STUDIES ON GREEN SYNTHESIS OF SILVER NANOPARTICLES FOR THE REMOVAL OF BRILLIANT GREEN DYE FROM AQUEOUS SOLUTION

Abstract

In order to remove Brilliant Green dye from an aqueous solution, the current study seeks to use an experimental evaluation of the biosorptive ability of synthetic nanoparticles with Tecomastans leaf extract. The XRD, FTIR, SEM, and FESEM analyses were used to describe the produced nanoparticles. The effects of agitation time, pH, BG dye concentration, biosorbent dosage, and temperature on BG dye removal were investigated in batch runs. The Response Surface Methodology (RSM) results are compared with the optimal settings that were empirically discovered. The experimental data is consistent with pseudo-first order kinetics and was fitted into the Temkin isotherm.

The thermodynamically possible, endothermic, and spontaneous natures of biosorption are revealed by thermodynamic investigations. The findings showed that Ag-TS-Nps can be used as good, affordable biosorbent for treatment of industrial waste waters.

Keywords: Brilliant green, Tecoma stans, Isotherms, Kinetics, Thermodynamics, Response surface methodology, Ag-TS-Np's.

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I. INTRODUCTION

Development of Science and technology contributes to society for better life but it also impact on the environment negatively. Treatment of industrial waste water is one of the issues in discharge water from industries. The effluent from textile industry, paper industry, carpet, leather and printing units may contain different dyes. Organic dyes are very difficult to biodegrade due to their complex nature and they are more stable. By absorbing sunlight, dyes can prevent photo synthesis in ecosystems. Brilliant green dye should be kept out of water sources because it is poisonous and carcinogenic, and because it has issues with detoxification and degradation. Brilliant Green dye, BG, is regarded as a biohazard substance [1-8]. In general chemical, biological, and physical processes are used to remove the dyes from waste water. In recent years, green synthesis by using plant extract or modified material has gained momentum compared to other processes. However, the commercial Solid State Technology and other chemical processes are quite expensive and has limited application. So the cost-effective alternative adsorbents are efficient to replace the chemical substances.

Different authors studied the potentiality of using low cost materials like Carica Papaya[9], Microalgae coalastrella[1], carboxymethylcellulose[10], PanusTigrinus[11] Znobiosilicananocomposite[12], Allium sativum[13], FumariaeHerba[14], Ulvalactuca [15], are used to remove dyes form waste water. Since the raw material is readily available, safe, and affordable, the current work aims to investigate the viability of employing Tecomastans leaf extract to remove Brilliant Green dye from aqueous solution.

Characterization of Nanoparticles: FTIR spectrum analysis was used to evaluate the adsorbent material's surface functional groups. Through analysis of the X-ray diffract gram, the phase of the produced adsorbent was determined. The FESEM and SEM micrographs are used to confirm that the particle size and shape were in the nano scale range.

II. MATERIALS AND METHODS

Chemicals of the analytical grade were employed during the experiment. Brilliant Green of analytical grade had been used as a dye. For the preparation of all stock and synthetic solutions, double distilled water is used. The pH of the dye solutions were adjusted to the correct amount by adding 0.1M $H2SO_4$ and 0.1M NaOH solutions to the stock solution, which contained 1g of dye Brilliant Green dye in 1.0 liter.

Table 2.1: Experimental values studied for dye

S.No.	Parameters	Values studied
1	Agitation time, t, min	1, 3,5, 10,15, 20,25, 30, 40, 50, 60, 90, 120, 150 &180
2	pH of dye solution	2, 3, 4, 5, 6, 7 and 8
4	Initial dye concentration, C_0, mg/L	20, 40, 60, 80 and 100
5	Adsorbent dosage, w, g/L	10, 20, 30, 40, 50 and 60
6	Temperature, ^0C	30,40,50,60 and 70

1. Preparation of the Leaf Extract Solution and Nanoparticles Formation

- **Preparation of Tecoma Stans leaf extract solution:** In this procedure, 10 gram of fresh cleaned TS leaves are placed in a magnetic stirrer. Distilled water 110 ml is then added, and the mixture is heated at 60 ^{0}C for 30 minutes. The solution is then filtered using Whatmann's filter paper in a 250 ml conical flask and set aside for further analysis. The resultant extract is in light yellow color.

- **Preparation of NanoParticles:** In order to produce nanoparticles, 70 ml of extract solution and 230 ml of 1.0 mM (0.17g) silver nitrate solution are put to a conical flask and placed in an orbital shaker incubator set to 30 degrees Celsius for five minutes. When silver nanoparticles formed, the solution's color shifted from pale yellow to brown .After being dried, this solution was used at different concentrations and dosages in a range of color degradation procedures.

2. Equilibrium Studies on Dye Decolourization

- **Effect of Contact Time:** 20 ml of aqueous solution (20ppm dye concentration) was taken in a test tube and 0.1 g of silver nanoparticles was added. This sample was taken and kept under the light for photosynthesis.Similarly,15 more samples were prepared in test tubes and analysed at different agitation time values (1, 3, 5, 10, 20, 25, 30, 40, 50, 60, 90, 120, 150 and 180 min). These samples were evaluated in UV spectrophotometer to determine final concentrations of dye. The equilibrium contact time was obtained from the data.

- **Effect of pH of the Aqueous Solution:** 20 ml of aqueous solution were poured into each of seven test tubes in order to examine the effect of pH on BG dye decolorization. In separate test tubes, the pH values of the solutions were changed to 2, 3, 4, 5, 6, 7 and 8 by adding the necessary amounts of 0.1N $H2SO_4$ or 0.1N NaOH. Separately, 0.1g of NP's powder was added to these test tubes. This sample was taken and kept under the light for photosynthesis. Then samples were allowed to settle down and color change was observed for equilibrium contact time. The various dye concentrations are determined by using UV spectrophotometer.

- **Effect of Initial Concentration of the Dye in Aqueous Solution:** 20 ml of aqueous solution containing 20 mg/L dye was taken in test tubes and 0.1g (5 g/L) of silver NP's is added. This sample was taken and kept under the light for photosynthesis. The sample was allowed to settle and color change is observed. In a UV spectrophotometer, the sample's final dye concentration is determined. For further initial dye concentrations in aqueous solution (20, 40, 60, 80, and 100 mg/L), the same process was repeated.

- **Effect of Dosage of Nanoparticles:** The experiments were carried out for six more dosages (10, 20, 30, 40, 50 and 60g/L) for equilibrium contact time, from the data optimum biosorbent dosage was identified.

  The percentage decolourization of dye is calculated as (Co-Ce) x 100/Co.

Where Co = Initial concentration of BG dye solution and Ce = Equilibrium concentration of BG dye solution

- **Effect of Temperature:** In this process the known quantity of broth solution of different leaves is taken in a magnetic stirrer and the temperature is changed for every solution. At first the solution is heated at 30^{o}C and is the solution is transferred to 250 ml conical flask by adding known quantity of NP's solution and this solution is kept on orbital shaker at room temperature and optimum time and temperature was maintained. The final (BG) dye concentration of the filtrate is evaluated in an UV Spectrophotometer. The similar process is done for other temperatures (30, 40, 50, 60,70^{o}C) for calculating optimum temperature.

III. RESULTS AND DISCUSSIONS

The goal of the current study is to determine how well nanoparticles work in decolorizing brilliant green dye in aqueous solution using experimental data from batch experiments. Contact time, solution pH, starting concentration, dosage, and aqueous solution temperature all have an impact on the decolorization of BG dye.

1. Characterization Studies

- **FESEM Analysis of NanoParticles:** FESEM (Field Emission Scanning Electron Microscope) image shown in fig.3.1 clearly indicates the small structures and different sizes of nanoparticles.

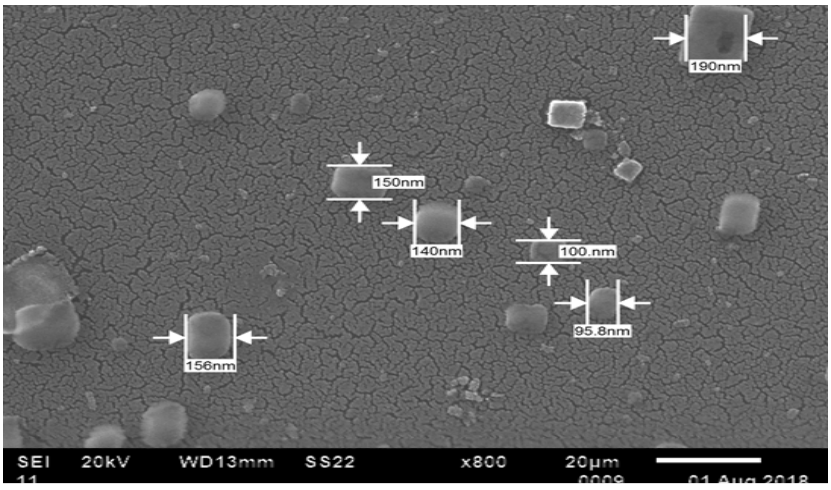


Figure 3.1: FESEM image of silver nanoparticles

For the best imaging, it offers very high steady probe currents and great resolution. The generated nanoparticles have a diameter between 95.8 and 190 nm.

- **Fourier Transform Infra-Red Spectroscopy (FTIR):** Infrared spectroscopy is one of the molecule-specific molecular vibrational spectroscopies that offers precise information about the functional groups, the character of their interactions, and their

orientations. Data from solid surfaces, liquids, and gases can be collected due to its sample requirements. The bands shifting and signal intensity variations allow for the identification of the functional groups involved in dye sorption.

- **FTIR Spectrum of Untreated Powder (a):** The untreated Ag-TS-Np powder's FTIR spectrum is shown in Figure 3.2. The peak at 1031.92 cm-^{1} indicates the participation and involvement of C=S stretching modes in adsorption. The presence of the C–H bent alkenes bond is indicated by the peak at 1238.30 cm-^{1}. The Amine N-H stretch bond is assigned to the peak at 2850.79 cm-^{1}.

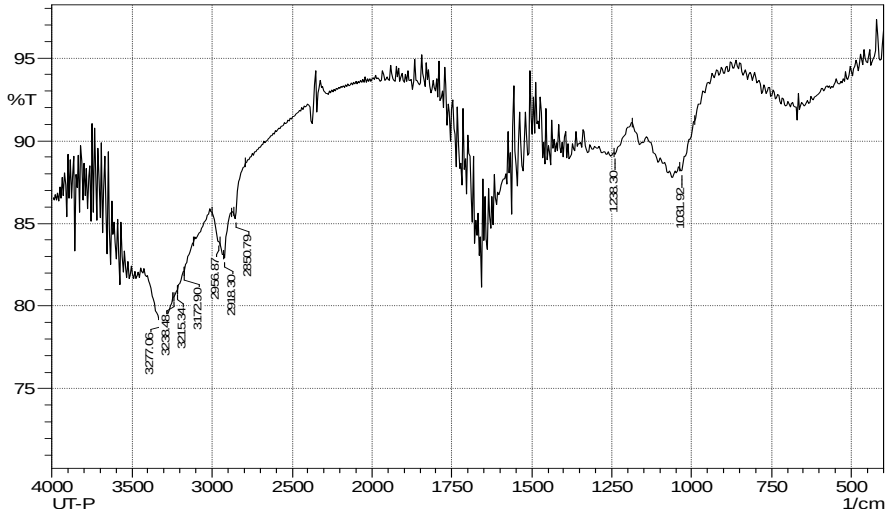


Figure 3.2: FTIR spectrum of BG dye untreated Ag-TS-Np's powder

The peaks at 2918.30, 2956.87 and 3172.90 cm^{-1} also designates the presence of Amine N–H stretch bonds. The peaks at 3215.34 and 3238.48 cm^{-1} denotes the presence of Asymmetric –CH_2–, symmetric –CH_3 and –CH_2– stretching vibrations. The peak at 3277.06 cm^{-1} denotes the presence of Amine N–H stretch bonds.

- **FTIR Spectrum of BG dye treated with Ag-TS-Np's Powder (b):** FTIR measurements for BG dye loaded with Ag-TS-Np's are shown in fig. 3.3 the peaks at 459.06 indicates C–Br stretch bands from alkyl halides. 1031.92 cm^{-1} is shifted to 1041.56 cm^{-1} indicates the presence of C=S stretching bonds in biosorption. The peaks ranging from 1238.30 cm^{-1} to 1251.80 cm^{-1} determines the presence of C–H bending alkenes. The peak at 2850.79 cm^{-1}determines that C=S stretching bonds remained same in both treated and untreated powder. The peak ranging from 2918.30 to 2920.23 cm^{-1} represents the Amine N–H stretching bond. The peak from 3277.6 to 3315.63 cm $^{-1}$wave length depicts the Amine N–H stretching vibrations. The peaks at 3331.07, 3346.50 and 3903.92 cm^{-1} (indicates the presence of aromatic C–H stretching or –NH_2 stretching respectively) are not shown in untreated analysis.

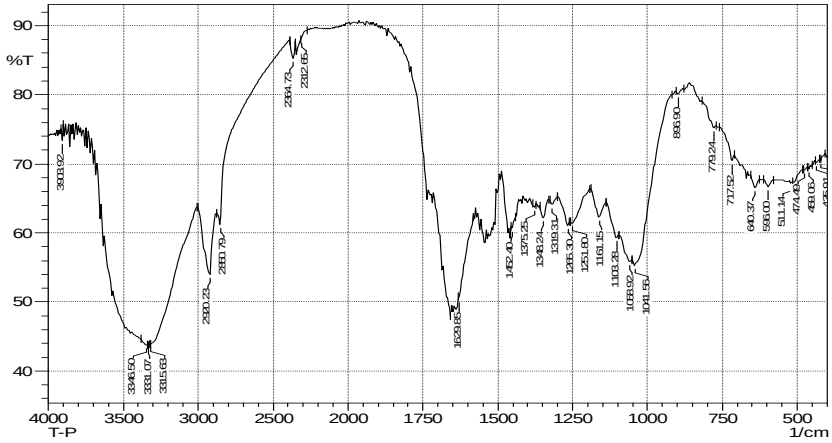
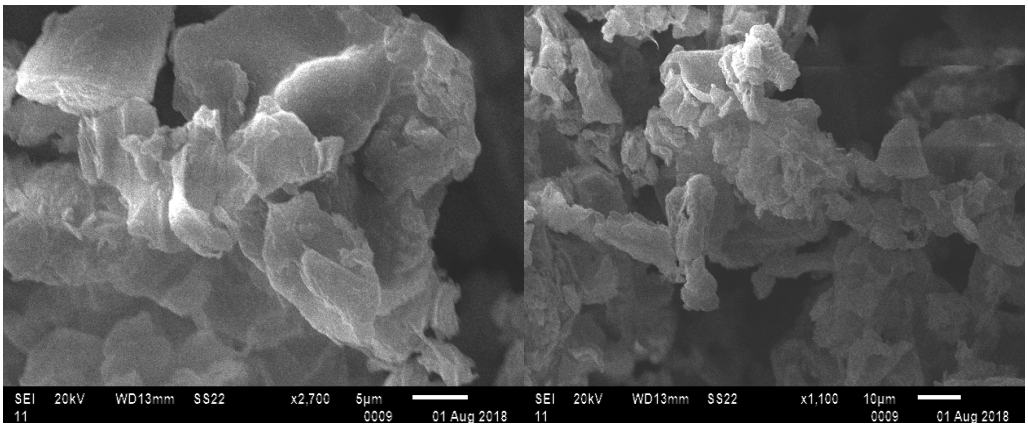


Figure 3.3: FTIR spectrum of BG dye treated Ag-TS-Np's powder

Further, three additional peaks at 1265.30, 1319.31 cm^{-1} denoting =C–H bend alkenes bonding and 1348.24 cm^{-1} for C=C stretching have been observed in BG dye treated powder. The peak at 1375.25, 1452.40 and 1629.85 cm^{-1} in BG dye treated powder is representing Alkyl C–H stretch mode and is not seen in native biosorbent. The alkyne ligand's C□C bands are involved in the peak at 2312.65 cm^{-1} that is obtained in treated biomass. This might be the result of the strong shaking physically disrupting the cell membranes and adjusting the pH.

- **Scanning Electron Microscopy (SEM):** The natural sorbent morphology and its modification derived from sorbate interactions can be studied from SEM technique. SEM is an electron microscope which provides images of the sample surface by scanning it with a high energy beam of electrons.

- **Scanning Electron Microscope for Untreated Ag-TS-Np's powder(a):** The SEM images of Ag-TS-Np's powder before and after biosorption are analysed. The SEM image in fig. 3.4 for untreated Ag-TS-Np's powder.



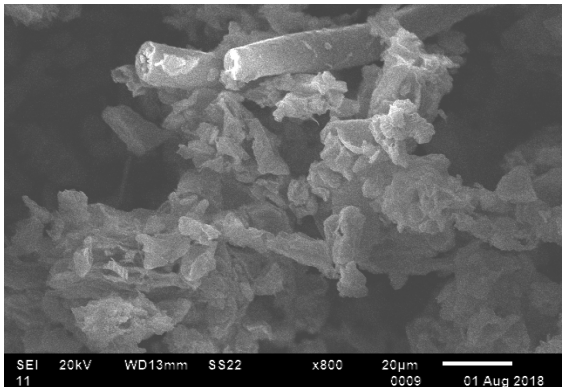


Figure 3.4: SEM image of untreated Ag-TS-Np's powder

The surface of the biosorbent had an uneven and rough physical structure. This morphological structure has a lot of pores and a greater biosorption surface for the biosorption of heavy metal ions.

- **Scanning Electron Microscope image for Treated Ag-TS-Np's powder (b):** After the binding of dye molecules, a significant change in the biosorbent surface was observed it became dull due to the coating of biosorbent particles with the dye molecules.

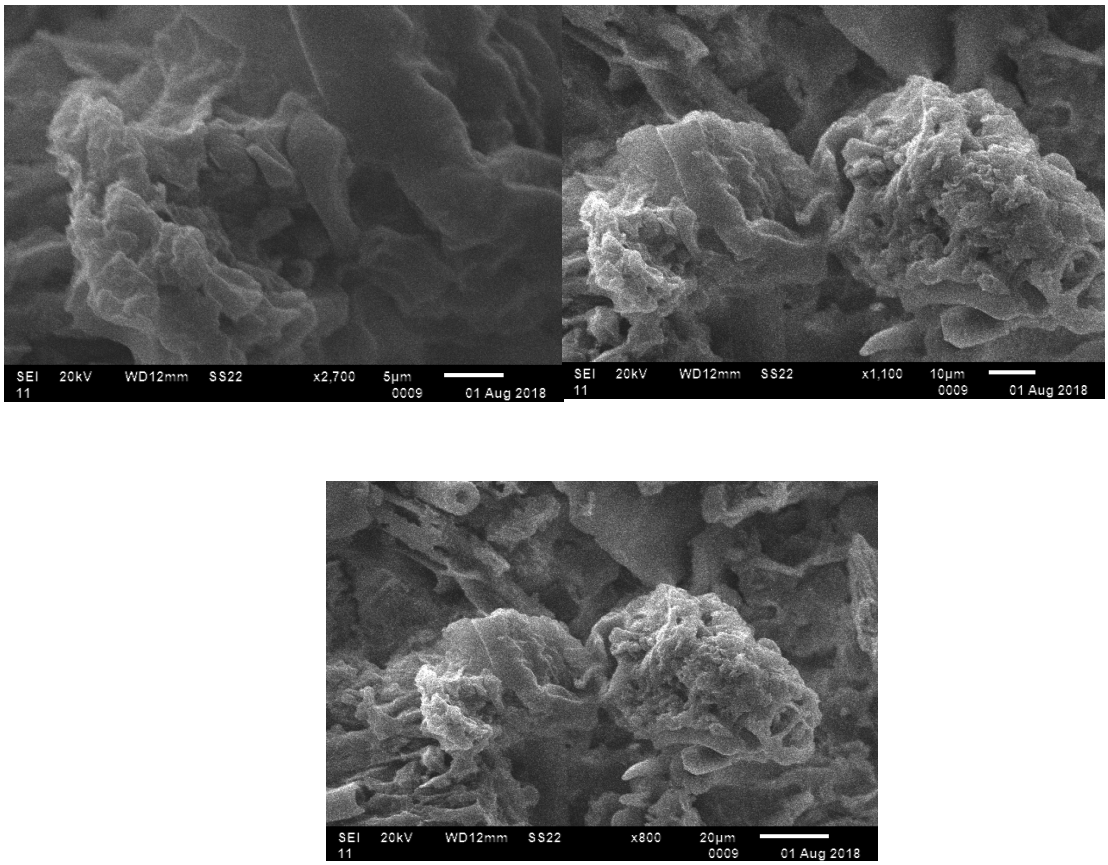


Figure 3.5: SEM image of treated Ag-TS-Np's powder

One can clearly see significant morphological changes on the sample surfaces. The scanning electron micrographs clearly show the biosorbent coated by dye molecules over the whole surface.

- **X-Ray DiffractionL:** A Rigaku Ultima model IV is used to take the powder samples' X-Ray Diffractograms (XRD). By comparing a series of "d" values and the accompanying intensities with the standards from the ICDD (International Center for Diffraction Data) files, different phases of the samples are to be determined.

- **XRD for BG dye untreated with Ag-TS-Np's Powder(a):** XRD patterns of untreated powder are shown in fig. 3.6 determines crystalline and amorphous nature. The peaks at 2θ values of 0.1513, 0.1998, 0.4077 and 0.5886 specifies the presence of AlO_4P, O_2Si, C_2N_2Zn and D_2 (ICDD files). Their corresponding d-values are 0.1003, 0.0668, 0.4345 and 0.1337.

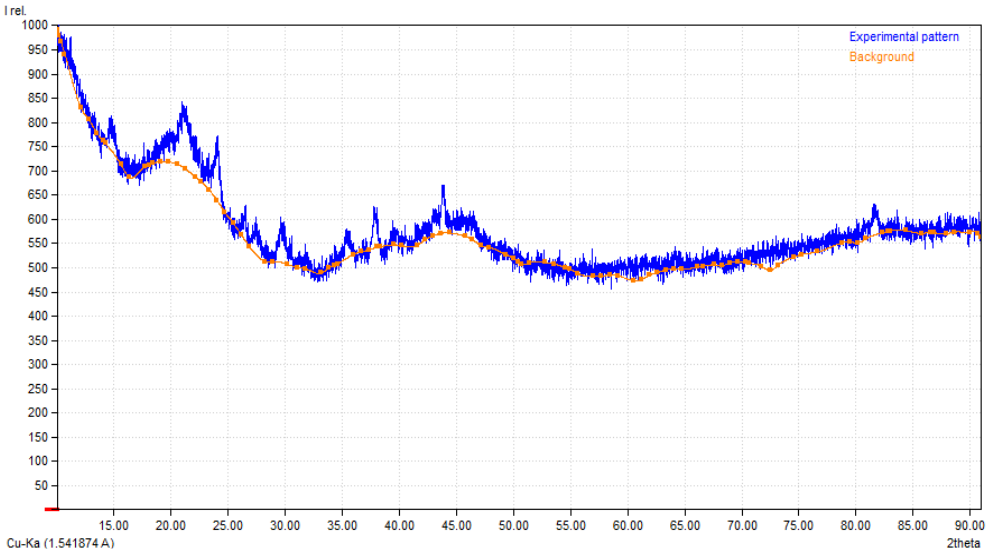


Figure 3.6: XRD pattern of BG dye untreated Ag-TS-Np's powder

- **XRD for BG Dye treated with Ag-Ts-Np's Powder(b):** XRD patterns for treated powder Fig. 3.7 determines good crystalline and amorphous nature and increase in surface area and porosity. The peaks at 2θ values of 0.3988, 0.1766, 0.1487, 0.3529 and 0.6672 indicates the presence of $C_{16}AlClN_{16}S_4$, $Bi_{38}Mo_5O_{15}Rb_{15}$, $F_{15}Mo_5O_{15}Rb_{15}$, $Al_{0.09}Ca_{1.87}K_{0.02}$, and $F_{3.48}Yb_{0.2}Zr_{0.8}$. Their corresponding d-values are 0.0334, 0.0334, 0.1671, 0.0334 and 0.1003.

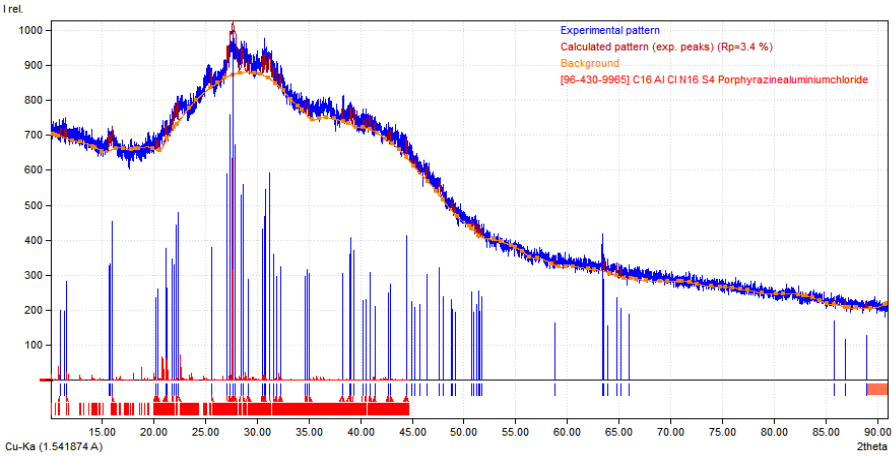


Figure 3.7: XRD pattern of BG dye treated Ag-TS-Np's powder

2. Equilibrium Studies

- **Effect of Contact Time:** Equilibrium biosorption is defined as the time needed for dye concentration in order to obtain an enduring value during biosorption. By plotting % biosorption from BG dye against contact time, as shown in fig.3.8 equilibrium contact times are determined for an interval of interaction between 1 and 180 minutes. In the earliest stage, biosorption is accelerated because of a suitable surface area for biosorbents.As time increases, more amount of BG dye gets biosorbed onto the surface of the biosorbent due to forces of interaction. The biosorbate is typically formed as a thin layer of one molecule thick covering the surface, if that monomolecular layer covers the surface and biosorption capacity has been exhausted. The rate at which adsorbates are transferred from the exterior to the interior regions of the adsorbent particles determines the maximum amount that can be utilised after surface adsorption sites are depleted. After 60 minutes, the maximum percentage removal—that is, 50%—is reached. Therefore, this agitation time is used for all subsequent studies.

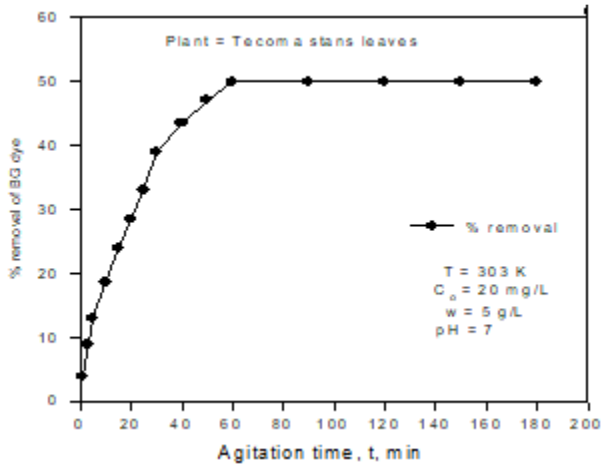


Figure 3.8: Effect of contact time on % removal of BG dye

- **Effect of pH:** The variation in pH for the dye decolorization in the range of 2 to 8 is shown in fig. 3.9, in the initial stage the pH is varying from 2 to 6, It increased rapidly due to the free movement of H^+ ions and at low pH depresses dye decolourization due to competition with H^+ ions for appropriate sites on the adsorbent surface.

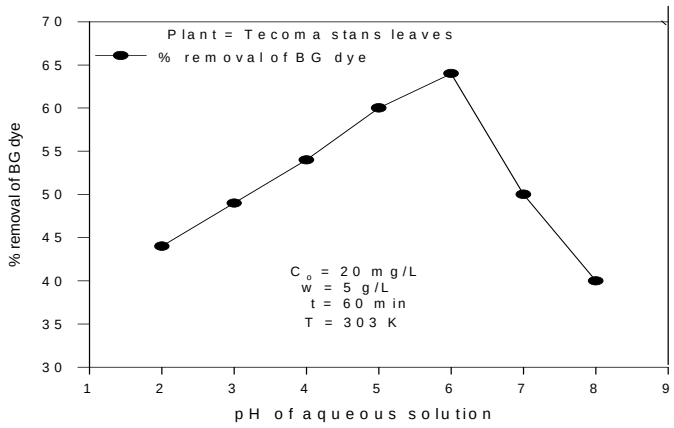


Figure 3.9: Effect of pH on decolourization of BG dye

However, with increasing pH, this competition weakens and brilliant green molecules replace H^+ ions which bound to the adsorbent, it causes a repulsive force between the dye and nanoparticles. The final optimum pH for BG dye is 6 and the percent removal is 64%. In this process the initial concentration and contact time were at 20 ppm and 60 min respectively.

- **Effect of Initial Concentration of Dye:** The effect of concentration parameter on decolourization of the dye is represented in below Fig 3.10. The plot reveals that as the concentration increases the % removal of dye decreases in the concentration range of 20-100 ppm. It is due to the vacant pores on the Tecomastans broth have been occupied by the dye molecules. By increasing the dye concentration, the adsorption sites available are already occupied and consequent adsorption is not as effective as in the beginning, it leads to decrease in % removal of dye. The percentage decrease may be due to lack of surface active sites of biosorbent to adsorb the dye molecules in the solution. Based on different concentrations (20-100 ppm) studied, the optimum concentration obtained for brilliant green dye is 20 ppm and the % removal is 64. Dye uptake curve is also represented in fig. 3.10.

  Dye uptake increases with concentration in the range of variables studied.

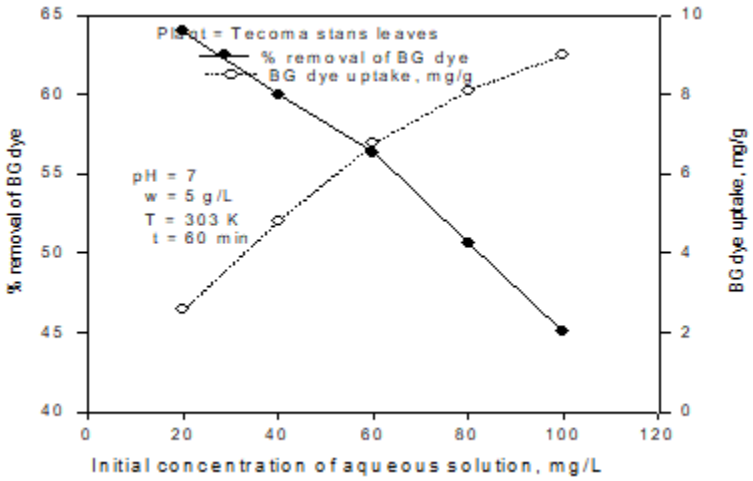


Figure 3.10: Effect of BG dye initial concentration

- **Effect of Nanoparticle Dosage:** The influence of dosage on decolorization of dye is shown in fig. 3.11 from 10g to 60g/L of silver nanoparticles. The other parameters like initial concentration (20 mg/L), pH (6), contact time (60 min), and temperature (303 K) are remained same in the whole process. The fig. 3.11 shows the variation of % removal of dye with increase in dosage. The plot shows that the percentage of dye removed grows along with the dosage. It can be stated that as the dosage of adsorbent is increased, surface area increases and removal efficiency increases as a result. The same picture also displays a dye uptake graph, which has a tendency opposite to the dose effect. These investigations have shown that the best MG dye dosage is 30 g/L and the removal percentage is 69.

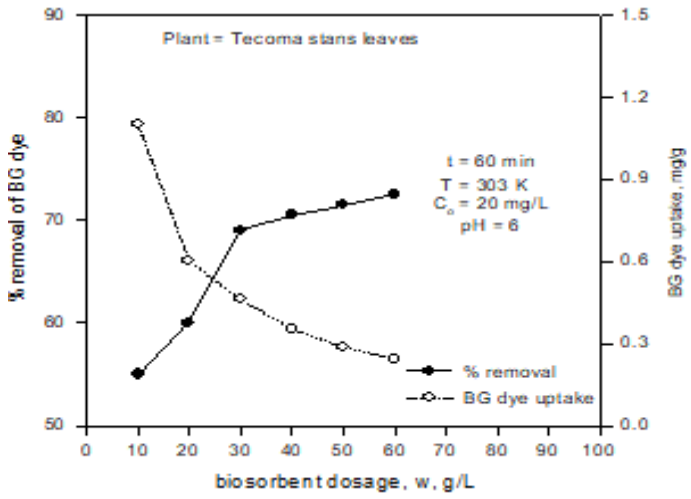


Figure 3.11: Effect of nano-biosorbent dosage

- **Effect of Temperature (T, K):** Figure 3.12 illustrates how a temperature change affects the percentage of dye removed. The dye containing Ag-TS-Np's at different temperatures is found to exhibit an increasing trend from the starting point of 30°C to

70°C, with an almost linear increase in the dye's percentage removal. Diffusion rates within the pores and across the exterior boundary layer both rise with temperature. Moreover, the equilibrium capacity will change as the temperature changes. Through batch studies conducted at five different temperature values (303, 313, 323, 333, and 343 K), the influence of temperature is examined. The Brilliant Green dye works best at 70°C, and its removal percentage is 82%.

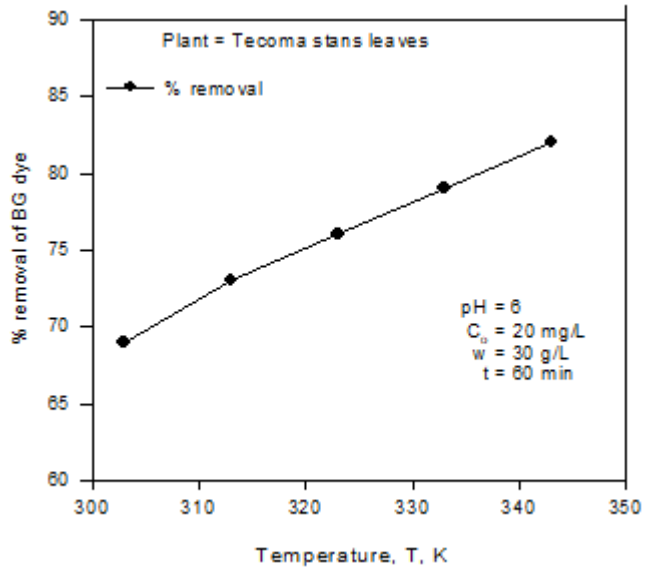


Figure 3.12: Effect of Temperature on Decolourization of BG dye

3. **Isotherms:** The values of the constants that define the isotherms express the surface characteristics and affinity of the biosorbent and can also be used to compare the biosorptive capacity of the biosorbent for various dyes. Three isotherm model equations—the Langmuir, Freundlich, and Temkin isotherms—were used in this study out of numerous isotherm model equations.

- **Langmuir Isotherm:** The Langmuir relationship is hyperbolic and the equation is,

$$q_e / q_m = \frac{bCe}{1+bCe} \text{.....3.1}$$

Where,

C_e is the equilibrium concentration (mg/L), q_e is the amount of dye biosorbed (mg/g), q_m is for complete monolayer (mg/g), b is Sorption equilibrium constant
The linear form of Langmuir isotherm equation is

$$C_e / q_e = 1 / (b\, q_m) + (1 / q_m)\, C_e \text{.....3.2}$$

Fig.3.13 is plot of [C_e] versus [C_e / q_e] which is straight line with slope $1/q_m$ and an intercept of $1/bq_m$.. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter (R_L) which is defined by the following equation,

$$R_L = 1 / (1+bC_0) \quad .....3.3$$

Where,

R_L = Dimensionless separation factor / equilibrium factor, which indicates sorption favourability, C_0 = Initial concentration (mg/L), b = Langmuir constant
The conditions for R_L are If R_L>1 Unfavourable sorption; R_L = 1; Linear 0< R_L

Value of R_L (0.8170) obtained in the present study are less than 1 which indicates the favorability of biosorption for Brilliant green onto silver NP's powder. Isotherm equation obtained for the present study isC_e/q_e= 0.0689Ce + 2.2162, R^2=0.9933.

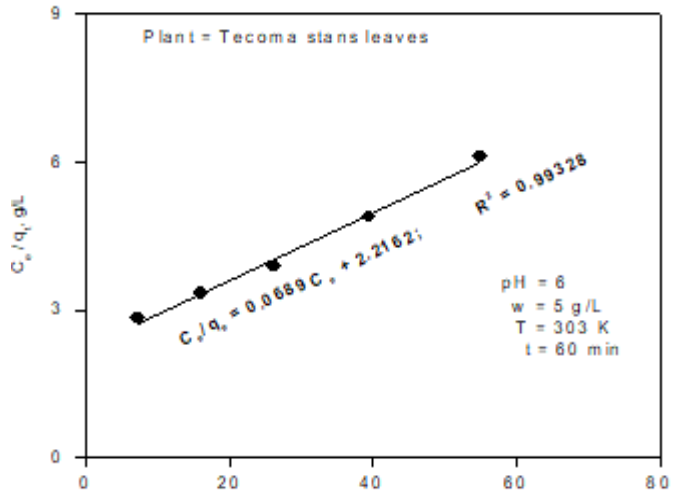


Figure 3.13: Langmuir isotherm for biosorption of BG dye

- **Freundlich Isotherm:** Freundlich Isotherm relationship is expressed by the following equation:

$$q_e = K_f C_e^{\,n} .....3.4$$

Linear form of Equation is

$$\ln (q_e) = n * \ln (C_e) + \ln K_f ..... 3.5$$

Where K_f and n are isotherm constants. The obtained equation is

$\ln q_e$ = 0.6284 $\ln C_e$0.23096, R^2=0.9763

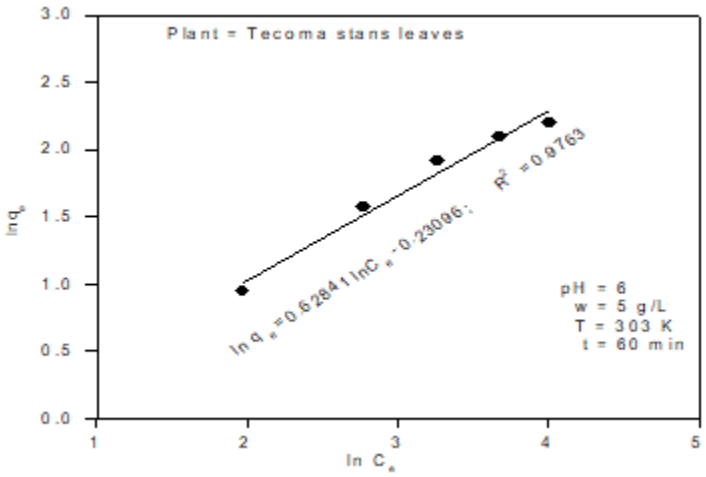


Figure 3.14: Freundlich isotherm for biosorption of BG dye

- **Temkin Isotherm:** Temkin isotherm relationship is expressed by the following equation:

$$q_e = (RT \ln (A_T C_e)) / b_T \ldots. \quad 3.6$$

The linear form of Temkin isotherm can be expressed as,

$$q_e = (RT / b_T) \ln C_e + (RT / b_T) \ln (A_T) \ldots. \quad 3.7$$

The obtained equation is $q_e = 3.2455 \ln C_e - 3.9445$, $R^2 = 0.9962$

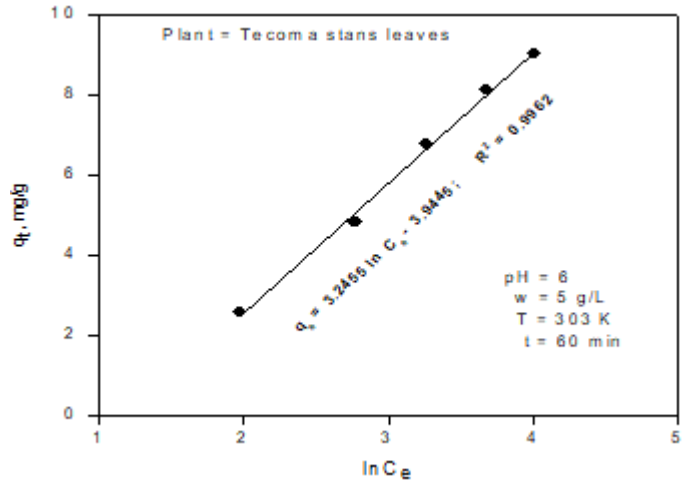


Figure 3.15: Temkin isotherm for biosorption of BG dye

Table 3.1: Isotherm Constants obtained for Various Models

Isotherm	Constants	R^2
Langmuir	q_{max}, mg/g = 14.51	0.9933
	b, L/g = 0.0311	
	R_L = 0.8170	
Freundlich	K_f = 0.7938	0.9763
	n = 0.6284	
Temkin	A_T = 0.2966	0.9962
	b_T= 776.1953	

Table 3.2: Dye uptake Capacities for different Biosorbents

Author	Dye Chosen	Biosorbent	q_{max}, mg/g
Rabia Rehman et al [17]	Brilliant green	Eugenia jambolana leaves	4.739
Aadil Abbas et al [18]	Brilliant green	Peanut Shell	19.92
Mohamed A. Salem et al [19]	Brilliant green	Psidium guajava Leaves Solanum tuberosum Peels	1.075 1.173
L.P. Thyagarajan et al [20]	Congo red	Silver Nanoparticles Synthesized from Bacillus sps	2
Present study	**Brilliant green**	**Silver nanoparticles synthesized from Tecomastans plant leaves**	**14.51**

4. Kinetics of Biosorption

- **Pseudo first order Kinetics:** The Lagergren first order equationis,

$$\mathbf{(dq / dt) = K_1 (q_e - q_t) \quad ..... \quad 3.8}$$

Where q_t and q_e are the amounts biosorbed at t (min) and equilibrium time and K_1 is the rate constant of the pseudo first order biosorption [16].
The derived form is:

$$\mathbf{\log (q_e - q_t) = \log q_e - (K_1 / 2.303)\, t \quad ..... \quad 3.9}$$

The Plot is drawn between the time (t) versus log (q_e- q_t) (fig.3.16) gives straight line for first order kinetics.
From Fig 3.16, the plot obtained represents the following model.
$\log(q_e - q_t) = -0.0231\, t + 0.3282\, t$, $R^2 = 0.9797$

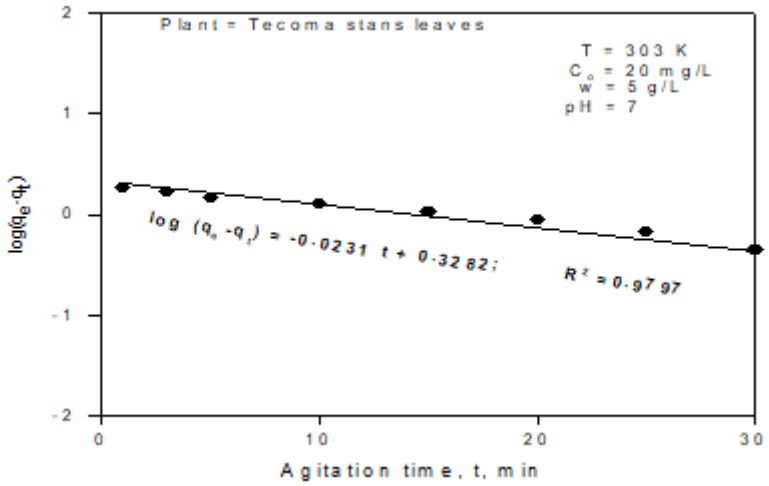


Figure 3.16: Pseudo first order kinetics for % biosorption of BG dye

- **Pseudo Second Order Kinetic Equation:** If the experimental results do not follow the above equation, pseudo second order kinetic equation is $(dq / dt) = K_2 (q_e - q)^2$ is applicable, where 'K_2' is the second order rate constant.

If results do not follow the first order kinetics, then data fitted in to Pseudo second order kinetic equation,

$$\mathbf{[dq/ (q_e-q)^2] = K_2\, dt \quad .... \ 3.10}$$

where 'K_2' is the second order rate constant Final equation for pseudo second order is

$$\mathbf{(t/q_t) = (1/K_2 q_e^2) + (1/q_e)\, t \quad ..... \ 3.11}$$

The Pseudo second order plot is shown in fig.3.17 is of time't' versus (t/q).
The obtained equation is $t/q_t = 0.3887t + 8.1280$, $R^2 = 0.9559$

Pseudo second order plot of time't' versus (t/q_t) shown in fig.3.17. From the results of kinetic data, the % biosorption of brilliant green onto silver tecomastans nano biosorbent powder data is well fitted with Pseudo first order kinetics.

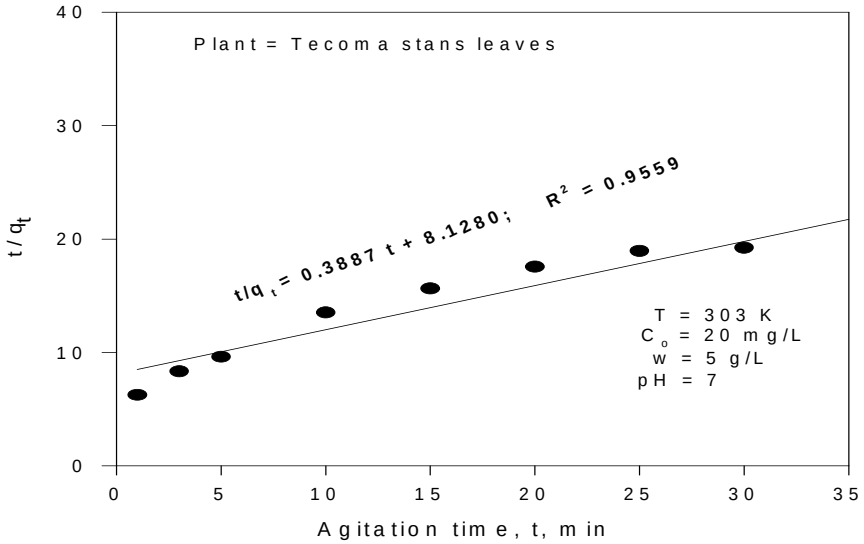


Fig. 3.17 Pseudo second order Kinetics for % Bisorption of BG dye

5. Thermodynamic Studies

The Gibbs free energy change of the sorption reaction given by the following equation:

$$\Delta G = - RT \ln K_a \text{ .....3.12}$$

Where,
The ΔG (free energy change) signify the reaction spontaneity
The Van'tHoff equation is,

$$\log (q_e / C_e) = - \Delta H / (2.303 RT) + \Delta S / (2.303 R) \text{ ..... 3.13}$$

Thermodynamic parameters for the biosorption process of brilliant green are computed from graph of a log (qe/Ce) versus 1/T.ΔH and ΔS values are calculated from the slope and intercept based on the data, it is determined that the biosorption of BG dye will result in a Gibbs free energy change ΔG of -8.549 KJ/mol. The biosorption is spontaneous and thermodynamically possible, as indicated by the negative ΔG value. The ΔH parameter has a value of 15.1243 J/mol. The endothermic character of biosorption is indicated by the positive ΔH. For BG dye biosorption, the ΔS parameter is found to be 28.26 J/mol K.The increased randomness at the solid/solution interface during biosorption is indicated by the positive ΔS value.

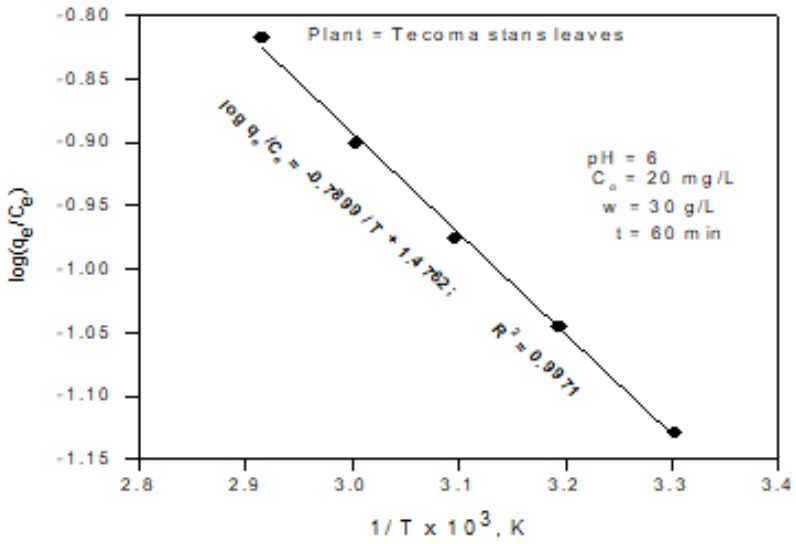


Figure 3.18: Vant Hoff's plot for thermodynamics

6. Optimization using Response Surface Methodology (RSM):

- **Optimization using CCD:** CCD (Box and Wilson, 1951) was used to optimize the levels of these variables. Based on the results of the pH (X_1,g/L), initial concentration (X_2, mg/L),preliminary dosage (X_3), and Temperature (X_4, K) were considered as the input variables and % removal of BG dye (Y) is the dependent output variable. The experiments with pH = 4-7, different BG dye concentrations of 10-30 mg/L, dosage ranging from 10-50 g/L and different temperatures of 283- 323 K were coupled to each other and varied simultaneously to cover the combination of variables in the Central Composite Design. In order to determine the ideal values and analyse the interactive impacts of these variables, a Central Composite Design (CCD) was used. Multiple regression analysis of the experimental data for the biosorption of BG dye is represented by the following equation.

$$\mathbf{Y = -2719.98 + 43.36\ X_1 - 3.12\ X_2 + 128.78\ X_3 + 17.11\ X_4 - 3.68\ X_1^2 - 0.11\ X_2^2 - 110.80\ X_3^2 - 0.03\ X_4^2 + 0.15\ X_1X_2 - 1.27X_1X_3 - 0.01\ X_1X_4 + 0.07\ X_2X_3 + 0.00\ X_2X_4 - 0.02\ X_3X_4} \quad \text{------ (3.14)}$$

A positive/negative sign of the coefficient represents an increasing/ decreasing trend for the increase in effect.

For the percentage biosorption of BG dye, the following parameters are expected to be ideal: pH of the aqueous solution: 5.9822; initial BG dye concentration: 20.15 mg/L; biosorbent dosage: 0.6010 g; temperature: 347.7894 K; and percentage removal of BG dye: 79.28000.

The Response surface plots for the interactive effect of dosage, Initial concentration, pH and Temperature were shown in figures 3.21-3.26. These plots represent different of combinations of two test variables keeping others at zero levels.

The maximum percentage removal of BG dye is indicated by the smallest surface curve (Circular or elliptical) of the contour. Optimum values compared are shown in table 3.3.

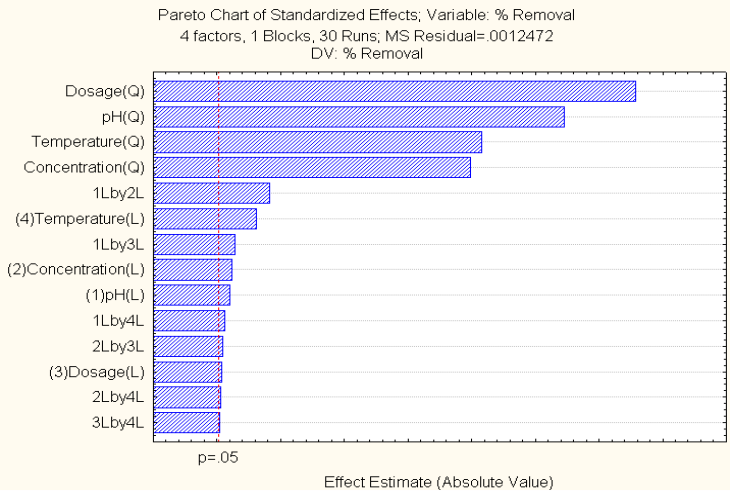


Figure 3.19: Pareto Chart

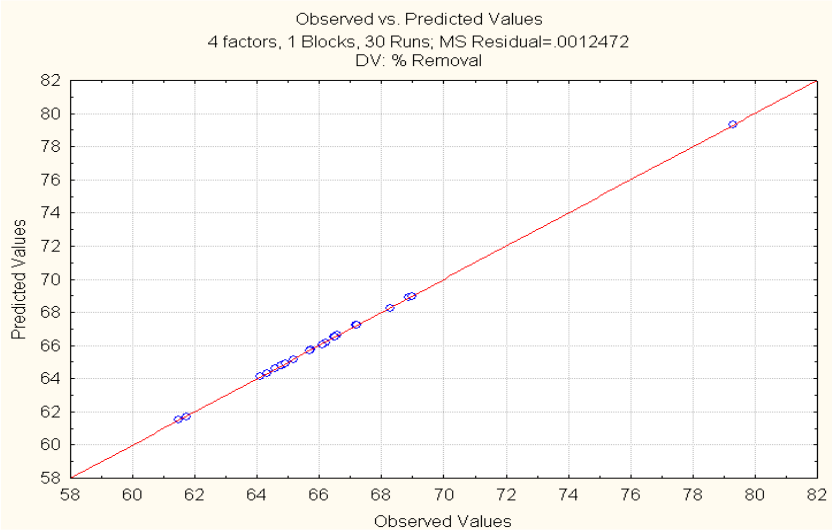


Figure 3.20: Normal probability plot for % biosorption of BG dye

The optimal set of conditions obtained with CCD are shown in table-3.3 along with experimental values.

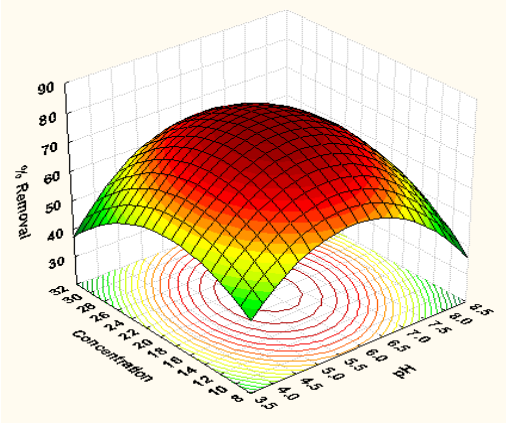


Figure 3.21: Surface contour plot for the effects the of pH and initial dye concentration

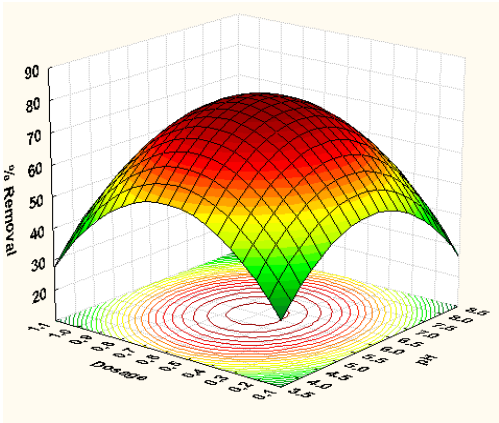


Figure 3.22: Surface contour plot for effects of dosage and pH

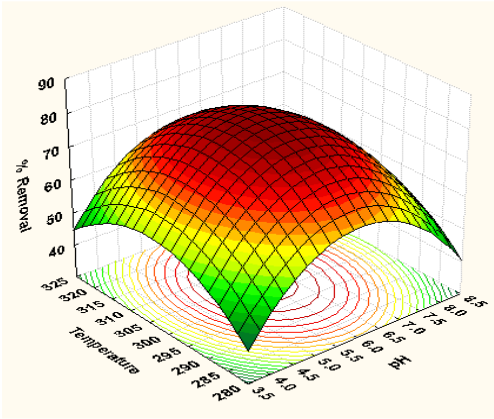


Figure 3.23: Surface contour plot for effect of Temperature and pH dosage

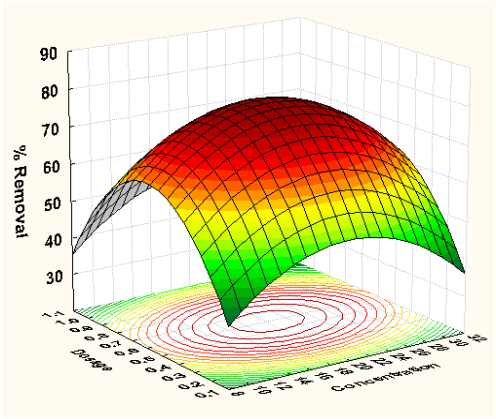


Figure 3.24: Surface contour plot for the effects of initial concentration and

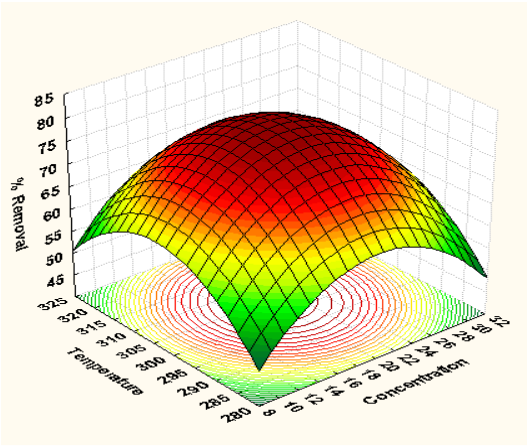


Figure 3.25: Surface contour plot for the effects the of concentration and Temperature

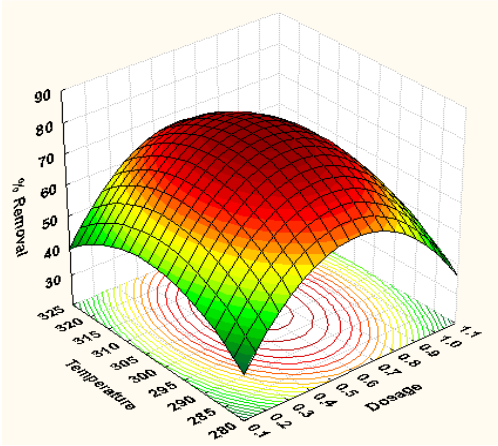


Figure 3.26: Surface contour plot for effects of Temperature and Dosage

Table 3.3: Comparison between optimum values from CCD and Experimentation

Variable	CCD	Experimental value
pH of solution	5.98	6
Initial dye concentration, mg/L	20.15	20
dosage, w, g	0.6010	0.6
Temperature, K	343.78	343
% biosorption	79.32	82

IV. CONCLUSIONS

Investigations are carried out to find out the equilibrium conditions for the decolorization of brilliant green dye from an aqueous solution using silver tecomastans nanoparticles. The analysis of the experimental data results in the following conclusions, Size of synthesized nanoparticles obtained by the analysis of FESEM was in range of 95.8 nm-190 nm.The equilibrium contact time obtained was 60 minutes. Percentage decolorization of dye or % removal of brilliant green dye from the aqueous solution changes significantly with pH of solution and the optimum obtained at a pH of 6 (64% removal). 20 ppm mg/L of dye was the concentration at which the maximum decolorization was achieved. The best nano-biosorbent dosage (30 g/L) was found to remove 69% of the brilliant green dye from an aqueous solution, or 0.6 g.A higher operating temperature resulted in a higher proportion of brilliant green biosorption; the maximum dye uptake measured was 14.51 mg/g, and the experimental data fit the Langmuir and Temkin models well. It is possible to further characterize the BG dye biosorption kinetics on Ag-TS-NP powder by using pseudo first order kinetics. The study finds that when ΔH is positive, it implies that biosorption is endothermic; when ΔS is positive, it indicates that biosorption is irreversible; and when ΔG is negative, it indicates that biosorption is spontaneous. The ideal variable values found in the experimental study and the values found using the Response surface methodology agreed upon quite closely.

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