Removal of Toxic Dye from Aqueous Solution Using Low Cost Adsorbent: Optimisation of Adsorption Conditions and Kinetic Studies

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Abstract: - **In this work, the potential of mustard seed husk powder (NIMSH) —a nutraceutical industrial waste to remove toxic dye Brilliant Blue R (BBR) from aqueous solution was investigated in a batch experimental set up. Adsorption conditions were studied with respect to initial solution pH, adsorbent dose, contact time, initial dye concentration and temperature. Equilibrium data were analyzed by two isotherms; the Langmuir isotherm and the Freundlich isotherm. The best fit to the data was obtained with the Freundlich isotherm. Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) were used to characterize the adsorbent material. FTIR analysis revealed functional groups responsible for the adsorption process. The temperature had a strong influence on the adsorption process and the rate of the adsorption reaction followed the pseudo-second-order kinetics. The results indicated that NIMSH can be used as a low-cost adsorbent for the removal of BBR dye from aqueous solutions.**

Key words: **Brilliant Blue R, Adsorption, Mustard Seed Husk, Kinetic studies**

I. INTRODUCTION

Due to urbanization and rapid growth of industries, a large quantity of wastes containing dyes and pigments have been discharged into the aquatic environment. It is reported that approximately 10–15% of the dye produced is lost during the textile dyeing processes and finishing operations [1]. The dye–bearing wastewater is not only disagreeable but also restrains sunlight from penetrating into the aquatic system which results in the disruption and gradual destruction of the aquatic ecosystem [2]. Moreover, many dyes and their products are potentially carcinogenic, mutagenic or allergenic and highly toxic to aquatic life [3]. The traditional methods for colour removal, including reverse osmosis, chemical precipitation and solvent extractions are limited because of the excessive usage of chemicals, high operational costs, expensive plant requirements, and accumulation of secondary concentrated sludge [4].

Carneiro et al. (2010) developed and optimized an accurate and sensitive analytical method for monitoring dyes like C.I. Disperse Blue 373 (DB373), C.I. Disperse Orange 37 (DO37) and C.I. Disperse Violet 93 (DV93) in environmental samples. The effluent treatments like pre-chlorination, coagulation flocculation and, flotation generally used by drinking water treatment plants, were not effective in removing these dyes. It was also confirmed by the detection of mutagenic activity in these wastewaters [5]. Hence the development of effective new method(s) for the removal of the dye is of paramount importance.

Brilliant Blue R (BBR) is a reddish-blue powder and belongs to the class of triarylmethane dyes. It is extensively used as a SDS-PAGE for the analysis of proteins [6] and recently it has been used in scientific experiments to treat spinal injuries in laboratory rats [7]. It is soluble in water, and has λ_{max} 588 nm. It is hazardous to aquatic environment. Currently, the process of biosorption, which is defined as the removal of materials (organic compounds, metal ions, dye molecules, etc.) by inactive, non-living biomass (materials of biological origin) is an eco-friendly technology as against the existing costly water treatment technologies due to its low initial cost, simplicity of design, ease of operation, insensitivity to toxic substances, and almost complete removal of pollutants even from dilute solutions [8-11].

The adsorbents derived from various agricultural waste, industrial waste and activated carbon and multiwall carbon nano tubes have been investigated intensively for removal of dyes from aqueous solutions [12-14]. To handle the large volume of effluents generated by food industry, spent/waste generated by nutraceutical industries which are available in large quantities could be appropriately used for the purpose.

NIMSH is a by-product from agriculture industry and generally available as a waste. Rapeseed/Mustard oil is commonly used for cooking medium in northern states of India, there are also other uses like lamp oil, in soap making, plastic manufacturing and as a high temperature, tenacious high-erucic acid lubricating oil [15]. Scientific studies on medicinal properties have opened some interesting doors for utilization of rapeseed meal. In numerous epidemiological studies, rapeseed meal phytochemicals has been associated with a decreased risk of chronic diseases such as cardiovascular disease, cancer, and asthma. It has high phenolic content which enhances antioxidant, antiinflammatory, antimicrobial and antimutagenic properties. It is the richest source of phytosterols and is useful in prevention of certain cancers. It also decreases serum and LDL cholesterol levels. Natural biosorbents are known to have high sorption properties and potential for ion exchange, biological materials are used as strong adsorbents [16]. The adsorption capabilities resulted due to net negative charge on the structure of biosorbent. This negative charge gives the capability to adsorb positively charged species and high porosity [17].

In recent years the use of mustard seeds as Nutraceutical is reported [18]. A nutracerutical is defined as, “a food or a part of a food that provides medicinal or health benefits, including the prevention or treatment of a disease”. The word Nutraceutical was used by Stephen DeFelice M D, founder and chairman of the foundation for innovation in medicine (FIM) [18]. The Nutraceutical differ from dietary supplements because Nutraceutical are not only supplement the diet but also aid in the prevention or treatment of disease and Nutraceutical are also represented as conventional food or as the sole item of meal or diet [19].

The Nutraceutical industrial Mustard Seed husk (NIMSH) biomass has been reported to exhibit excellent adsorption capacities in removing heavy metal ions [20]. Yet, this potential biosorbent has not been applied for remediation of dye-laden wastewaters. The NIMSH has the largest surface area and cation exchange capacity. Chemically it is hydrated cellulose along with other species [21]. It is used as a nano adsorbent and is applicable in the areas to reduce the environmental burden. The NIMSH is highly effective for the purification of waste water. It can also be used as a desiccant due to its adsorption properties [22] and photochemical reaction field [23]. Hence, as a novelty and in view to fulfil in the paucity of published data on the use of biomass based adsorbents for removing BBR, in the present study, the removal of chemical grade BBR was studied using NIMSH.

The present investigation is targeted to use the NIMSH powder as a potential adsorbent for the remediation of BBR dye. Various factors affecting adsorption capacity like pH, initial dye concentration, adsorbent dosage and temperature have been evaluated. Different models of isotherms and adsorption kinetics are fitted to the experimental data to establish the removal capacity of this adsorbent. The Fourier transform infrared spectroscopy (FTIR) analyses are used to study the adsorbent material before dye adsorption.

II. MATERIAL AND METHODS

Materials

Brilliant Blue R, sodium has chemical name as 3-[[4-[[4-(4-ethoxyanilino)phenyl]-[4-[ethyl-[(3-sulfonatophenyl)methyl] azaniumylidene]cyclohexa-2,5-dien-1-ylidene]methyl]-N ethylanilino]methyl]benzenesulfonate and it is a triarylmethane dye with chemical formula $C_{45}H_{44}N_3NaO_7S_2$ and molecular weight of 825.971, absorbance maximum (λ_{max}) 588 nm is classified as C.I. 42660 was procured from Sigma Aldrich Private Limited, Mumbai, India. All the chemicals used throughout this study were of analytical-grade reagents and the adsorption experiments were carried out at room temperature (28 ± 2 °C), 30°, 40° and 50°C. A stock dye solution of (1000 mg/L) was prepared by dissolving accurately weighed amount of the dye in distilled water. All working solutions of required concentrations were obtained by diluting the stock solution with distilled water for later use. The molecular structure of BBR is shown in Fig. 1.

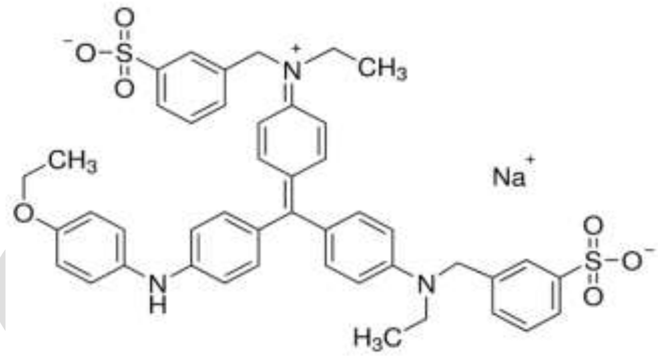


Fig. 1 Chemical Structure of Brilliant Blue R

Preparation of adsorbent

NIMSH was procured from a local industry. The NIMSH was dried at 60°C for 24 h in an oven. The dried NIMSH was ground and passed through ASTM sieve 80μ mesh to get the particle size of ≤ 177μm, and stored in plastic jar for later use. Prior to adsorption process no other chemical or physical treatments were given to NIMSH.

Surface characterization

NIMSH was observed through Scanning Electronic Microscope (Zeiss Evo/LS15, Germany). The functional groups present in the adsorbent were identified by FTIR spectrometer (Inter-spec 2020, Spectro Lab, UK).

Adsorption

Adsorption of BBR from aqueous solution by NIMSH was investigated by batch method. The effects of various parameters affecting adsorption such as initial dye concentration, adsorbent dosage, temperature and pH were studied.

Batch adsorption experiments were carried out by adding a fixed amount 50 mg of NIMSH into 250 mL Erlenmeyer flasks containing 50 mL of initial dye concentration (10-100 mg/L). The flasks were agitated (Kemi Orbital Shaker, India) at 170 rpm at 28±2°C for 180 min, until equilibrium was reached. The samples were centrifuged at 3000 rpm for 10 min. The supernatant liquid containing un-adsorbed dye solution was removed carefully using micropipette and the absorbance of the colored solution was measured by a double beam UV/Vis spectrophotometer

(Perkin Elmer- Lambda 25, USA) at 588 nm. The amount of BBR adsorbed at equilibrium, qe (mg/g) was calculated using following equation (1).

$$q_e = (C_0 - C_e)\frac{V}{W} \ldots \ldots (1)$$

Where, C_0 and Ce are concentrations (mg/L) of BBR at initial and at equilibrium respectively, V is solution volume (L) and W is adsorbent weight (g). For kinetic studies, the same procedure was followed. The concentrations of BBR were similarly measured. The amount of BBR adsorbed at any time, qt (mg/g), was calculated using equation (2).

$$q_t = (C_0 - C_t)\frac{V}{W} \ldots \ldots (2)$$

Where, C_t (mg/L) is the concentration of BBR measured at time t. Initial concentrations of 5, 10 and 20 mg/L of the dye and adsorption time of 15 min (2 min intervals) were used. For determining optimum amount of adsorbent per unit mass of adsorbate, 50 mL of dye solution was mechanically stirred in an orbital shaker with different amounts of NIMSH (0.025-0.200 g/L) until it reach equilibrium .To study the influence of pH on dye adsorption, 50mg of NIMSH along with 50 mL of dye solution of concentration 200 mg/L were agitated using orbital shaker. The experiment was done with pH values of 2-12. The pH was adjusted with dil HCl and/or NaOH solution. Solution pH was determined by pH meter (Systronics 802, India). Agitation was continued for 180 min. It is observed that 140-150 min and with constant agitation speed of 170 rpm is sufficient to reach the equilibrium. However, agitation speed of 170 rpm for 180 min was fixed for all studies. At equilibrium, the dye concentration was measured using double beam UV/Vis spectrophotometer at 588 nm. The extent of removal of dye was determined by following equation (3).

$$\text{Dye removal efficiency } \% = \frac{(C_0 - C_e)}{C_o} \times 100 \ldots \ldots (3)$$

Where, C_o and C_e are concentrations (mg/L) of BBR at initial and at equilibrium.

Modelling studies

Adsorption isotherms

Adsorption isotherm models provide information about interaction mechanisms, surface properties and affinities of adsorbent. The most accepted models for single solute system with two parameters are Langmuir and Freundlich. The models were used to test the equilibrium adsorption at ambient temperature.

The non-linear forms of isotherm models studied are shown below.

Freundlich isotherm: $\ln q_e = \ln K_F + (1/n) \ln C_e$ (4)

Langmuir isotherm: $C_e / q_e = (1/bq_{max}) + (1/q_{max})C_e$ (5)

Where, q_e is the amount of dye at equilibrium in unit mass of adsorbent (mg/g), C_e is concentration of dye solution at equilibrium (mg/L), q_{max} and b are the Langmuir coefficient related to adsorption capacity (mg/g) and adsorption energy (L/mg), respectively. K_F and n are the Freundlich coefficient related to adsorption capacity [(mg/g) / (mg/L) 1/n] and adsorption intensity of adsorbent, respectively. In our present work only Freundlich model fits to the data.

Adsorption kinetics

The controlling of the adsorption process was done by fitting experimental data with pseudo-first-order and pseudo-second-order. The controlling mechanism of the adsorption process was found by fitting the experimental data with the respective kinetic equations.

Thermodynamic parameters

Energy and entropy enable to understand the feasibility and mechanism. In the present study, thermodynamic parameters, including standard free energy (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were estimated by using rate law and also kinetic data to find out the extent and enthalpy of the adsorption process.

$$\text{Log (qem/Ce)} = \Delta S^o / 2.303R + (-\Delta H^o / 2.303RT) \quad (6)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (7)$$

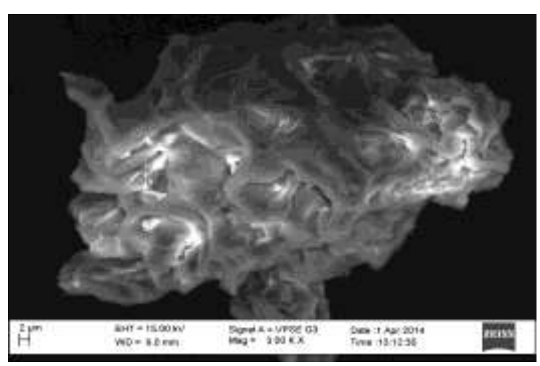
Where, m is the adsorbent dose (g/L), Ce is concentration of dye solution at equilibrium (mg/L), qe is the amount of dye adsorbed at equilibrium in unit mass of adsorbent (mg/g), q_e/C_e is the adsorption affinity. ΔH^o, ΔS^o and ΔG^o are change in enthalpy (kJ/mol), entropy (J/mol/K) and free energy (kJ/mol),respectively, R is the gas constant (8.314 J/mol/K) and T is the temperature (K).The values for ΔH^o and ΔS^o were obtained from the slopes and intercepts respectively. From the Van't Hoff plots of log (qem/Ce) verses 1/T, ΔG0 values were obtained from Equation 7.

III. RESULTS AND DISCUSSION

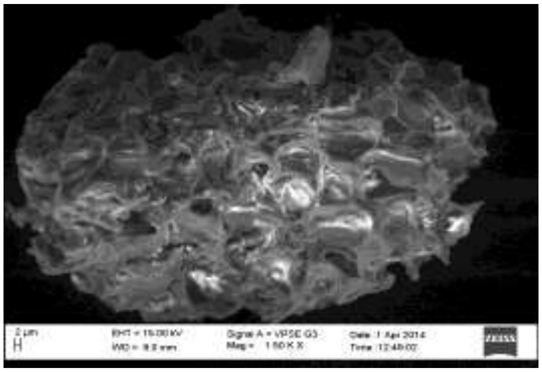
Surface characterization

Scanning Electron Microscopy

The NIMSH morphology obtained by SEM exhibited fibrous and porous structure as shown in Fig 2(A). This structure enhances dye adsorption as observed in Fig 2 (B) where the pores and voids between the spaces are occupied by the dye.



(A)



(B)

Fig. 2 SEM Image of NIMSH before (A) and after (B) adsorption

FTIR characterization of NIMSH

As seen in Fig. 3, The FTIR spectroscopy of NIMSH showed the broad band around 3178 cm^{-1} is attributed to the surface hydroxyl groups, linked in cellulose and adsorbed water, Band at 1621.99 cm^{-1} is due to C=C stretching of olefins. The band at 1406.95 cm^{-1} indicates methyl groups. The band at 1082.7 cm^{-1} is due to the presence of cellulose in adsorbent.

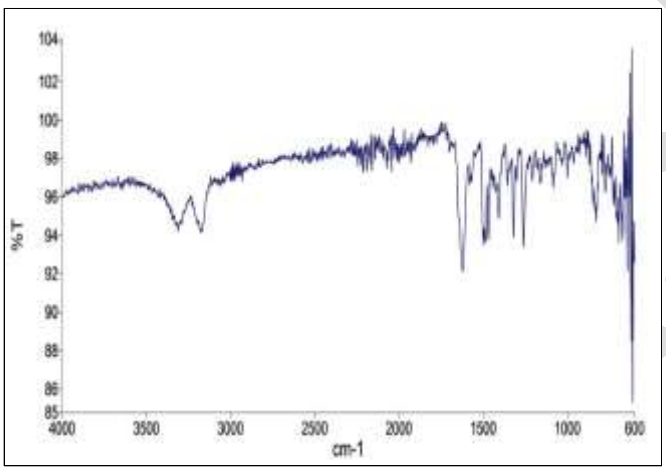


Fig. 3 FTIR of NIMSH

Adsorption of BBR onto NIMSH

Effect of initial dye concentration

As seen in Fig. 4, the dye uptake increased from 9 to 85 mg/g of NIMSH with the increase in dye concentration from 10 to 100 mg/L respectively. This indicates that there is an increase on the driving force of the concentration gradient due to the increase in the initial dye concentration. Adsorption was rapid initially due to the dye getting adsorbed onto exterior surface. Later, the dye molecules, probably entered into pores (interior surface), which is relatively a slow process. The adsorption of BBR was more with higher concentration and remained almost constant after equilibrium time.

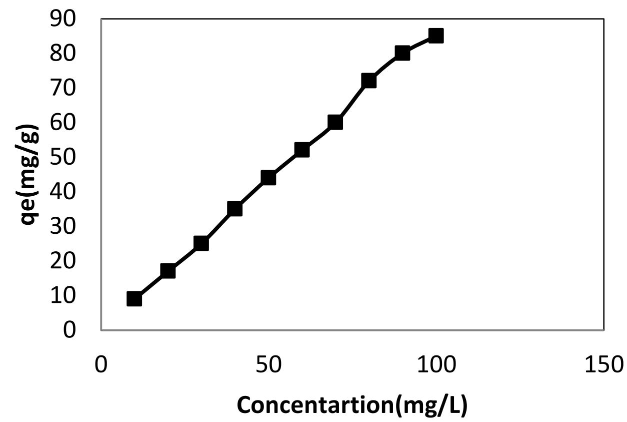


Fig. 4 Effect of initial dye concentration on adsorption of BBR

Influence of adsorbent dosage

The influence of adsorption of the dye onto NIMSH increased with the enhancement in the adsorbent dosage from 0.025 g to 0.200 g. This may be due to the binding of almost all dye molecules on the adsorbent surface and establishing equilibrium of dye molecules and the adsorbent. Hence dye adsorption increased with adsorbent dosage and reach equilibrium at certain dosage the results are shown in Fig. 5.

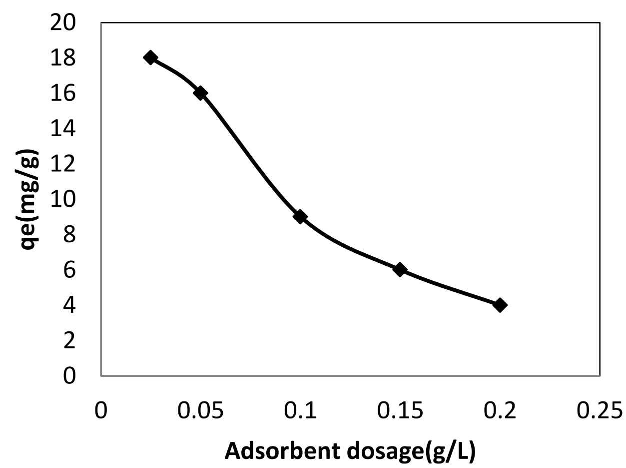


Fig. 5 Effect of adsorbent dosage on adsorption of BBR

Effect of Temperature

Temperature is an influencing factor in the adsorption process and it was studied at 30^oC, 40^o and 50^oC and the results are shown in Fig. 6. It can be observed that with the increase in temperature, the adsorption capacity increases marginally, which indicates that the process is exothermic in nature. The increase in adsorption with temperature is may be due to the increase in the mobility of the dye molecule with increase in their kinetic energy. The slight increase in removal of dye due to increasing temperature may be due to higher interaction between adsorbate and adsorbent.

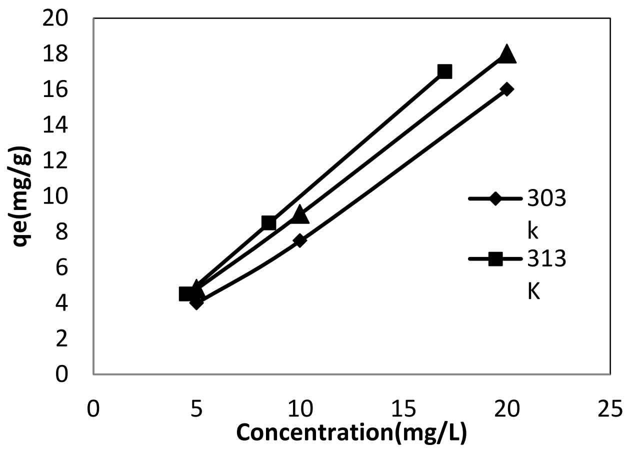


Fig. 6 Effect of Temperature on adsorption of BBR

Effect of pH

The very important parameter in adsorption process is pH. It controls the adsorption capacity by influencing adsorbent surface properties and ionic forms of dye. The adsorption capacity of NIMSH slightly increased with increase in solution pH and maximum adsorption capacity of BBR was under acidic condition. In acidic pH an excess of H+ ions compete with cations of the dye for adsorption sites. This result in increased adsorption and increase in pH decreases the adsorption results are depicted in Fig. 7.

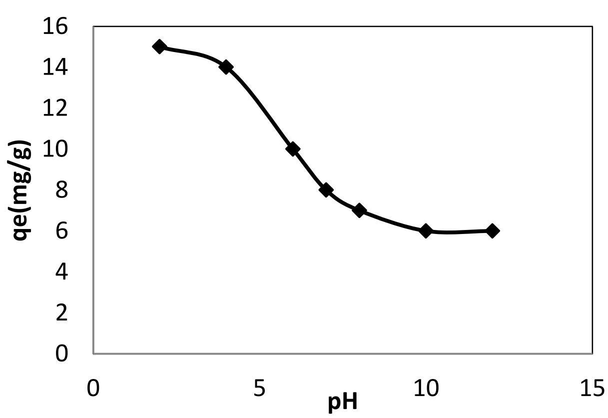


Fig. 7 Effect of pH on adsorption at 20 ppm concentration of BBR

Adsorption isotherms

The equilibrium experiments were conducted for different initial concentrations of BBR in the range of 10-100 mg/L. The adsorption of the dye onto adsorbent using Langmuir Model assumes the monolayer adsorption on to the surface of adsorbent containing finite number of identical adsorption sites of uniform energies [24]. The Langmuir isotherm parameters q_{max} and b were determined from slope ($1/q_{max}$) and intercept ($1/bq_{max}$) of the plot of C_e/q_e verses C_e (Fig. 8), respectively. The values of Freundlich constants n and K_F were obtained from the slope (1/n) and intercept ($\ln K_F$) of the plot of ln q_e verses ln C_e (Fig. 9), respectively. The plot gives a straight line and this shows that adsorption of BBR on NIMSH also follows the Freundlich isotherm.

Freundlich isotherm model [25] is an empirical equation which assumes that the adsorption process takes place on heterogeneous surface. The heterogeneity factor (n_F) indicates whether the nature of adsorption is linear (n_F=1), chemisorption (n_F< 1), or physisorption (n_F>1). In the present study, the values of n_F is 1.096 indicate that the adsorption is physisorption and favours normal Langmuir isotherm. The fitting of Langmuir and Freundlich isotherms to the experimental data R^2 is 0.27 and 0.85 respectively; where, R^2 is the correlation coefficient shows that the data fits well. The results are presented in Fig 8 and 9. Hence it is inferred that the adsorption of BBR on NIMSH is favourable and the process is physisorption. The Langmuir and Freundlich isotherms constants and regression coefficients are listed in Table 1.

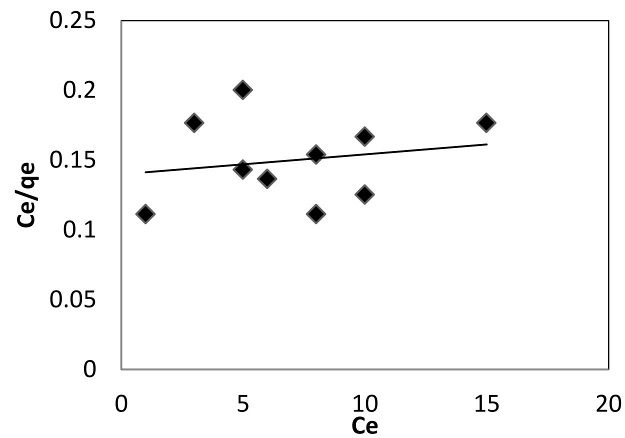


Fig. 8 Fitting of experimental data to Langmuir model

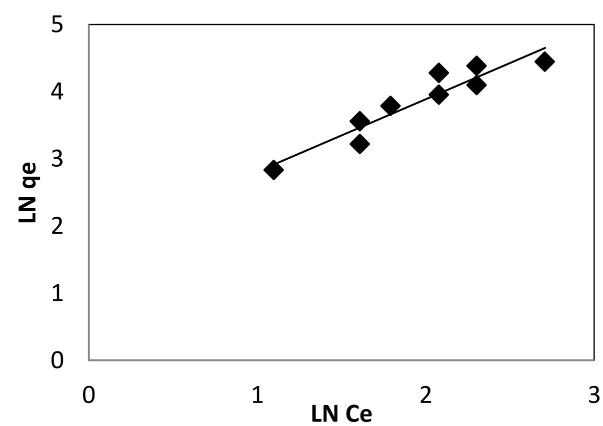


Fig. 9 Fitting of experimental data to Freundlich model

Table 1: Isotherm parameters for BBR adsorption on NIMSH

Freundlich Constants			Langmuir Constants		
K_F	n_F	R2	q_{max}	b	R^2
5.643	0.927	0.888	714.28	0.010	0.036

Adsorption kinetics

The rate constants for the adsorption of BBR on NIMSH were obtained using the pseudo-first order and pseudo-second order kinetic models.

Pseudo-first order kinetic model

When the adsorption is preceded by diffusion through a boundary, the kinetics in most cases follows the pseudo-first order rate equation. The differential rate equation is as follows

$$dqt/dt = k_1 (qe - q\,t) \qquad (8)$$

Where, q_t and q_e are the amounts of dye adsorbed at time t (mg/g) and at equilibrium (mg/g), respectively and k_1 is the pseudo-first order rate constant (min^{-1}). Integration of the above equation by using the boundary condition, $q_t = 0$ at $t = 0$ gives equation 9 [26]:

$$\log (q_e - q_t) = \log q_e - (k_1/2.303)\, t \qquad (9)$$

The values of k_1 and q_e were calculated from the slopes and intercepts of the linear plots of log ($q_e - q_t$) verses t, and presented in Table 2. Therefore, it may be concluded that the adsorption of BBR onto NIMSH is not followed the pseudo-first order kinetic model.

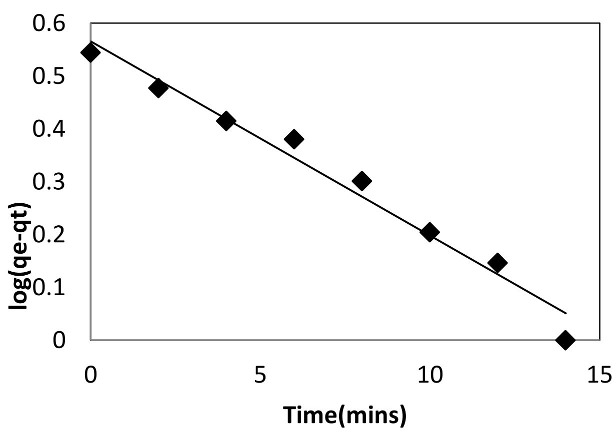


Fig. 10 Pseudo-first order kinetic model for 5ppm of BBR

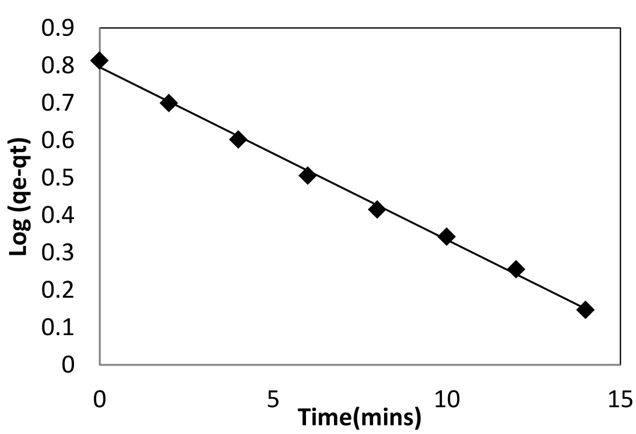


Fig. 11 Pseudo-first order kinetic model for 10 ppm of BBR

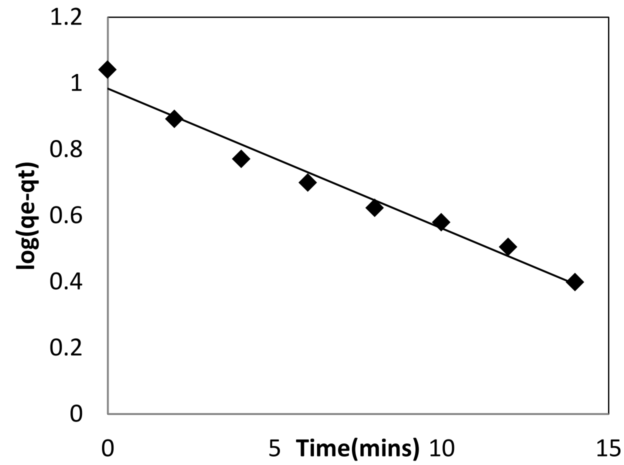


Fig.12 Pseudo-first order kinetic model for 20ppm of BBR

Pseudo-second order kinetic model

The pseudo-second order kinetic model [27] is presented in equation 10:

$$dqt/dt = k_2 (q_e - q_t)^2 \qquad (10)$$

Where, q_t and q_e are the amount of dye adsorbed at time t (mg/g) and at equilibrium (mg/g), respectively and k_2 is the pseudo-second order rate constant (g/mg min). Integrating the above equation using the boundary condition, $q_t = 0$ at $t = 0$ leads to equation 11:

$$t/qt = 1/k_2\, qe_2 + t/\, qe \qquad (11)$$

The values of k_2 and q_e were calculated from intercepts and slopes of the linear plots of t/qt verses t respectively and presented in Table 2. Table 2 shows that the calculated q_e values are very close to that of experimentally obtained q_e and the values of correlation coefficients (R^2) are closer to unity confirms that adsorption of BBR onto NIMSH follows pseudo-second order kinetics.

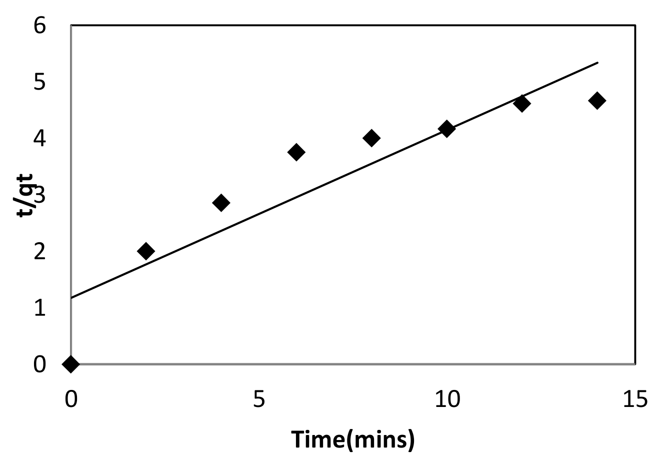


Fig. 13 Pseudo-Second order kinetic model for 5ppm of BBR

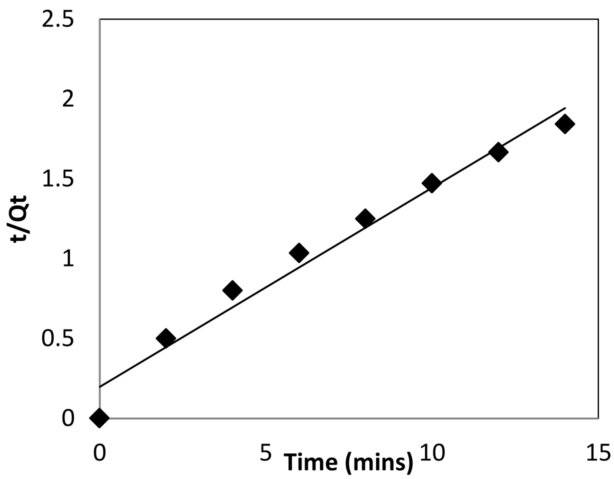


Fig. 14 Pseudo-Second order kinetic model for 10ppm of BBR

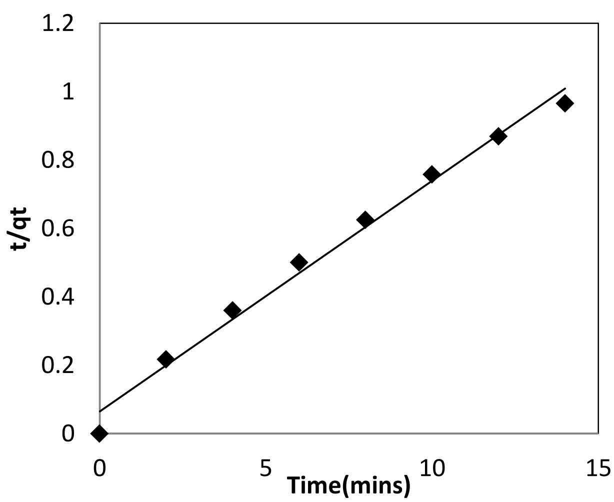


Fig. 15 Pseudo-Second order kinetic model for 20ppm of BBR

Table 2: Kinetic parameters for BBR adsorption on NIMSH

Concentration of Dye (ppm)	Pseudo first order			Pseudo second order		
	q_e (mg /g)	K_1 (min^{-1})	R^2	q_e (mg /g)	K_2 (min^{-1})	R^2
5	1.760	0.084	0.974	3.364	2.858	0.833
10	2.215	0.106	0.997	8.019	40.644	0.972
20	2.675	0.097	0.974	14.814	229.33	0.988

Effect of Adsorption thermodynamics

The Gibbs free energy, entropy and enthalpy changes of adsorption were calculated by Van’t Hoff and Gibbs-Helmholtz equations. As seen in Table 3, the positive ΔH° value suggests the endothermic nature of adsorption while the low magnitude and very similar values of enthalpy irrespective of changes in initial dye concentration also clearly indicate that the adsorption is physical i.e., involving weak interactions. The ΔG° is negative for all studied temperatures indicating that the adsorption of BBR onto NIMSH follows a spontaneous and favourable trend. The decrease in ΔG° with increase in temperature indicates increase in adsorption at higher temperatures. The positive value of ΔS° suggests good affinity of BBR towards the adsorbent and increased randomness at the solid solution surface.

Table 3: Adsorption thermodynamic parameters of BBR on NIMSH

Concentration (mg/L)	ΔH^0	ΔS^0	$-\Delta G^0$		
	(kJ/mol)	(J/mol/K)		(kJ/mol)	
			303 K	313 K	323 K
5	72.38	263.3	7.39	10.02	12.66
10	44.65	169.9	6.82	8.52	10.22
20	32.72	132.5	7.42	8.74	10.07

IV. CONCLUSIONS

The major conclusions of this study are:

- NIMSH has been developed as efficient, environmental-friendly and cost-effective biosorbent for the remediation of dye Brilliant Blue R.
- Operational parameters such as; initial dye concentration, adsorbent dose, temperature and pH, influenced the adsorption efficiency of NIMSH.
- The experiments and analyses of the results for adsorption isotherms and kinetic studies confirmed the complexity involved in the dye adsorption mechanism.
- Thermodynamic study demonstrated the spontaneous and endothermic nature of biosorption process. It also confirmed that the adsorption is physical in nature.
- An alternative use of Mustard Seed Husk as a biosorbent will help to reduce carbon foot print.
- NIMSH is appropriate ready-to-use matrix in field of adsorption science.
- The authors envisage that the concept demonstrated will help overcoming resource depletion through utilization of agro-based spent which has neither feed or fertilizer value.

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