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Development of Sustainable Dye Adsorption System using Nutraceutical Industrial Black Cumin Spent – Studies with Acid Violet 49

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ABSTRACT: First-ever study on the use of inexpensive nutraceutical industrial black cumin spent (NIBCS) as a biosorbent for the removal of Acid violet 49 (AV49) from aqueous media has been tried. The effects of initial dye concentration, adsorbent dosage, contact time between adsorbent and adsorbate, speed of agitation and pH were studied. The experimental equilibrium data collected were analyzed by two-parameter isotherm models of Langmuir, Freundlich, Jovanovic, Dubinin-Radushkevich, Harkin-Jura and Temkin. The pseudo-first order and pseudo-second order models were applied for adsorption kinetic studies. The kinetic data fitted well to pseudo-second order model. Thermodynamic analysis showed that the adsorption is favourable (negative values for ΔG°) and endothermic ($\Delta H^{\circ}=12-20$ kJ mol⁻¹) for the initial dye concentrations of 50, 100 and 150 ppm. The low ΔH° value indicates the physical process of adsorption involving weak chemical interactions like hydrogen bonds and van der Waals interactions. SEM images of NIBCS show highly fibrous matrix with hierarchical porous structure. FTIR analysis of the spent confirmed the presence of cellulosic and ligno-cellulosic material imparting hydrophilic and hydrophobic properties. The two-level approach and the analysis of variance (ANOVA) yielded maximum rate of adsorption 35.84 mg/l. The ANOVA also indicated the influence of each parameter and their combinations on the final adsorption capacity of the system. The investigation indicates that BCS is a cost-effective and efficient biosorbent for the remediation of toxic AV49 dye.

KEYWORDS: Nutraceutical industrial black cumin spent, Acid violet 49, Adsorption studies, Kinetics, Isotherms

I. INTRODUCTION

Water is the most vital among the natural resources, and is critical for the survival of all living organisms. The quality of water gets affected by human activities and is declining due to the rise of urbanization, population growth, and industrial production amongst other factors. The resulting water pollution is a serious threat to the well-being of ecosystem. Amongst many industries, textile industry is one among the top ten most polluting industries [1]. Textile industries use varied varieties of chemicals. Dyes are one of the most prominent classes of chemicals which are used extensively.

Indian dyes and dye Intermediates industry has achieved substantial growth, particularly in the last 15 years. In this span of last 15 years, the production tonnage has increased 3 times, whereas the export value in Rupees has increased 79 times. At present, export of dyes and dye intermediates contributing to 50% of the total export of chemicals from India. During the production of dyes and dye intermediates, hazardous wastes are generated which are to be managed in an environmentally safe manner. Hazardous wastes, in the present context, by virtue of their physical, chemical, reactive, toxic, flammable, explosive or corrosive characteristics causes danger or likely to cause danger to health or environment, either alone or in contact with other wastes or substances including dyes.

Triphenylmethane dyes are one of the oldest classes of synthetic dyes. They exhibit high tinctorial strength, relatively less expensive, and can be applied to a large number of substrates. Interest in this class of dyes was revived with the introduction of polyacrylonitrile fiber. Triphenylmethane dyes are readily adsorbed on this fiber and show high lightfastness and wash fastness properties, compared with these dyes on natural fibers. AV49 (C.I. 42640) belongs to

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triamino derivatives of triphenylmethane dyes of the fuchsine, rosaniline, or magenta series (CI 42500–42800); extensively used in wool, silk and polyamide fiber dyeing.

Textile dyes discharged into the water stream from dyeing process is estimated to be 12–14%. The presence of these dyes in water inhibits the penetration of light and photosynthetic activity of water plants [2-3]. Many types of diseases such as allergy, skin irritation, dermatitis and cancer are caused due to synthetic dyes [4]. Therefore, treatment of hazardous industrial wastewaters containing dyes is essential for sustainable life and development [5-8]. Wastewater containing dyes is normally treated by flocculation, membrane filtration, electrokinetic coagulation, ion exchange, irradiation, precipitation and ozonation. However, these technologies are generally ineffective in color removal, expensive and less adaptable to all types of dye wastewaters [9-10]. Researchers have tried different biosorbents but so far they have ended up with any excellent and efficient biosorbent.

Nutraceutical industrial spent (NIS) can be considered as one of the best alternative to many of the agricultural wastes proposed in the literature as it has such characteristics as: available in abundance at very low price; minimal alternate use(s); ready-to-use form without requiring any pre-processing; and high pore structure which permit maximum adsorption. Our research school has extensively studied about the use of NIS as filler material for the fabrication of thermoplastic and thermoset composites [11-18] and as biosorbent for the remediation of toxic dyes [19-21]. Besides, we also developed NIS amenable to simple and cost-effective technology to make reusable the sludge/toxic biomass produced after the remediation process as filler material for fabrication of composites [19]. Nutraceutical Industrial Black Cumin Spent is likely to be suitable candidate having the required properties besides it is a ready-to-use biosorbent, as it has already undergone mechanical, thermal and chemical processes; thus not requiring any further chemical pre-treatment which reduces E-factor [22].

Nutraceutical industrial sector is one of the fast growing sectors in the US and Asia-Pacific regions and its market is estimated to rise to US\$ 278.96 billion by 2021, recording a CAGR of 7.3% for the period 2015-2021 [23]. Nutraceuticals are the phytochemicals and/or food components derived from herbal or botanical raw materials. Their use with desirable therapeutic properties with reduced side effects, as compared with other therapeutic agents is well known and these are going to change the nature of food industry by the year 2025.

Nutraceuticals act like pharmacological model and prevent types of acute and chronic maladies. The active component(s) derived from the botanicals varies from 5 to 20%. The large amounts of waste/spent generated by nutraceutical industries presents great problem of disposal. Although exact figures are not available, processing the vast volume generated is estimated as millions of tons per year.

Black cumin (*Nigella sativa*-family Ranunculaceae) is a nutraceutical with wide spectrum of pharmacological potential. It is native to Southern Europe, North Africa and Southwest Asia and it is cultivated in Middle Eastern Mediterranean region, South Europe, India, Pakistan, Syria, Turkey, and Saudi Arabia [24]. In India Black Cumin is an important umbelifer growing wild in dry temperature regions of Jammu-Kashmir and Himachal Pradesh. The seeds are rich in essential oil, and are used for culinary purposes and for flavoring foods and beverages. Most of the pharmacological properties of Black Cumin are mainly attributed to quinine constituents [25].

The seeds of Black Cumin contain protein (26.7%), fat (28.5%), carbohydrates (24.9%), crude fibre (8.4%) and total ash (4.8 %). The seeds have good amount of various vitamins and minerals like Cu, P, Zn and Fe. The seeds contain carotene which is converted by the liver to vitamin A. Roots and shoots have vanillic acid [26] and the seeds contain alpha- herein, a water soluble pentacyclic triterpene and saponin, a potential anticancer agent [25-27].

Different methods are applied to extract essential oil from black cumin seeds, which include use of solvent at high pressure, or using Super-Critical Fluids. The portion remaining after extraction of oil is discarded as spent. The major disadvantages of NIS includes that it cannot be used as feed or fertilizer as it has undergone mechanical, thermal and chemical processes. It cannot be used as a fuel also as the porous structure traps moisture providing either low calorific value or incomplete combustion and toxic gases generation like carbon monoxide and fused pyrenes. Presently, it is used in boilers which leave carbon foot print. This is neither economically feasible nor ecologically acceptable as it creates an unprecedented problem of pollution.

Attempt has been made in this paper to illustrate the first-ever-use of NIBCS as a low-cost biosorbent for the removal of AV49 extensively used in wool, silk, polyamide fiber dyeing from water and optimization of parameters have been made for getting maximum output such as dye concentration, absorbent dose, pH and contact time.

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II. MATERIALS AND METHODS

Materials

The dye used for this experiment is Acid Violet 49 (AV49) or Acid Pale Purple 5B [C.I. = 42640; CAS registry number = 1694-09-3; chemical formula is $C_{35}H_{40}N_3NaO_6S_2$; molecular weight is 733.87; absorbance maximum (λ_{max}) = 549 nm. The molecular structure of the dye is shown in Fig. 1.

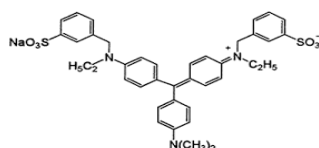


Fig.1. Structure of Acid Violet 49

Adsorbent preparation and characterization

1. Adsorbent preparation

NIBCS initially was obtained from a local factory (Fig. 2) in order to be as close to real world application as possible. The NIBCS was initially dried in sunlight, crushed and finally ground using a ball mill and sieved as per ASTM standard particle size of $\geq 125 \mu m \leq 177 \mu m$ (ASTM 80 mesh particles).

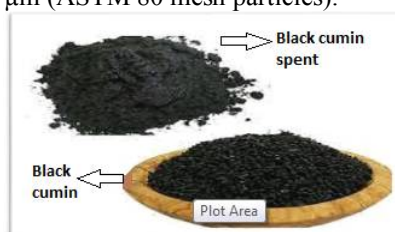


Fig. 2. Nutraceutical Industrial Black Cumin Seeds and Spent

2. Surface characterization

Electronic Microscope (LEO 435 VP model, Japan) was used to scan and visualize the surface morphology of NIBCS. FTIR was used to identify the functional groups present in the adsorbent. A FTIR spectrometer (Inter-spec 2020, Spectro Lab, UK) was used to measure the Infrared spectra of the control sample (NIBCS before adsorption of AV49) and the AV49-loaded samples.

3. Batch adsorption experiments

Batch experiments conducted included different parameters. The common preliminary preparation involved the setting up of 250-ml flasks with 50 ml working aqueous solution of AV49 (100 mg/L). After the initial preparation was complete, 50 mg of NIBCS were introduced into each flask. A temperature controlled shaker was used to agitate the contents of the flasks at 175 rpm for 3 h. Evaluations were conducted with varying dosage of NIBCS (0.025, 0.050, 0.075, 0.100, 0.150, 0.200, 0.300); AV49 concentration (25, 50, 75, 100, 125, 150, 175 and 200 mg L⁻¹), orbital shaker for rotation speed (75, 100, 125, 150, 175 and 200 rpm), contact time (15, 30, 45, 60, 90, 120, 150 and 180 min), pH (2, 4, 6, 7, 8, 10 and 12) and temperature (303 K, 313 K and 323 K) with dye concentrations of 50, 100, 150 ppm. Samples were centrifuged for 5 min to remove the leftover particulate matter. UV-Vis Spectrophotometer (Perkin Elmer-Lambda 25, USA) measured the absorbance of the filtrate at 549 nm. Controls were maintained by using the adsorbent in distilled water and an adsorbent-free AV49.

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4. Adsorption isotherms

The Langmuir, Freundlich, Tempkin, Harkins–Jura, Jovanovic, and Dubinin-Radushkevich were used as adsorption isotherm models for studying surface for single solute systems for the equilibrium adsorption at ambient temperature. Analysis was done on adsorption isotherms to describe the interaction between the adsorbate and adsorbent using the data obtained from the batch experiments for the effect of initial AV49 concentration studies. The results of parameters studied in different models provided information about interaction mechanisms, surface properties and affinities of the adsorbent.

5. Adsorption kinetics

Erlenmeyer flasks were used to conduct the adsorption kinetics experiments. The flasks were populated with 50 mg of BCS and 50 ml of AV49 solution of 50 ppm, 100 ppm and 150 ppm concentrations and temperatures 303K, 313K and 323K and the readings were recorded, up to 120 min, when the maximum adsorption capacity was almost reached. The experimental data was fit-in to the pseudo-first-order and pseudo-second-order kinetic models to investigate the controlling mechanism of the adsorption process.

6. Thermodynamic parameters

To evaluate the feasibility and enthalpy of the adsorption process the rate law and kinetic data were used to estimate the thermodynamic parameters, such as standard free energy (ΔG°), entropy change (ΔS°) and enthalpy change (ΔH°).

7. Statistical optimization by Response Surface Methodology using Central Composite design

The effects on the final adsorption capacity was described from adsorption time (A), process temperature (B), Initial dye concentration (C), orbital shaker, agitation speed (D), adsorbent dosage (E) and pH (F). A standard experimental design was set up with 6 factors at 2 levels Table 1. ANOVA was conducted and a general quadratic regression equation was obtained. Using this equation optimization was done based on the central composite design. Surface and contour plots indicated the effect of individual as well as interaction between parameters on the adsorption capacity.

Table 1. Experimental design of high and low levels of different factors studied

Factor	Name	Units	Minimum	Maximum
A	Time	Minute	15	180
B	Temperature	°C	27	50
C	Concentration	mg/L	25	200
D	Orbital shaker	rpm	75	200
E	Absorbent dosage	g/L	0.025	0.300
F	pH		2	12

III. RESULTS AND DISCUSSION

Characterization of the adsorbent

1. Surface characterization

The SEM image of NIBCS displayed slightly porous structure (Fig. 3a). Upon adsorption some pores were completely filled with the adsorbate (AV49) forming a thin film over the particle (Fig. 3b). IR spectra of NIBCS provided the functional groups present (Fig. 4). Absorption at 3322 cm^{-1} is due to stretching of hydroxyl groups of cellulose,

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hemicellulose and lignin present in NIBCS. The bands at 2924 cm^{-1} is due to C-H stretching of saturated carbon. The bands at 1633 cm^{-1} is due to C=C stretching. The bands at 1029 cm^{-1} are assigned to C-N bending, which is due to aliphatic amines often overlapped. Bands at 667 cm^{-1} , 652 cm^{-1} , 639 cm^{-1} and 608 cm^{-1} are C-X vibration are due to chloroalkanes stretching respectively. The finger print region of the biological material NIBCS indicates complex bands and accurate assignment of the peaks without the help of standard sample is difficult. However, the presence of cellulose and lignin indicate for hydrophilic and hydrophobic properties of spent.

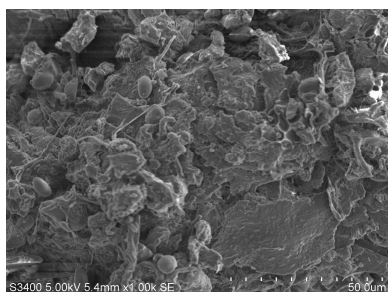
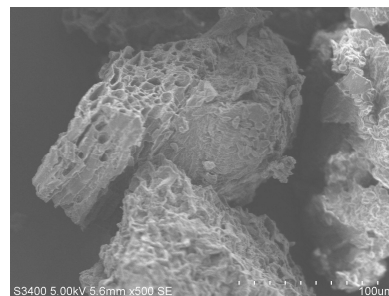


Fig. 3. (a) SEM image of NIBCS



(b) SEM image of AV49-NIBCS

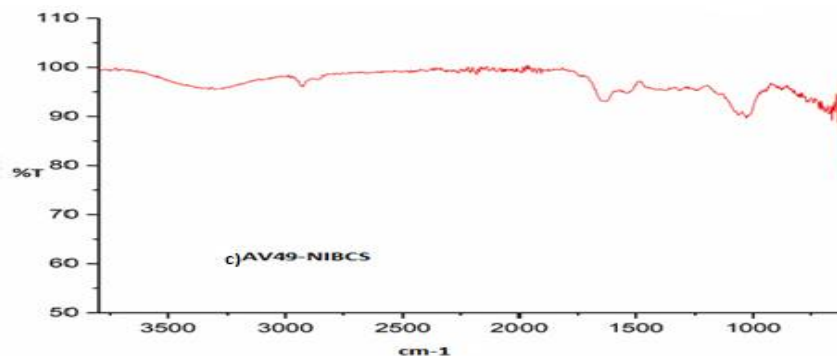
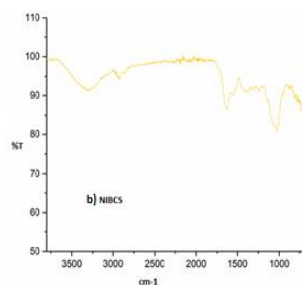
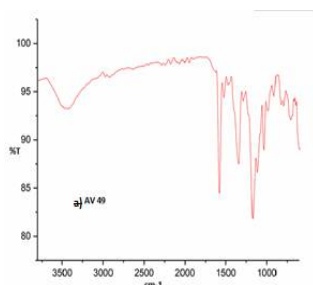


Fig. 4. FTIR spectra of a) AV49, b) NIBCS and c) AV 49 adsorbed on NIBCS

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2. Batch adsorption studies

a) Effect of initial dye concentration and adsorbent dosages:

The maximum adsorption capacity of 50 mg/g was reached for initial AV49 concentration of 100 mg/L (Fig. 5.a) with 27. With the increase in BG concentration to 100 mg/L the percentage adsorption decreased (Fig. 5.b). There was an increase followed by decrease in adsorbent dose at 50 mg/g (Fig. 5.c).

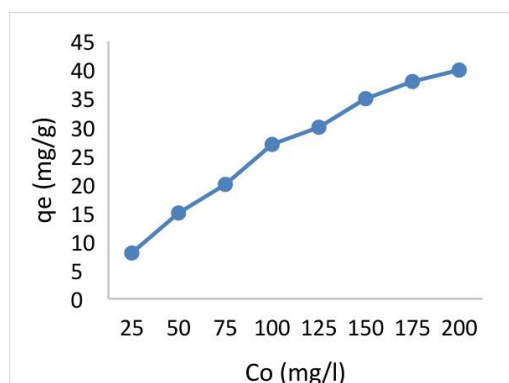


Fig. 5.a Effect of Initial dye concentration

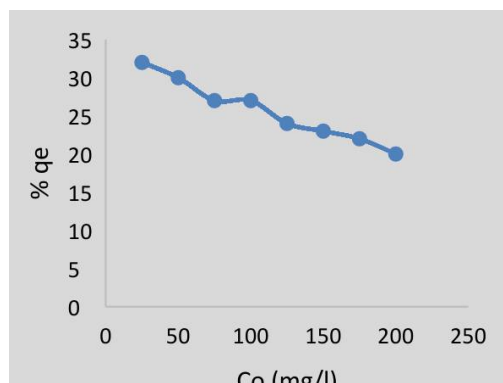


Fig. 5.b Effect of Initial dye concentration with % qe

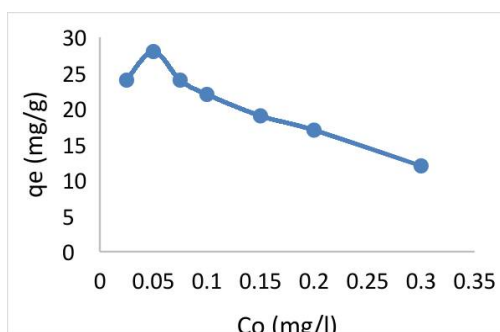


Fig. 5.c Effect of adsorbent dosage

b) Effect of contact time and speed of agitation

The contact time studied in the range of 15–180 min showed ($q_e = 25$ mg/g) in 120 minutes. Hence all parameters were studied at 120 min. The adsorption capacity versus the contact time at optimum AV49 concentration (Fig. 6.a) showed that as the AV49 concentration increased, the value of q_e increased, this was due to mass transfer resistance and magnify driving force and the interaction between AV49 and NIBCS. For speed of agitation, the adsorption experiments were conducted by agitating 50mg/L of AV49 dye solution with 50mg/g of NIBCS in an orbital shaker with the agitating speed from 75 – 200 rpm. Adsorption increased as the agitation speed was enhanced from 75 to 175 rpm then decreased at 200 rpm (Fig. 6.b).

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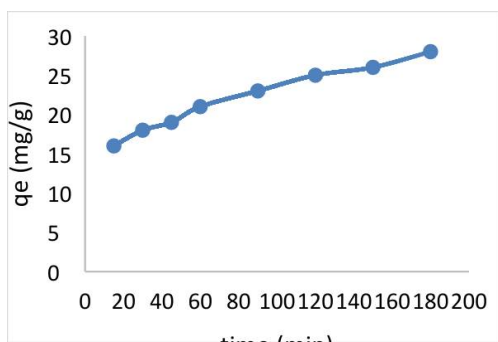


Fig.6.a Effect of contact time

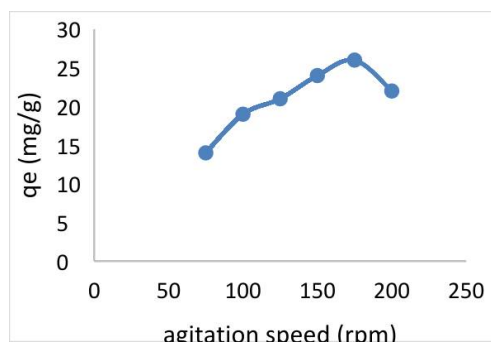


Fig.6.b Effect of speed of agitation

c) Effect of pH

Adsorption increased gradually as the pH increased from 2 to 6, and from pH 7 to 12 it decreased moderately. Maximum AV49 dye removal by NIBCS was achieved at pH 6.0 ($q_e = 25 \text{ mg/g}$) with initial concentration of 100 mg/L . Fig. 7 it is clear that as the solution pH increases, the adsorption capacity also increases. Increasing the pH increases the negatively charged sites, which helps for the attraction between dye and biosorbent surface. In the pH range of 6 to 8 net positive charge decreases with increasing pH resulting in decrease in repulsion between the adsorbent surface and the dye, thus decreasing the biosorption capacity.

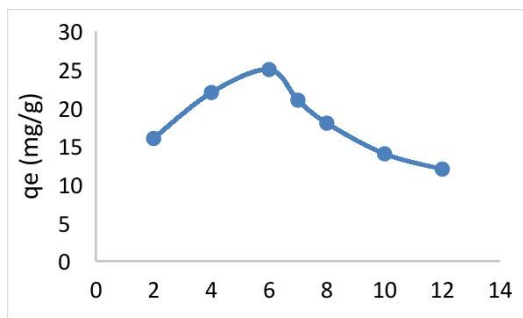


Fig. 7. Effect of pH on adsorption

3) Adsorption isotherm

The interaction between the adsorbent and adsorbate, can be understood by fitting the adsorption data to different adsorption isotherms which are based on different mechanisms. The values for maximum adsorption (q_m), correlation coefficient (R^2) and other parameters for all isotherms are shown in Tables (2 and 3). The Langmuir isotherm [28] assumes that adsorption takes place on a homogeneous surface with equal energy and all points on it are equally available for interaction with the adsorbate. This assumption holds good only for monolayer adsorption, which suggests that there is no transmigration of the adsorbate molecule on the surface. In the present study a predicted maximum adsorption capacity (Q_m) value of 78.58 mg/g Langmuir isotherm was obtained which is significantly higher compared to the experimental value of 27 mg/g (Fig. 8.1). Since the Langmuir isotherm is derived from thermodynamic principles, an important metric called the separation factor (R_L), can be estimated [29]. The separation factor indicates whether the adsorption in the system studied is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). In the present work, for the concentration range of $50\text{--}150 \text{ mg L}^{-1}$, the obtained values between

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0.80 and 0.42, indicate favorable adsorption of AV49 dye on to NIBCS. The decrease in R_t with increase in the initial concentration of the dye indicates that the adsorption is more favorable at high concentrations as expected.

The Freundlich isotherm assumes that heterogeneous layers of adsorbate can be formed and an empirical model can be used to describe this process [30]. The metric heterogeneity factor (n_f) estimated from the Freundlich isotherm, indicates whether the adsorption is linear ($n_f = 1$), chemisorption ($n_f < 1$), or a physisorption ($n_f > 1$). This parameter can also be used to quickly identify if a process follows normal Langmuir isotherm ($1/n_f < 1$) or cooperative adsorption ($1/n_f > 1$). The values of $n_f = 1.522$ and $1/n_f = 0.657$ obtained in the present study indicates that the adsorption was physisorption and it fits the normal Langmuir isotherm. The fitting of Langmuir and Freundlich isotherms with experimental data ($R^2 = 0.9809$) are shown in Fig. 8.a. Most of the other isotherms are expanded forms of either the Langmuir or Freundlich isotherms, an expanded form of Langmuir isotherm is Jovanovic isotherm [31] which describes a model considering a monolayer and no lateral interactions, but with an added exponential term to account for deviances of the experimental results from the Langmuir isotherm. Looking at q_m , χ^2 and R^2 values Langmuir appears to be the better fit than Jovanovic model (Table 3). The fits of Dubinin - Radushkevich isotherm ($R^2 = 0.837$), Jovanovic isotherm ($R^2 = 0.975$) shown in Fig. 8.b, whereas Harkin-Jura isotherm ($R^2 = 0.984$), and the Tempkin isotherm ($R^2 = 0.925$) to the experimental data are shown in Fig. 8.c.

An empirically determined Tempkin isotherm model explains the heterogeneous adsorption systems by building on the Langmuir isotherm. Since most models used are mathematically of higher order equations the validity of data fitting cannot be confirmed by R^2 value alone as it is mostly used with linear models. χ^2 values provide a better validity because if data from model were similar to the experimental data, χ^2 would be a small number and inversely so for models which do not fit with the experimental data. From the isotherms analysis and the most important parameters, q_m , χ^2 and R^2 (Table 3) the isotherms could be according to their capacity to predict their efficiency of AV49-NIBCS system. With respect to q_m value (closest to actual value to farthest from actual value): Jovanovic > Langmuir, while, as per χ^2 the order will be Harkin-Jura > Dubinin-Radushkevich > Tempkin > Freundlich > Jovanovic > Langmuir.

Table 2 Calculated parameters of two-parameter isotherms

Two Parameter Isotherms											
Langmuir		Freundlich		Jovanovic		Harkins-Jura		Dubinin-Radushkevich		Tempkin	
Q_m	78.58	K_f	1.49	Q_m	51.33	A_{HJ}	985	Q_s	39.15	b_T	0.09
K_s	0.007	n_f	1.522	K_j	9.66	B_{HJ}	3.2	K_{ad}	2.49	k_T	168.83

Table 3 Statistical parameters for isotherm model fitting

Isotherms	Langmuir	Freundlich	Jovanovic	Harkins-Jura	Dubinin-Radushkevich	Tempkin
SSE	4.30	12.600	3.80	494.40	114.50	22.300
χ^2	0.16	0.640	0.16	37.77	9.95	1.490
R^2	0.974	0.995	0.980	0.980	0.840	0.925

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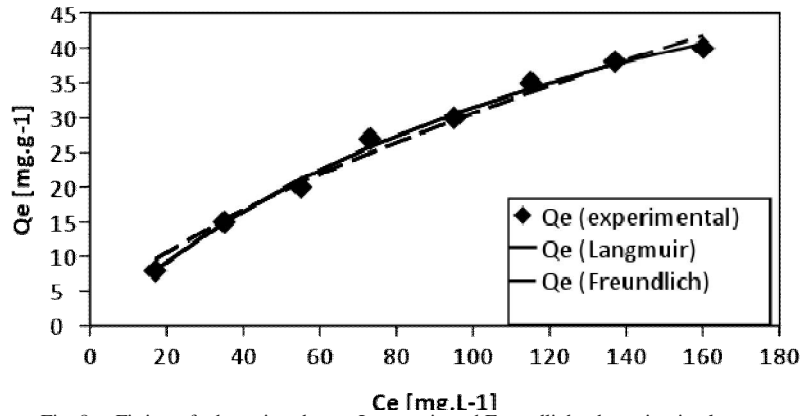


Fig. 8.a. Fitting of adsorption data to Langmuir and Freundlich adsorption isotherm

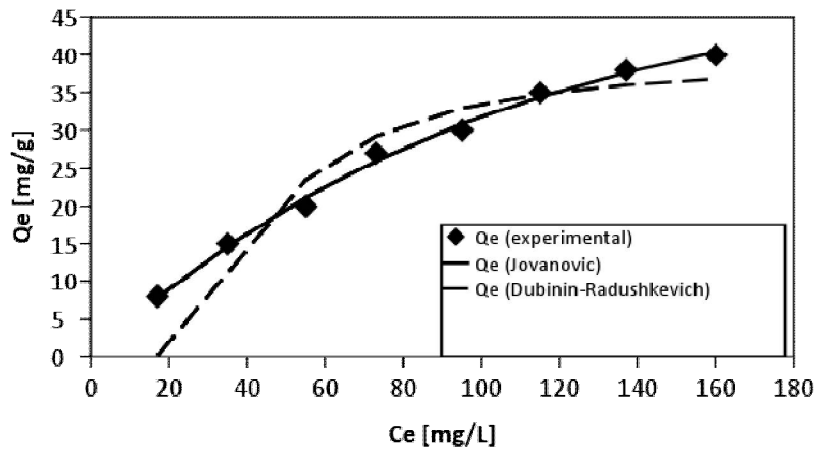


Fig. 8.b. Fitting of adsorption data to Jovanovic and Dubinin-Radushkevich adsorption isotherms

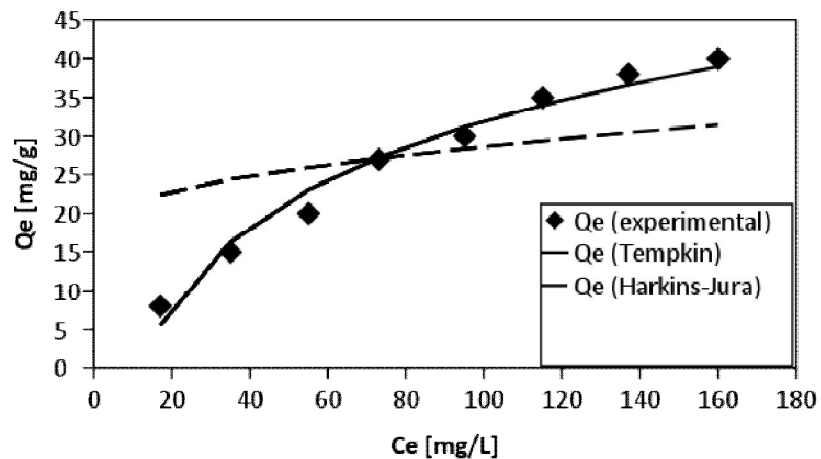


Fig. 8.c. Fitting of adsorption data to Temkin and Harkins-Jura adsorption isotherms

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4) Adsorption kinetics

The initial AV49 concentrations employed during kinetic studies were 50, 100 and 150 ppm and these are similar to other studies reported [32, 33]. Study of kinetics at 303 K, 313 K and 323 K provides the changes in rate of adsorption at different temperatures. The kinetic data for both adsorption and desorption were analyzed by non-linear analyses (MS Excel 2010) using pseudo-first order [34] and pseudo-second order [35] kinetic models. The estimated parameters are shown in Table. The coefficients of determination (R^2) and chi-square values (χ^2) indicate that the pseudo-second-order model, was the best fit with the experimental data for all initial AV49 concentrations (50, 100 and 150 ppm) (Figs. 9a, 9b and 9c). The rate of adsorption initially is very high and retards over time and becomes stagnant as it achieves the maximum adsorption potential. The adsorption capacity (q_e) increases with increase in temperature. Based on these results, the adsorption processes were not rate-limiting step. The data indicate that the adsorption process occurs in multiple steps involving transport of solute molecules from the bulk solution to the solid-surface of the adsorbent and then into the interior of the pores of the NIBCS. Adsorption kinetics is not controlled by single mechanism, as evident from the experimental data, where in all solute concentrations multiple levels of linearity is evident. At lower initial concentration (50 ppm) and lower temperature, adsorption rate is high and it is followed by a shift in the rate taking a different linear trajectory and the rate stabilizes at the end with respect to time. At higher temperatures the rate is more linear and at higher concentrations of solute (150 ppm) there is less apparent changes in the rate of adsorption. This is more so when fitting the higher temperature data to the pseudo-second order model [36] as seen in Fig. 9. The data shows good adherence to the model with high R^2 and χ^2 values. This infers that at higher temperatures the adsorption rate is negligibly hindered by diffusional limitations, implying that diffusion is the rate limiting process. The solute initially gets absorbed quickly onto the surface of the particles forming a film which retards further diffusion and this explains for the changes in absorption rates.

Table 4 Experimentally determined and theoretically predicted parameters for absorption kinetics models.

Initial Concentration [ppm]	Temp [K]	$Q_{e_{\text{expt}}}$ [mg.g ⁻¹]	Pseudo First order				Pseudo Second order			
			$Q_{e_{\text{pred}}}$ [mg.g ⁻¹]	k_1	R^2	χ^2	$Q_{e_{\text{pred}}}$ [mg.g ⁻¹]	k_2	R^2	χ^2
50	303	16	12.10	1.62	0.95	0.64	15.77	8.07	0.95	0.47
	313	17	12.11	2.12	0.91	0.80	16.87	1.26	0.93	0.54
	323	18	12.49	2.61	0.88	0.93	17.73	1.74	0.90	0.58
100	303	22	19.82	3.33	0.78	1.84	23.99	1.62	0.84	1.08
	313	23	20.49	3.70	0.75	1.87	24.50	1.83	0.83	1.06
	323	25	22.58	3.71	0.80	1.65	27.09	1.63	0.87	0.87
150	303	29	25.40	4.88	0.63	2.35	29.54	2.16	0.77	1.29
	313	31	27.60	4.52	0.68	2.46	32.25	1.82	0.80	1.32
	323	33	29.42	4.79	0.66	2.61	34.11	1.87	0.79	1.40

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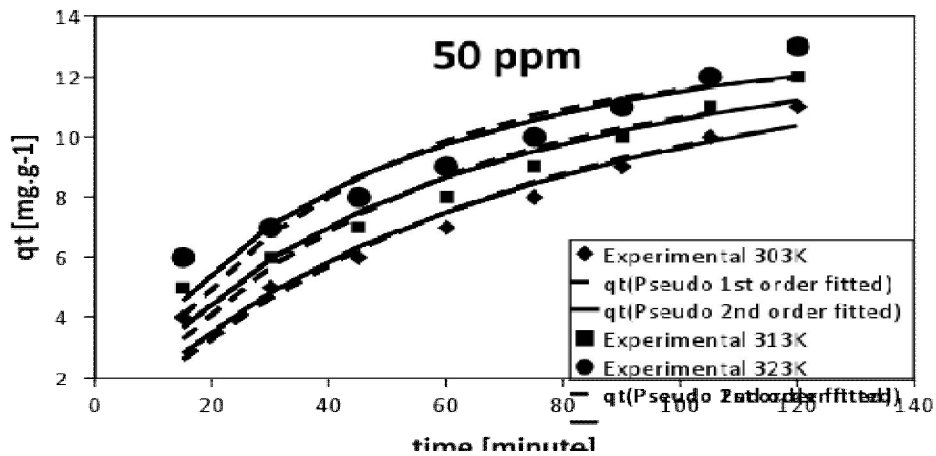


Fig. 9.a. Kinetic model fits for 50 ppm initial concentration of AV49 on NIBCS system at different temperatures

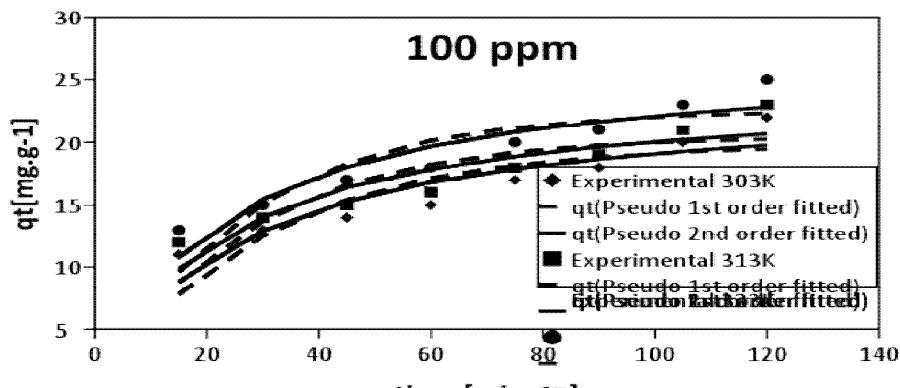


Fig. 9.b. Kinetic model fits for 100 ppm initial concentration of AV49 on NIBCS system at different temperatures

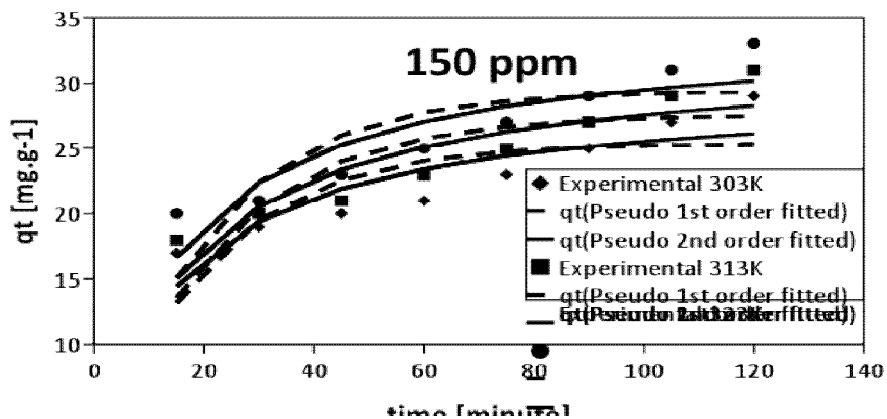


Fig. 9.c Kinetic model fits for 150 ppm initial concentration of AV49 on NIBCS system at different temperatures

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5) Adsorption thermodynamics

Both energy and entropy are the main factors to be considered in the interaction process design. The standard Gibbs free energy change (ΔG°) indicates the extent of spontaneity of the adsorption process. Significant adsorption can occur, if the free energy change (ΔG°) of adsorption is negative. The Gibbs free energy, entropy and enthalpy changes of adsorption were calculated by Van't Hoff and Gibbs-Helmholtz equations

$$K_L = C_{ac} C_e \quad (1)$$

$$\Delta G^\circ = -RT \ln K_L \quad (2)$$

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (3)$$

Where, K_L is the thermodynamic equilibrium constant ($l \text{ mol}^{-1}$) and T is the temperature (K). C_{ac} and C_e are the initial and equilibrium concentration (mg l^{-1}) of dye in solution respectively. ΔH° and ΔS° can be determined from the slope and the intercept of Van't Hoff plots of $\ln(K_L)$ vs. $1/T$.

Table 5 Thermodynamic parameters of AV49-NIBCS system.

Initial Concentration [ppm]	Temperature [K]	ΔG° [kJ mol ⁻¹]	ΔS° [J mol ⁻¹ K ⁻¹]	ΔH° [kJ mol ⁻¹]	ln A	Ea [kJ mol ⁻¹]
150	303	-0.69	4.66	0.72	4.73	0.28
	313	-0.74				
	323	-0.78				
100	303	-0.83	6.51	1.15	9.20	0.35
	313	-0.89				
	323	-0.96				
50	303	-0.97	24.45	6.45	17.62	38.44
	313	-1.16				
	323	-1.46				

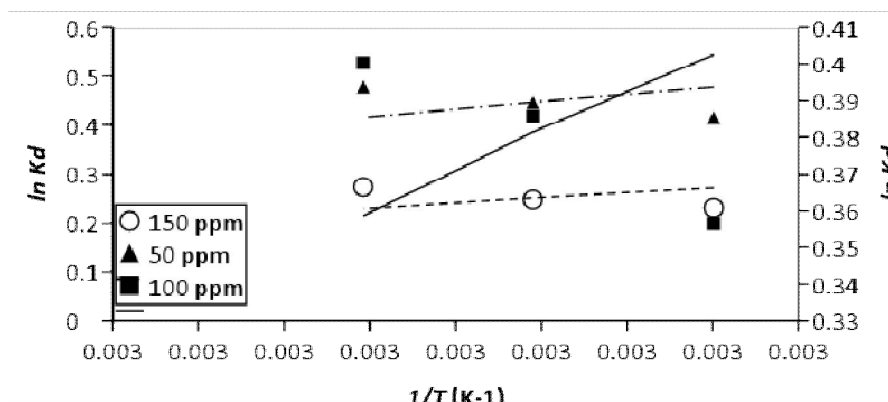


Fig. 10.a. Plot of thermodynamic equilibrium constant vs $1/T$ to determine the enthalpy and Gibbs free energy of the process

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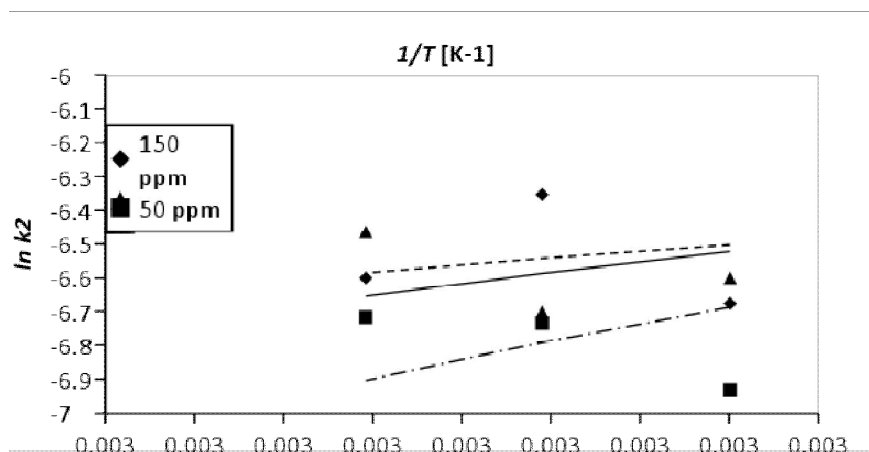


Fig. 10.b Plot of pseudo – second order kinetic constant vs 1/T to determine the activation energy of the process

Thermodynamic parameter estimates are provided in Table. The positive ΔH° value suggests the endothermic nature of adsorption and the negative ΔG° values indicate the feasibility and spontaneity of the adsorption process. The ΔG° is negative for all studied temperatures indicating that the adsorption of AV49 onto BCS would follow a spontaneous and favorable trend. The ΔG° value decreases with increase in temperature indicating increase in adsorption at higher temperatures. The positive value of ΔS° suggests good affinity of AV49 towards the adsorbent and increased randomness at the solid solution surface. Extremely low ΔH° value suggests that the adsorption process is highly physical as the standard enthalpy change for chemical reaction is normally $>200 \text{ kJ mol}^{-1}$. This has been further confirmed by activation energy values of the adsorption process at concentrations of 50, 100 and 150 ppm which ranged from ~ 0.3 to 39 kJ mol^{-1} (Table 5) using the Arrhenius equation and the kinetic constant from the Pseudo second order model.

6) Statistical optimization by central composite design

The first step in the optimization was to determine and fit an appropriate model regression to the experimental data obtained based on a central composite design

$$\text{Biosorption} = 17.53 + 6.77*A + 2.73*B - 0.78*C + 4.06*D - 7.59*E - 3.64*f + 1.20*AB + 2.50*AC + 1.63*BC - 0.82*A^2 - 0.75*B^2 - 18.13*C^2 - 4.76*D^2 + 0.23*E^2 - 8.94*F^2$$

Cross product of factors like AD AE etc. are zero hence excluded from the equation

The optimal values of the variables determined by maximization of the second-order polynomial equation with interaction terms obtained by multiple regression analysis based on a central composite experimental design model and the input parameters were established (Table 5) with an agitation speed of 175 rpm at the temperature of 30°C , pH of 5.9, biosorbent dosage of 0.03 g/L and initial dye concentration of 122 mg/L with adsorption time of 180 min. The predicted sorption capacity for these optimal values was 35.84 mg/g.

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Table 6 ANOVA for central composite design

Source	Sum of Squares	Degree of freedom	Mean Square	F Value	P- Value
Model	2910.19	15	194.01	147.78	< 0.0001
A	768.15	1	768.15	585.1	< 0.0001
B	265.16	1	265.16	201.98	< 0.0001
C	10.03	1	10.03	7.64	0.0068
D	73.34	1	73.34	55.86	< 0.0001
E	228.19	1	228.19	173.81	< 0.0001
F	37.16	1	37.16	28.30	< 0.0001
AB	16.44	1	16.44	12.52	0.0006
AC	42.06	1	42.06	32.03	< 0.0001
BC	28.52	1	28.52	21.73	< 0.0001
A ²	5.75	1	5.75	4.38	0.0388
B ²	6.70	1	6.70	5.11	0.0260
C ²	1350.78	1	1350.78	1028.89	< 0.0001
D ²	22.38	1	22.38	17.05	< 0.0001
E ²	0.06	1	0.06	0.05	0.8302
F ²	146.47	1	146.47	111.57	< 0.0001
Residual	132.60	101	1.31		
Lack of fit	123.35	84	1.47	2.70	0.1190
Total	3042.79	116			

Significant figures

+ Suggestive significance (P value: 0.05 < P < 0.10)

* Moderately significant (P value: 0.01 < P < 0.05)

** Strongly significant (P value : P > 0.01)

R-Squared	95.6%
Adj R-Squared	95%
Pred R-Squared	88.4%
C.V. %	6.11%

The fit of the quadratic polynomial equation to the experimental data was confirmed by both the regression coefficient, which is quite high with a value of 0.956, and the analysis of variance (ANOVA) (Table 6). The P-value for the F-test with value lower than 0.5 indicates that the equation is statistically significant regression model. Thus it can be successfully used in optimization of AV 49 biosorption. The results confirm the accuracy of approximation by the quadratic equation.

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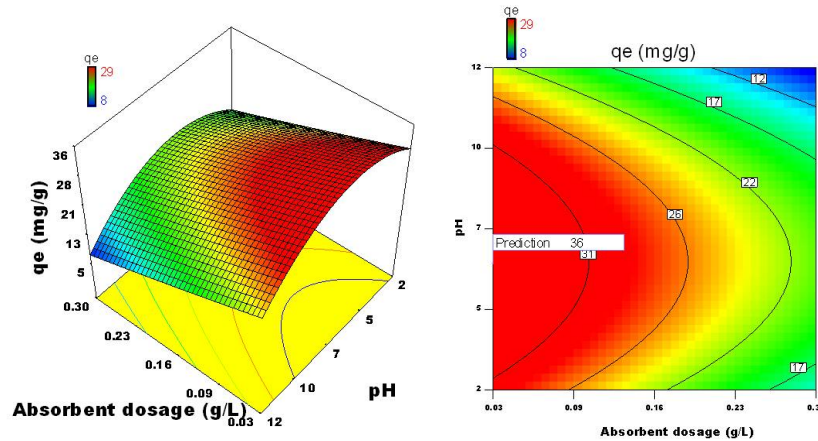


Fig. 11. (a) 3D surface plot and (b) contour plot showing the variation of adsorption capacity with adsorbent dosage and pH

The last step of the statistical optimization was the analysis of 3D response surface plots (Fig. 11) as a function of two independent variables, which served the purpose of determining the interaction effects between two parameters keeping others at a fixed value (in this case the optimum value). Statistical process optimization, in a given range of parameter values, allows not only for calculating the optimal condition, but also for determining the effect of the process conditions on the biosorption. In Fig.11 it can be observed that the lower the biosorbent dosage (E) and at almost neutral pH (E), higher is the sorption capacity (qe). The values of the regression coefficients indicate the effect of the parameter on the adsorption capacity. Positive values indicate incremental effect, for example, an increase in the initial dye concentration (C) causes a significant increase in sorption capacity. Likewise, a positive negative value indicates a detrimental effect, as seen in the case of pH (E), an increase in pH increases the adsorption capacity of the adsorbent. This is graphically represented in the surface and contour plots (Figs. 11-13).

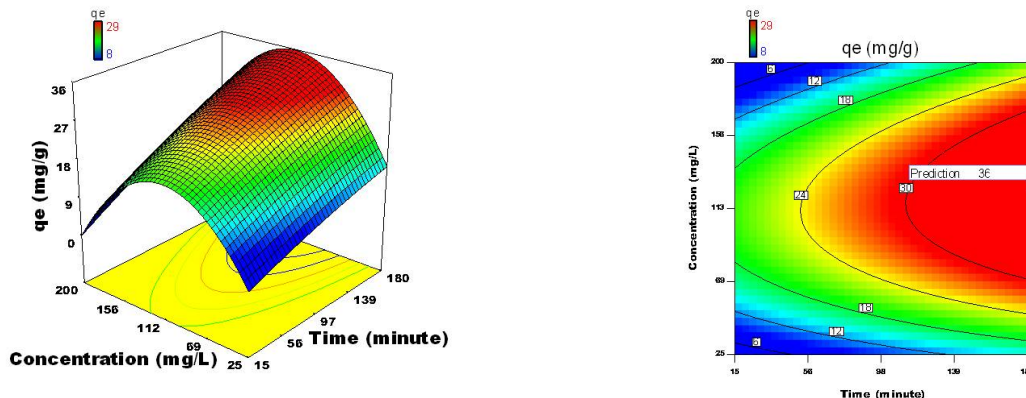


Fig. 12. (a) 3D surface plot and (b) contour plot showing the variation of adsorption capacity with initial dye concentration and process time.

As the values of process time, process temperature and initial dye concentration increase there is an observable increase in absorption capacity, whereas, when considering their combined effect (i.e., for example effect of process time and process temperature on adsorption capacity) there is almost negligible effect (reflected by the coefficient value). Similarly, individually, the adsorbent dosage and pH have positive values for co-efficient, indicating that as their value increases the adsorption capacity increases.

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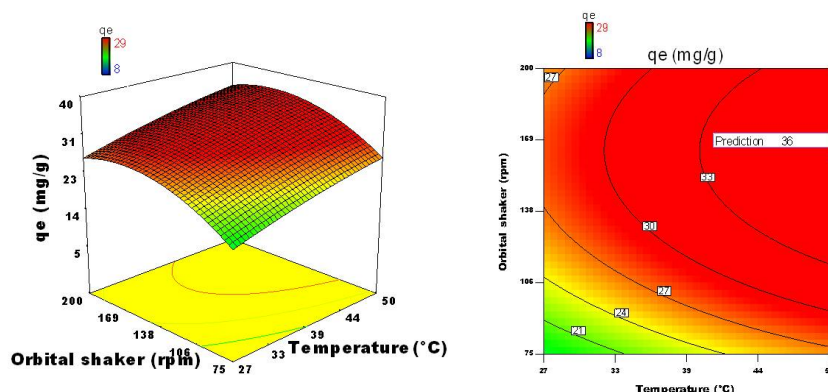


Fig. 13. (a) 3D surface plot and (b) contour plot showing the variation of sorption capacity with orbital shaker i.e., agitation speed and temperature.

The dependence of the sorption capacity on the initial dye concentration indicates the occurrence of a maximum of about 35.84 mg/L, which was confirmed by maximization of obtained quadratic polynomial expression. Increasing the speed of agitation of adsorbent with increase temperature should lead to removal of a pollutant from an aqueous solution and the results reflect this.

Table 7 Optimized conditions obtained from the statistical response optimizer

Time	Temperature	Concentration	Orbital shaker	Absorbent dosage	pH	Qe
180	50	122.09	160.17	0.03	5.9	35.84

The statistical significance of each operating factor was evaluated by F-test and P-values (Table VII). The F-test for testing the significance of the individual terms of the model is based on the test statistic that is calculated by dividing a regression coefficient by its variance. The results of F-test and associated P-values with confidential level >95% reveal that the most significant are A, B, D, F and BC effects, while the others seems to be unimportant.

IV. CONCLUSION

The AV49 adsorption from aqueous solution by Nutraceutical Industrial Black Cumin Spent (NIBCS) is dependent on contact time, initial pH of the solution, adsorbent dose and initial AV49 concentration. Based on the isotherm analysis and taking into consideration the value of Q_m , the adsorption data of NIBCS adsorbent is well described by Jovanovic isotherm model, while, with respect to χ^2 in the descending order Harkin-Jura > Dubinin-Radushkevich > Tempkin > Freundlich > Jovanovic > Langmuir and the adsorption kinetics fitted the pseudo-second order kinetics model. The optimal values of the variables determined by maximization of the second-order polynomial equation with interaction terms obtained by multiple regression analysis done as per central composite experimental design model and the input parameters, the predicted sorption capacity of NIBCS for those optimized values was 35.84 mg/g. It is envisaged that cost-effective and ready-to-use NIBCS derived from nutraceutical industry for the removal of AV49 dye from water is not only feasible but also is a commercially challenging proposition.

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