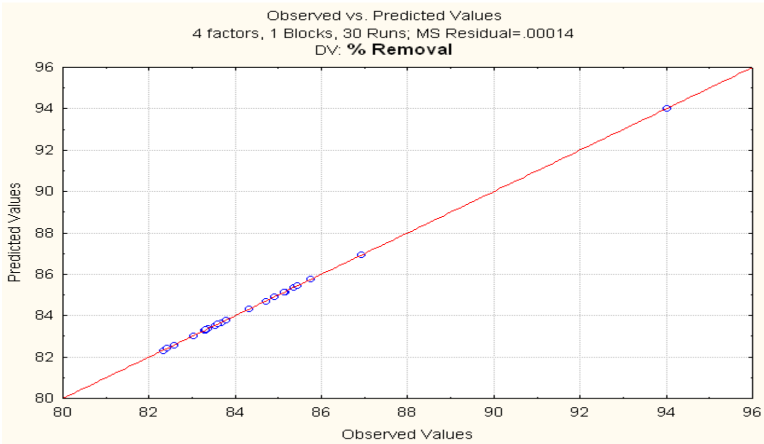

Figure 10: Normal probability plot for % biosorption of Indigo Caramine dye

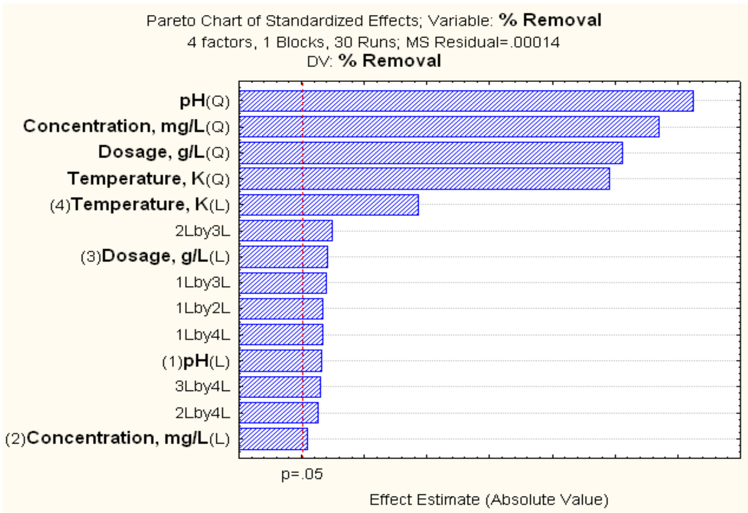

Figure 11: Pareto chat

Interaction effects of biosorption variables:

The response surface plots in three dimensions are shown in Fig. 12. The figures 12 demonstrate how pH has a significant impact on the percentage of dye biosorption of Indigo Caramine.

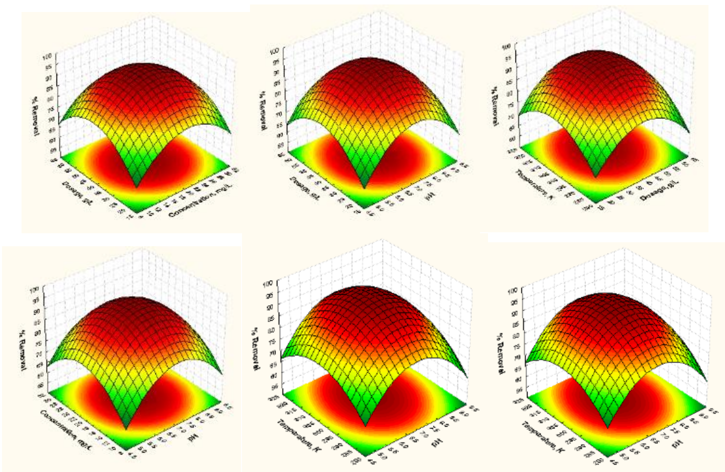

Figure 12: Response surface plots

Conclusion

According to the results of the current studies, quisqualis indica leaf powder has the potential to be an adsorbent for removing IC dye from the aqueous phase. The sorption revealed that in low pH ranges, adsorption is high. With rising temperatures, sorbent mass, falling pH, and increasing solution concentrations, the quantity of dye absorption at equilibrium increased. The study results indicate that Quisqualis indica leaf powder has great promise for application in removing IC from wastewater; nevertheless, more research is needed to boost the powder's adsorption capacity. It took 25 minutes to reach the equilibrium of IC dye biosorption. The proportion of IC dye that is biosorbed from the aqueous solution drops (from 70 to 50 percent) when the initial concentration of IC dye in the solution rises (20 to 200 mg/L). Seven is the ideal pH, and seventy percent is the ideal biosorption rate. With a biosorption percentage of 90.81381 percent, the CCD-optimized conditions are as follows: w = 40.8386 g/L, pH = 6.7560, C0 = 19.6451 mg/L, and T = 306.1284. Hence it might be concluded that quisqualis indica leaf powder is capable of removing Indigo Caramine dye.

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