Biosorption of Malachite Green by Raphanus Raphanistrum Leaves-Experimentation and Process Optimization

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***Abstract*— The study was focused on identification and describing the binding mechanism of the dye by Raphanus Raphanistrum in a biosorption process optimized by Response Surface Methodology based on the Central Composite Design (CCD). The parameters influencing the biosorption capacity, such as contact time, solution pH, temperature, biosorbent dosage, average biosorbent size and initial dye concentration were investigated. Langmuir, Freundlich and Temkin sorption isotherms were applied to the biosorption equilibrium data. The biosorption isotherm data was found to fit the Freundlich model. Pseudo-first order, Pseudo second order, Elovchi models were used to describe the biosorption kinetic studies. Pseudo-second order kinetics gives the rate of biosorption and mass transfer kinetics. Thermodynamic analysis revealed that the biosorption process is spontaneous and exothermic in nature. Using Central Composite Design (CCD) the process parameters like contact time (min), solution pH, initial dye concentration (mg/L) and temperature (K) were analyzed. The second-order polynomial equation, response surface plots were used to quantitatively determine the relationships between dependent and independent variables.**

Keywords*— Malachite green, Raphanus Raphanistrum Leaves (RRL), Biosorption Isotherms, Kinetics, thermodynamic studies, Central Composite Design (CCD).

INTRODUCTION

Out of various industries, the dyeing industry is an important sector of the chemical industry. Dyes are substances capable of coloring fabrics to such an extent that the color cannot be removed by rubbing or washing. Dyes are widely used for the manufacture of textiles, paper, leather, fur, hair, food, drugs, cosmetics, wax, grease, petroleum products, and plastics [1]. India's dye industry produces many types of dyes and pigments. Production of dyestuff and pigments in India is close to 80,000 tones. India is the second largest exporter of dyestuffs and intermediates among the developing countries, after China. These dyes are being used in the textile industry at nearly 80%. However, a recent study conducted under the National Biodiversity strategy and Action Plan (BSAP) has revealed that chemical colors have all but wiped out India's wonderful vegetable dyes. Color removal has become a major scientific interest, and hence significant attention has been directed towards the exploration of various biosorbent materials [2].

The Indian textile industries now predominantly use synthetic organic dyes like direct dyes; disperse dyes, vat dyes, acid dyes, reactive dyes, etc. The large variety of dyes and chemicals used in an attempt to make more attractive popular shades of fabrics for a competitive market render the effluent very complex. During the last decade, environmental issues associated with dyestuff production and their applications have grown significantly [3].

Malachite green (MG) dye has been used as a food coloring agent, food additive, medical disinfectant as well as a dye in silk, wool, jute, leather, cotton, paper and acrylic industries [4]. It is also extensively used as a topical fungicide [5] and echo parasiticide in aquaculture industries throughout the world [6]. The dye has been reported to cause serious health effects including effect on immune system and reproductive system as well as its genotoxic and carcinogenic potentials [6]. Researchers have been working on different ways of removing dyes from wastewater for many years. Dye wastewater is very difficult to treat, because of its synthetic origin and complex aromatic structure. Therefore, different procedures have been developed: adsorption onto materials such as activated carbon [3, 6] or waste products [7, 8], physical and chemical degradation [9, 10] in addition to a large number of other techniques; Fenton's oxidation, electro coagulation [11], ozonization . Biosorption is the fast, economic, feasible and eco-friendly technique which also utilized the waste generated from industrial processing. In the present work, Raphanus Raphanistrum powder was tested for removal of Malachite green (MG) dye from aqueous solutions. The equilibrium, kinetics and thermodynamic data of the biosorption process were investigated. Information has been reported on the statistical optimization of experiment conditions for the biosorption of MG dye by RR biosorbent.

MATERIALS AND METHODS

Preparation of Raphanus Raphanistrum Leaf powder preparation procedure

Raphanus Raphanistrum leaves were collected from Vignan's Engineering College, Vadlamudi.

The collected leaves were washed several times with deionized water until the wash water contains no dirt. These washed leaves were completely dried under sunlight for 30 days and were powdered using domestic mixer. The dried powder was sieved for 63-212 µm.

Preparation of stock solution

Malachite green dye solution was prepared. A known weight of 0.1 g of dye was weighed and a standard stock solution of concentration 1000 mg/L was prepared in double distilled water and further working solutions of concentrations (25, 50, 75 and 100 mg/L) were prepared in stoppered bottles and stored.

EXPERIMENTATION

Batch biosorption studies were carried out at 303K on a rotary shaker at 180 rpm with time intervals of 5-135 min. The biosorption studies were completed under effective process parameters of solution pH 2-10, dye concentrations 25-100 mgL^{-1}, weight of the biosorbent 0.02-0.2 g and particle size of the biosorbent vary from 63 (242 mesh) -212 (72 mesh) µm. The mixed biosorbent solutions were taken out, filtered and analyzed for Malachite green dye concentration in an UV Spectrophotometer at 618nm. By varying the initial concentration of the dye solution from 25-100mg/L at equilibrium biosorption time=90 min, pH=6, dosage=0.1g and temperature=303K along with thermodynamic parameters which gives the feasibility of the process, 26 experiments were designed by the Design Expert Software with the optimized parameters.

The % biosorption is given as

$$\% \text{ Biosorption} = (C_i - C_f)/C_i * 100 \qquad (1)$$

The dye uptake onto RR is obtained by:

$$q_t = \frac{V(C_i - C_f)}{1000w} \qquad (2)$$

Where q_t is the amount of dye adsorbed on the RRL biosorbent surface *(mg/g),*

C_i is the initial concentration of solute in the solution before biosorption *(mg/L),*

C_f is the final concentration of solute in the solution after biosorption *(mg/L*),

V is the volume of the dye solution *(ml)* and

w is the weight of the Biosorbent (g).

RESULTS AND DISCUSSION

Effect of contact time:

The biosorption efficiency for different initial dye concentrations from 25 mg/L - 100 mg/L, with respect to contact time is represented in Fig.1. More active sites are available for biosorption at the initial stages of contact period. At 90 min, the %biosorption was constant even after increase in contact time, which indicates availability of less number of accessible vacant sites on the biosorbent surface. At 25 mg/L of initial dye concentration, the biosorption efficiency was increased from 82.64% to 97.76% with a contact time of 90 min.

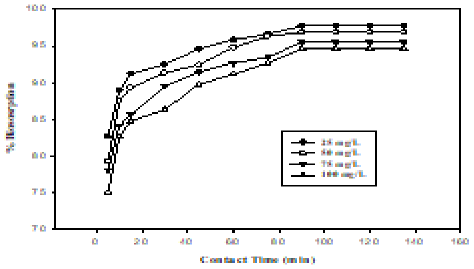

Fig.1: Effect of contact time on the biosorption efficiency of MG dye onto RR biosorbent

Effect of solution pH

Biosorption Capacity is highly influenced by the solution pH. The degree of biosorption onto biosorbent surface is due to the surface charge on the biosorbent, which in turn influenced by the solution pH. Dissociation of functional groups present on the surface and subsequently shift in reaction kinetics and equilibrium characteristics takes place with change of solution pH. The effect of solution pH on biosorption efficiency of MG dye is shown in Fig.2. The biosorption efficiency increases with an increase in pH gradually and attains equilibrium at pH 6. At pH 6, the maximum % biosorption obtained was 97.76% for an initial dye concentration of 25 mg/L.

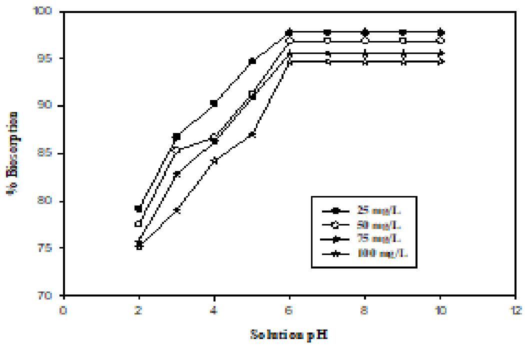

Fig.2: Effect of solution pH on the biosorption efficiency of MG dye onto RR biosorbent

Effect of Initial dye concentration:

Dye removal is highly influenced by initial dye concentration.Fig.3. shows that with an increase in initial dye concentration the percentage biosorption was decreased and dye uptake was increased. At low concentration, most of the dye molecules adsorb on active sites and hence % biosorption was high at the initial dye concentration. The percentage of biosorption was decreased and dye uptake was increased with an increase in initial dye concentrations, increased number of dye molecules could not accommodate number of active sites for a fixed dosage of biosorbent. The dye uptake was increased from 12.22 to 47.34 mg/g with an increase in initial dye concentration from 25 to 100 mg/L at 303K.

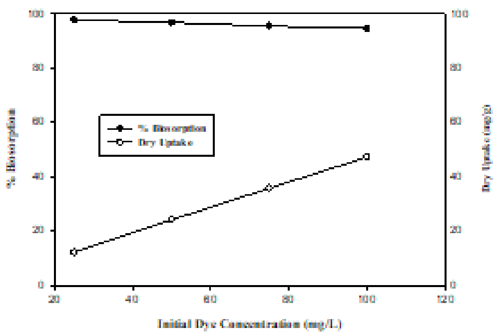

Fig.3: Effect of initial dye concentration on the biosorption efficiency of MG dye onto RR biosorbent

Effect of Biosorbent dosage

The effect of biosorbent dosage on biosorption capacity of RR biosorbent is shown in Fig.4. With an increase of biosorbent dosage from 0.02 to 0.1g, the % biosorption increased gradually and attained a maximum % biosorption at 0.1g. The percentage biosorption increases proportionally with an increase of weight of the biosorbent dosage. The increase in biosorption with the increasing dosage of biosorbent is basically due to binding of almost all dye molecules and establishment of dynamic equilibrium between dye molecules on the surface and in aqueous solution. The % biosorption was increased from 81.84 to 97.76% with an increase of biosorbent dosage from 0.02 to 0.2 g for an initial concentration of 25 mg/L.

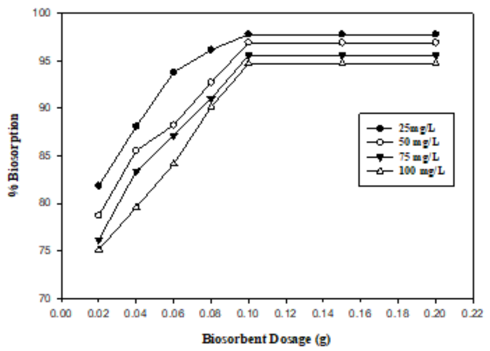

Fig.4: Effect of biosorbent dosage on the biosorption efficiency of MG dye onto RR biosorbent

Effect of average biosorbent size

The influence of average biosorbent size on biosorption with different initial dye concentrations is shown in Fig.5. The percentage biosorption decreased from 98.8% to 79.6% with an increase of particle size from 63µm to 212 µm for an initial concentration of 25mg/L. When compared with larger particles, the smaller biosorbent particles will have more specific surface area, where rapid biosorption process takes place with high mass transfer.

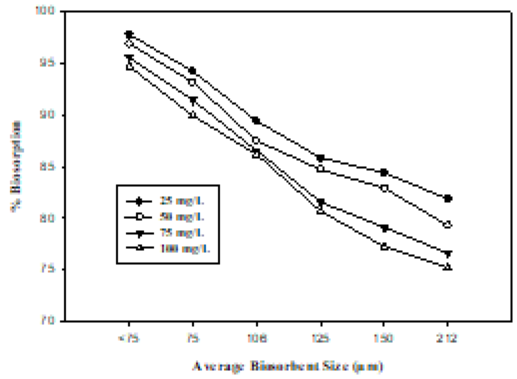

Fig.5: Effect of average biosorbent size on the biosorption efficiency of MG dye onto RR biosorbent

Effect of temperature

The effect of temperature on biosorption for different initial dye concentrations is shown in Fig.6. As the temperature increases the percentage biosorption decreases gradually, due to physico-chemical bonds present between dye molecules and surface of biosorbent may be weakened resulting in the low percentage biosorption. Moreover, at high temperatures the solubility of dyes in aqueous solution increases, thus attractive forces between dye molecules and solution were stronger than attractive forces between dye molecules and surface. At a contact time of 90 min, the maximum biosorption was observed as 97.76% at 303K for an initial concentration of 25mg/L.

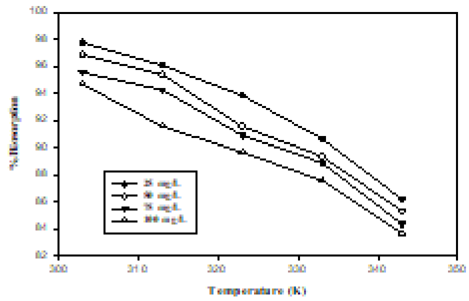

Fig.6: Effect of temperature on the biosorption efficiency of MG dye onto RR biosorbent

Biosorption Isotherms

The applicability of Langmuir isotherm model indicates the homogeneity with finite number of active sites on the surface of biosorbent. The Langmuir model also suggests the possibility of uniform coverage of biosorbent surface with dye molecules. The equation applied to analyze the Langmuir constants are:

$$\frac{1}{q_e} = \frac{1}{q_{max} K_L C_e} + \frac{1}{q_{max}} \qquad (3)$$

where C_e is the concentration of the dye in the solution at equilibrium (mg/L), q_e is the quantity of dye adsorbed at equilibrium (mg/g), q_{max} is the maximum biosorption capacity of the dye (mg/g) and K_L is Langmuir constant (L/mg). A plot of C_e vs. C_e/q_e was plotted. The values of constant and maximum biosorption are evaluated from equation (3). The high value of biosorption capacity (q_{max}) indicates the availability of high surface area.

Equation (4) gives the separation factor (R_L) values represented in Table-1. C_i is the initial concentration (mg/L). The values of R_L which are between 0 and 1 indicate that biosorption is favourable with an increase in the initial dye concentration.

$$R_L=1/(1+K_LC_i) \quad (4)$$

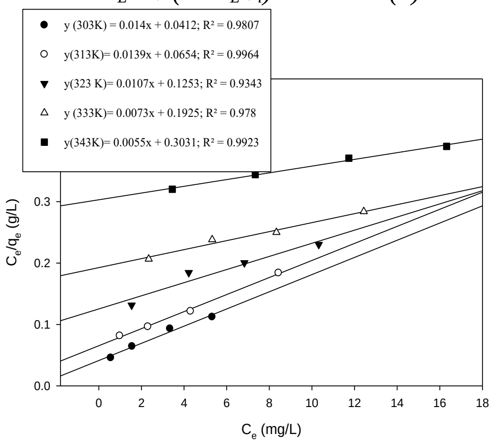

Fig.7: Langmuir isotherm at different temperatures for biosorption of MG dye onto RR biosorbent

For a heterogeneous surface with a non-uniform multilayer coverage of biosorbent surface with dye molecules, the Freundlich isotherm is derived. The Freundlich isotherm model is given by

$$\ln q_e = \ln K_f + \frac{1}{n_f} \ln C_e \quad (5)$$

q_e and C_e are the quantity of dye adsorbed at equilibrium (mg/g) and concentration of the dye in the solution at equilibrium (mg/L) respectively. A plot of lnC_e vs. lnq_e is plotted in Fig.8. Freundlich constant values of K_f and $1/n_f$ were calculated by using equation (5). With an increase of temperature, the values of K_f decreased which indicates the exothermic nature of biosorption. The n_f values are greater than one indicates the process was favourable and due to chemical interactions between biosorbate and biosorbent. The constant values are indicated in Table-1. The R^2 value represents Freundlich isotherm best suits for the data.

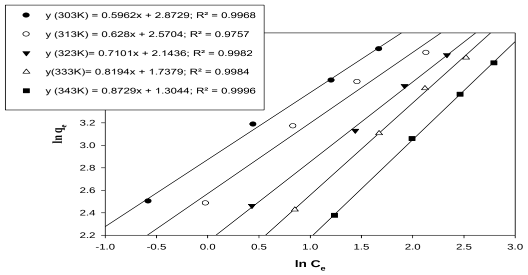

Fig.8: Freundlich isotherms at different temperatures for biosorption of MG dye onto RR biosorbent

Temkin isotherm equation is given as

$$q_e = B_T \ln (A_T) + B_T \ln (C_e) \quad (6)$$

The biosorption potential and the biosorption energy variations in biosorption process are studied under Temkin isotherm. q_e and C_e are the quantity of dye adsorbed (mg/g) and concentration of the dye in the solution at equilibrium (mg/L) respectively. Equation (6) gives the values of temkin constants B_T and A_T. A graph of ln C_e vs. q_e was plotted and the values are tabulated in Table-1. Furthermore, Freundlich isotherm was best fitted with data than Temkin isotherm.

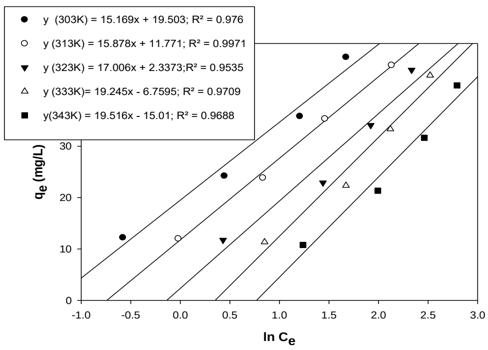

Fig.9: Temkin isotherms at different temperatures for biosorption of MG dye onto RR biosorbent

Isotherm Model	Parameters	Temperature (K)				
		303	313	323	333	343
Langmuir	q_{max} (mg/g)	71.42	71.9	93.4	136.9	181.8
	K_L (L/g)	0.33	0.21	0.08	0.03	0.018
	R^2	0.98	0.99	0.93	0.97	0.9923
	$R_L=1/(1+K_LC_o)$	0.10	0.15	0.32	0.519	0.689
Freundlich	K_f (mg/g)/(L/g)^n	17.68	13.07	8.53	5.68	3.68
	n_f (L/g)	1.67	1.59	1.40	1.22	1.14
	R^2	0.9	0.97	0.99	0.998	0.99
Temkin	A_T (L/g)	3.61	2.09	1.14	0.703	0.463
	B_T(L/mg)	166.07	163.8	157.9	143.8	146.12
	R^2	0.97	0.99	0.95	0.970	0.968

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Kinetic Modeling

Studies of biosorption kinetics provide the necessary information to evaluate the biosorption rate and to identify other factors that influence the biosorption process which in turn are used to optimize the efficiency of the biosorption process. The kinetic studies were conducted using pseudo-first-order, pseudo-second-order and Elovich kinetic models to best fit the data. The pseudo-first-order model generally expressed as

$$\ln(q_e - q_t) = -k_f t + \ln q_e \qquad (7)$$

Where k_f (min^{-1}) is the first-order biosorption process rate constant and q_t (mg/g) is the weight of MG dye adsorbed on biosorbent surface at time t. Fig.10. shows a graph of t verses $ln\ (q_e - q_t)$ at different concentrations (25 – 100 mg/L) using the dye at optimum conditions of pH 6 and temperature 303K. The values of Pseudo-first-order kinetic model are shown in Table-2. The values of R^2 are low which suggest the non-applicability of pseudo-first order kinetic model.

Pseudo second-order kinetic model is expressed as

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_s q_e^2} \qquad (8)$$

where k_s (g mg^{-1} min^{-1}) is the second-order biosorption process rate constant. A plot of t vs. t/q_t was plotted as shown in Fig.11 represents the second-order kinetic model. The constants are evaluated from equation (8). The increase of R^2 value suggested the applicability of pseudo second order kinetics model.

The applicability of second order model represents the presence of both physisorption and chemisorption process. The overall biosorption process can be limited by chemisorption. The pseudo second order was fitted with the data well.

Elovich model gives the information about the physisorption or chemisorption mechanism. Elovich model is used to describe the second order kinetics of chemisorptions and it is based on the assumption that the adsorption surface is energetically heterogeneous. The Elovich model is expressed as

$$q = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \qquad (9)$$

Where α is initial rate and β representing activation energy (g/mg). A graph of ln t vs. q is drawn where the constants are evaluated from equation (9). The constants and correlation coefficients are given in Table-2, indicate that for higher concentrations the Elovich model was not suitable to fit the data.

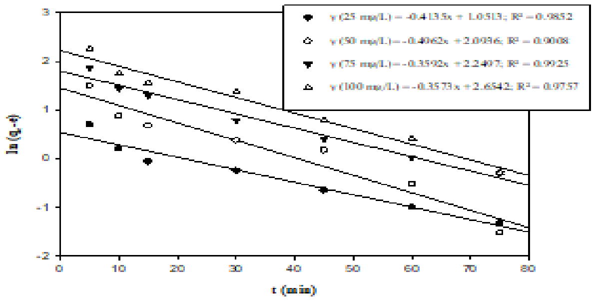

Fig.10: Pseudo First order Kinetic model for biosorption of MG dye onto RR biosorbent

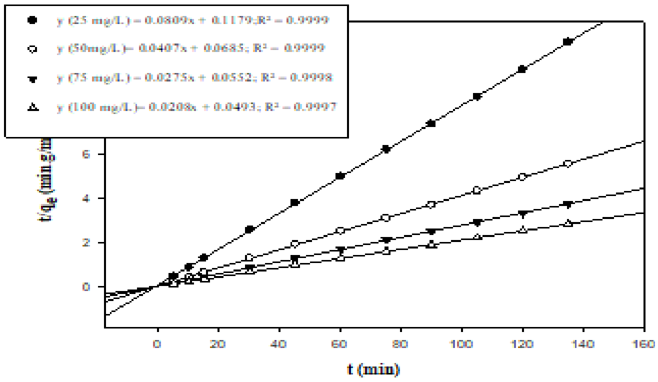

Fig: 11. Pseudo Second order Kinetic model for biosorption of MG dye onto RR biosorbent

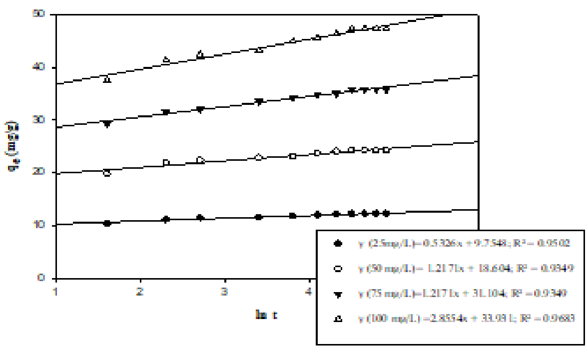

Fig: 12. Elovich kinetic model for the biosorption of MG dye onto RR biosorbent

Table.3: Kinetic rate constants for MG dye biosorption onto RR

C_i mg/L	Pseudo-first-order			Pseudo-Second-order			Elovich Model		
	k_f	q_e	R^2	k_s	q_e	R^2	β	α	R^2
25	1.1	2.2	0.9	0.12	11.7	0.9	2.5	2.525×10^{10}	0.8
50	1.0	4.8	0.9	0.05	23.0	0.9	1.1	1.089×10^{9}	0.8
75	0.9	9.5	0.9	0.02	34.3	0.9	0.5	2.046×10^{6}	0.9
100	1.1	14.5	0.9	0.01	44.4	0.9	0.4	2.863×10^{6}	0.8

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Thermodynamic studies

Thermodynamic parameters give the feasibility of biosorption process. Thermodynamic studies provide information about the effect of temperature on biosorption process, which is essential for the estimation of energy requirement. The thermodynamic parameters are represented in Van't Hoff equation as

$$\ln K_D = \Delta S^o/R - \Delta H^o/RT \quad (10)$$

Where *ΔH^o^ is standard enthalpy*, *ΔS^o^ is standard entropy*, and ΔG^o is standard Gibbs free energy, R is the universal gas constant (8.314 J/mol K), T is the absolute temperature, K. ΔG^o represents the feasibility and spontaneous nature of the biosorption process. The enthalpy (ΔH^o) and entropy (ΔS^0) are calculated from the equation (10) ΔG^o and K_D *are related* by the following equation,

$$\Delta G^o = -RT \ln K_D \quad (11)$$

A plot was plotted between 1/T vs. ln K_D, shown in Fig.13. for different initial dye concentrations. The values of ΔH^o, ΔS^o and ΔG^o are represented in Table-3. The negative values of ΔH^o represents the reaction is exothermic. The negative value of ΔS^o indicates an increase in the randomness at the solid-solute interface during biosorption. With an increase of temperature, the feasibility of biosorption decreased with simultaneous decrease in negative values of ΔG^o.

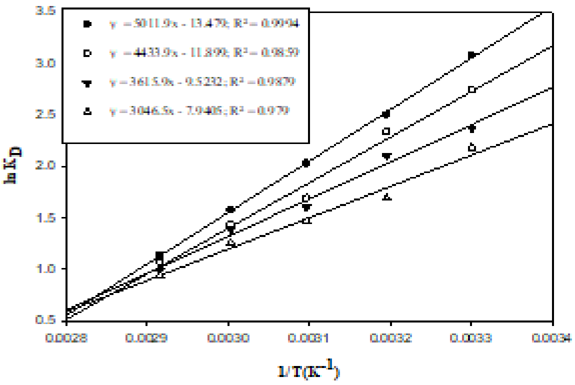

Fig.13: Thermodynamic studies at different concentrations for biosorption of MG dye onto RR biosorbent

Table.3. Thermodynamic energy parameters for the biosorption of MG dye using RR biosorbent

C_i (mg/L)	$-\Delta H^o$ (kJ/mol)	$-\Delta S^o$ (kJ/mol. K)	$-\Delta G^o$(kJ/mol)				
			303K	**313K**	**323K**	**333K**	**343K**
25	41.66	0.11	8.33	7.23	6.13	5.03	3.93
50	36.85	0.09	9.58	8.68	7.78	6.88	5.98
75	30.06	0.07	8.85	8.15	7.45	6.75	6.05
100	25.32	0.06	7.14	6.54	5.94	5.34	4.74

Optimization using RESPONSE SURFACE METHODOLOGY (RSM)

Response surface methodology (RSM) is a collection of mathematical and statistical technique that is useful to model and analyze problems in which a response of interest is influenced by several variables. The independent and dependent variables in biosorption process are optimized using the RSM modeling technique. The most important effects, interactions and analysis of variance (ANOVA) are performed using Design Expert software. The four parameters opted for the process optimization: contact time (min), solution pH, initial dye concentration (mg/L), temperature (K).

By using the least square regression methodology, a second order multiple regression analysis equation along with process parameters are obtained.

$$Y = \alpha_o + \sum_{i=1}^{k} \alpha_i x_i + \sum_{i=1}^{k} \alpha_{ii} x^2{}_i + \sum\sum_{i<j}^{k} \alpha_{ij} x_i x_j + \in$$

Where Y is the % removal, α_o is the constant, α_i is the incline or straight impact of the data element x_i, α_{ii} is the quadratic effect of input factor x_i, α_{ij} is the linear by linear interaction effect between the input factor x_i and ϵ is the residual term

A second-order polynomial equation was developed from Table-6 as regression equation:

$$\% \text{ Removal } (Y) = -5266.07 + 11.12X_1 + 13.64X_2 - 4.17X_3 + 35.52X_4 - 0.05X_1^2 - 0.31X_2^2 - 0.07X_3^2 - 0.05X_4^2 + 0.13X_1X_2 + 0.02X_1X_3 - 0.01X_1X_4 - 0.01X_2X_3 - 0.07X_2X_4 + 0.02X_3X_4$$

Where X_1, X_2, X_3 *and* X_4 are the code values for the independent variables (contact time, solution pH, initial dye concentration, temperature), X_1X_2, X_1X_3, X_1X_4, X_2X_3, X_2X_4, X_3X_4, X_1^2, X_2^2, X_3^2 and X_4^2 are the significant model terms for the biosorption of MG dye. A plot of experimental values versus predicted values is plotted in Fig.14. The interaction between the variables is represented by the response surface plots. (Fig.15 (i-vi)) The surface plot (Fig. 15 (i) to 15(vi)) had a clear peak, where the optimum conditions falls inside the design boundary.

Prediction of optimal values

By using RSM, the maximum biosorption efficiency obtained was 98% under the optimal conditions of t=88.8 min, *pH*= 5.9, C_o =23.7mg/L, and *T*=301.2K. The biosorption efficiency was 97.76% under experimental process conditions.

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Table 4. Experimental variables and their levels.

Variable	Process parameter	Range of Process parameters				
		-2	**-1**	**0**	**1**	**2**
X_1	Contact Time (min)	80	85	90	95	100
X_2	Solution pH	2	4	6	8	10
X_3	Initial dye concentration (mg/L)	15	20	25	30	35
X_4	Temperature (K)	293	298	303	308	313

Process parameters	**Initial observed**	**Critical values**	**Final observed limits**
Contact time (min)	80	88.81	100
Solution pH	2	5.96	10
Initial effluent concentration (mg/L)	15	23.77	35
Temperature (K)	293	301.26	313

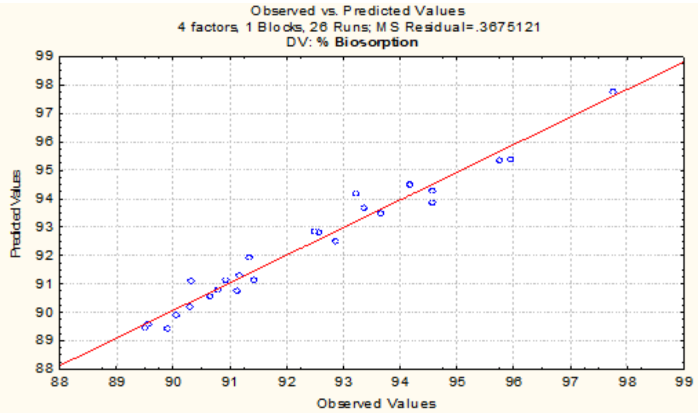
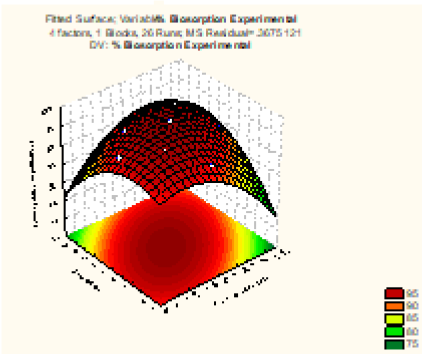
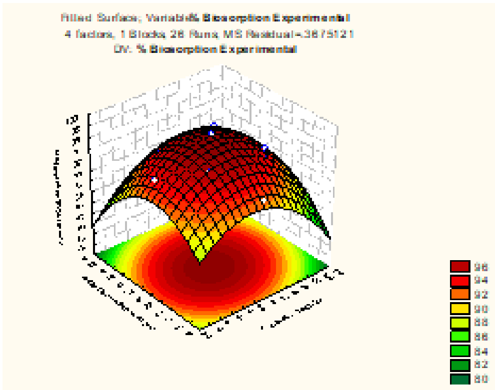
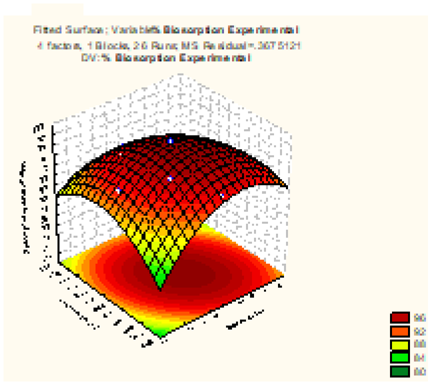


Fig 14. values for the biosorption of MG dye.







Surface Plots

CONCLUSIONS

1. The present study confirms that Raphanus Raphanistrum as an effective biosorbent for the removal of Malachite green from an aqueous solution.
2. The batch experiments show that biosorption of dye onto Raphanus Raphanistrum is highly dependent on contact time, solution pH, initial dye concentration, biosorbent dosage, average biosorbent size and temperature.

3. The percentage biosorption increases with contact time, pH and biosorbent dosage and decreases with initial dye concentration, average biosorbent size and temperature.
4. The equilibrium data were analyzed by non-linear Freundlich isotherm model with an increase in R^2 values.
5. The biosorption kinetic uptake for Malachite green by Raphanus Raphanistrum at various initial dye concentrations was analyzed by non-linear curve fitting analysis method to fit the pseudo-second order equations.
6. The negative values of enthalpy indicate that the process is exothermic, and the negative values of entropy indicates that the process is random and the negative value of Gibb's free energy represents that the process is feasible and spontaneous in nature.
7. The experimental optimum values of biosorption are t=90 min, pH=6, C_i=25mg/L and a T= 303 K having a percentage biosorption efficiency of 97.76%.
8. RSM results showed the optimum process parameter values as t=88.8 min, pH=5.9, C_i= 23.7 mg/L and T=301.2 K having a percentage biosorption efficiency of 98%.

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