Influence of Operating Conditions on the Removal of Brilliant Vital Red Dye from Aqueous Media by Biosorption using Rice Husk

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Summary: Biosorption is emerging as an economical and ecofriendly methodology for the removal of hazardous and toxic chemicals from waste water. The operating conditions have a great influence on the efficiency of this process. Conventional and indigenous biosorbents like baggase, wheat husk and rice husk have been evaluated for their removing efficiency of Brilliant Vital Red dye from water. Rice husk is proved better among them. The effect of important operating conditions for the removal of the dye using rice husk were studied. The observed optimum values for various factors are; 0.2 g of biosorbent, 25 ppm initial dye concentration, 30°C temperature, 15 minutes contact time, 300 rpm stirring speed and 2.0 pH. Langmuir adsorption isotherm model was also applied to evaluate maximum adsorption capacity of rice husk for Brilliant Vital Red dye. Q_{max} value was 15.06 which indicated that rice husk can effectively be used for the removal of Brilliant Vital Red dye from wastewater using the optimized operational conditions. This study would be accommodative with regard to practical wastewater treatment.

Introduction

Dyes and pigments are released into water streams as wastewater from several industrial sources, primarily from the dye manufacturing, leather, paper and textile finishing. Wastewaters from the textile dyeing processes contain unused dyes and auxiliary chemicals along with bulk of water [1]. Various dyes and their break down products are harmful and lethal for the living organisms. The presence of dyes in water causes reduction in light penetration which has a dangerous effect on photosynthesis. There are many structural varieties of dyes like acidic, basic, disperse, azo, diazo, anthraquinone based and metal complexes [2]. Cationic dyes, commonly known as basic dyes, are widely used in acrylic, nylon, silk, and wool dyeing. Due to the complex chemical structure of these dyes, they are resistant to breakdown by physical, chemical and biological methods. Moreover, degradation by any physical, chemical or biological means may produce toxic and carcinogenic intermediates or the final products [3, 4].

A single treatment is not adequate for the complete removal of impurities from waste water [5, 6]. Various techniques in combination with one another are employed for this purpose [7-12]. Formal physical and chemical methods are either costly, e.g., activated carbon, or produce concentrated sludge or may not capable of treating large volumes of effluent without the risk of clogging, e.g., membrane filtration [13]. Among several physical and chemical methods, the biosorption has been found to be superior as compared to other techniques for wastewater treatment in terms of its capability for efficiently adsorbing a broad range of adsorbates and its simplicity of design [14]. Biosorption is a relatively new technique that has been emerged in 1980s and gained an appreciable amount of attention because it can remove contaminants from effluents in an environment friendly manner [15, 16]. Biosorption refers to the passive or physicochemical attachment of chemical species to the biopolymers present in a biosorbent [17]. Biosorbents are generally economical because they are either naturally plentiful or found as waste materials from certain processes. It has been revealed that different kinds of cheap dead biomasses can be used as biosorbents to sequester toxic contaminants from water and wastewater. Biosorbents may be classified according to their sources: bacteria, algae, fungi, plant-derived and animal-derived [18].

In the present work, various indigenous agricultural by-products like bagasse, wheat husk and rice husk are tested as biosorbents for dyes with a model system of aqueous Brilliant Vital Red dye solution. Rice husk is selected from these biosorbents for further evaluation of the effects of various parameters which affect biosorption. Brilliant Vital Red dye is also called Ditolyldiazo-3,6-disulfo-β-naphthylamine-*β*-naphthylamine-6-sulfonic acid sodium salt. Its chemical structure is shown in Fig. 1. Various physical properties of this dye are mentioned

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in Table-1 [19]. It has been identified as a high priority for action as it was found to be persistent, bioaccumulative and inherently toxic to aquatic organisms [20]. It is used for blood volume determinations in clinical tests and as a textile dye for cotton fabrics. Once textile dyeing is completed, the material is washed several times to remove unfixed and hydrolyzed dye. Therefore dyeing processes do not run to total completion and residual reactive and hydrolyzed dyes are left in the process water and are discharged in the waste water leaving the site [21, 22].

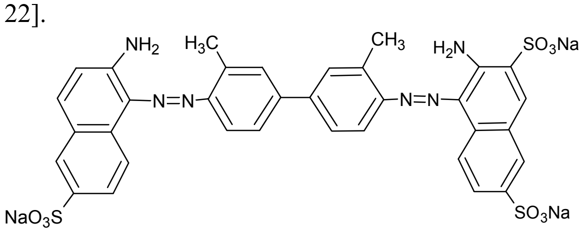

Fig. 1: Brilliant Vital Red dye.

Table-1: Properties of Brilliant Vital Red dye.

Name of Property	Characteristics
Color	Cherry red
Chemical group	Discrete organics
Class	Organic azo dyes
Chemical formula	$C_{34}H_{25}N_6Na_3O_9S_3$
Molecular weight	826.76 amu
Absorption max	500 nm (aqueous solution)
Synonyms	Direct Red 34, Brilliant Congo R
Percent Composition	C= 49.39%, H= 3.05%, N= 10.17%, Na= 8.34%, O= 17.42%, S= 11.64%

Different agricultural waste materials like bagasse, wheat husk, rice husk are used as biosorbents for removing various harmful and toxic substances during the treatment of waste water [23]. The conditions for treatment of wastewater varied with varying biosorbent and adsorbate. So different influencing parameters are tested and optimized in the following study for the treatment of wastewater containing Brilliant Vital Red dye. Rice husk has been chosen among different biosorbents in this study. It has been reported as a good adsorbent for many metals and dyes. Rice husk is also being used to treat textile dyes such as Malachite green, [24, 25] Congo red, [26] Methylene blue [27] and Acid yellow 36 [28]. Rice husk is an agricultural waste and accounts for about 20% of the whole rice. It contains about 20% silica. It has a grainy structure. It is insoluble in water and has chemical stability with high mechanical strength. Adsorption of dyes from aqueous solution requires adsorbents possessing not only large capacities but also significant pore volume and surface area contributed by mesopores, due to the size of dye molecules which are relatively large [29]. The physicochemical properties of the adsorbent used like porosity, surface area, and pore volume are mentioned in Table-2 and its typical chemical composition is mentioned in Table-3 [30]. The focus of this piece of research work was to evaluate the adsorption potential of the rice husk in removing Brilliant Vital Red dye from aqueous solutions. Langmuir adsorption isotherm model is also applied in this regard to quantify maximum adsorption capacity of rice husk for this dye.

Table-2: Physicochemical characteristics of rice husk [30].

Characteristics	Values
Bulk density (g/ml)	0.73
Solid density (g/ml)	1.5
Moisture content (%)	6.62
Ash content (%)	45.97
Particle size (mesh)	200-16
Surface area (m^2/g)	272.5
Surface acidity (meq/gm)	0.1
Surface basicity (meq/gm)	0.45

Table-3: Typical composition of rice husk [30].

Composition	Percent
Cellulose	32.24
Hemicellulose	21.34
Lignin	21.44
Extraetives	1.82
Water	8.11
Mineral ash	15.05
Chemical composition in mineral ash:	
SiO_2	96.34
K_20	2.31
MgO	0.45
Fe_2O	0.2
Al_2O_3	0.41
CaO	0.41
K_2O	0.08

Results and Discussion

Three different biosorbents are compared for their biosorption efficiency of Brilliant Vital Red dye from water, *i.e.* bagasse, wheat husk and rice husk. The result is shown in Fig. 2. It clearly indicates that percentage adsorption of biosorbent is maximum when rice husk is used. Then effect of various factors which influence biosorption of Brilliant Vital Red dye on rice husk have been evaluated in this study.

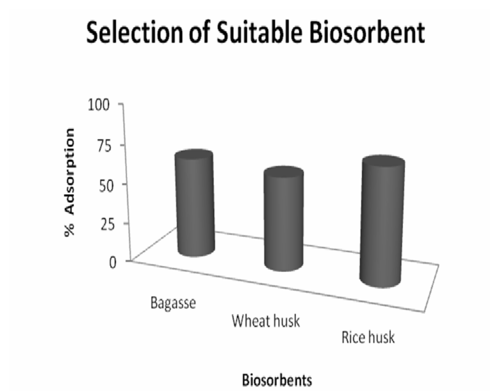

Fig. 2: Selection of suitable conventional biosorbent for Brilliant Vital Red dye.

The effect of particle size on adsorption was studied by using different mesh sized rice husk. The results are shown in Fig. 3. Adsorption was 1.2 % for the particle size of 80-100 microns to maximum adsorption value 6.9 % for the particle size of 40-60 microns. It was observed that smaller the biosorbent size, with more surface area, enhanced adsorption capacity of the biosorbent. The adsorption capacity depends on the surface active sites, *i.e.* specific surface area available for solute surface interaction which is accessible to the solute. It is expected that removing efficiency will be increased with a larger surface area. It is also supported by the literature. Adsorption being a surface phenomenon, smaller biosorbent size will offer comparatively larger surface areas and higher adsorption will occur at equilibrium [30].

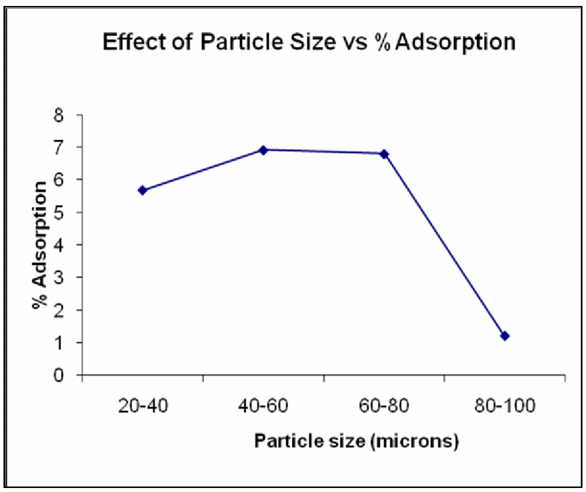

Fig. 3: Effect of particle size of rice husk (biosorbent) on percentage adsorption of Brilliant Vital Red dye.

The effect of variation in the adsorbent dose on the adsorption of Brilliant Vital Red dye was studied. The results are shown in Fig. 4. It was observed that the percentage adsorption is increased as the adsorbent dose decreases. The minimum adsorption was 5.9 % for 2.0 g to maximum adsorption value 11.8 % for the dose 0.25 g. This increase in adsorption with decrease in adsorbent dose was due to the availability of more adsorption sites. Another reason may be due to the particle interactive behavior like aggregation, resulted from high adsorbent dose. Such aggregation would lead to the decrease in total surface area of the biosorbent and hence the adsorption is decreased.

The effect of various contact intervals on adsorption was studied. The results are shown in Fig. 5. The minimum adsorption was 1.4 % for 5 minutes and maximum value was 6.7 % for 15 minutes. These adsorption characteristics indicated a rapid uptake of the adsorbate. The adsorption rate decreased to a constant value with increase in contact time because of all available sites was covered and no active site available for binding.

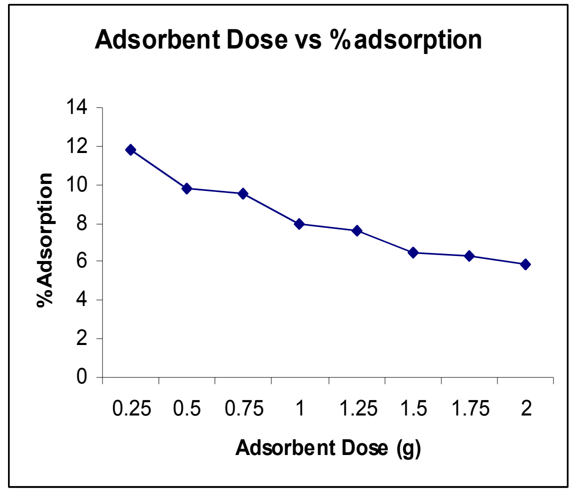

Fig. 4: Effect of adsorbent dose on percentage adsorption of Brilliant Vital Red dye.

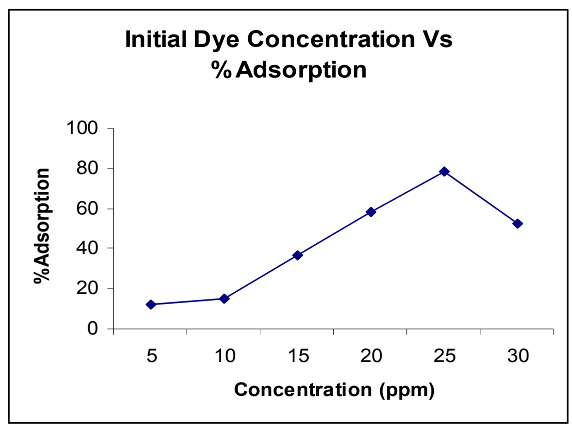

Fig. 5: Effect of initial concentration of dye (Brilliant Vital Red) on percentage adsorption.

The effect of initial dye concentration on biosorption was studied. The results are shown in Fig. 6. It was observed that adsorption increased with increase in initial concentration of the dye. The minimum adsorption was 12.04 % for 5.0 ppm to maximum adsorption value 78.48 % for 25 ppm concentration of dye solution. This may be due to available active sites on biosorbent and increase in the driving force of the concentration gradient, as an increase in the initial concentration of the dye.

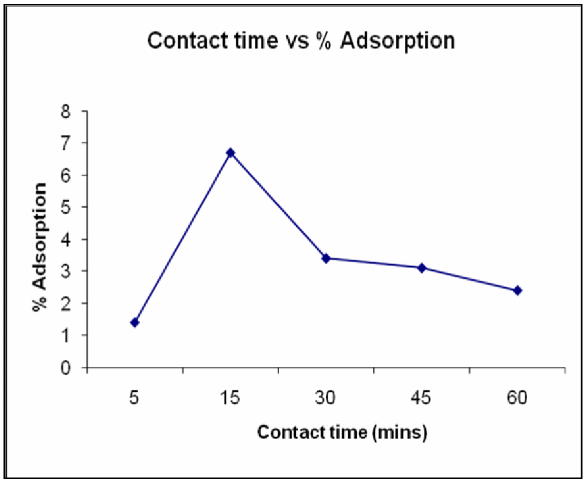

Fig. 6: Effect of contact time of rice husk with Brilliant Vital Red dye solution on percentage adsorption.

The pH of the aqueous solution is clearly an important parameter that controls the biosorption process. The percentage of adsorption was studied as a function of pH in the range of 2-10. The results are shown in Fig. 7. The minimum adsorption was 1.6 % at pH = 8 and maximum adsorption value was 95.7 % at pH=2. The maximum adsorption occurred in the acidic media. This indicated that rice husk is an efficient biosorbent for Brilliant Vital Red dye in acidic conditions. This might be due to the force of attraction like hydrogen bonding between the oxygen atoms of adsorbate and hydroxyl groups of biosorbent that contributed in increased percentage adsorption [31].

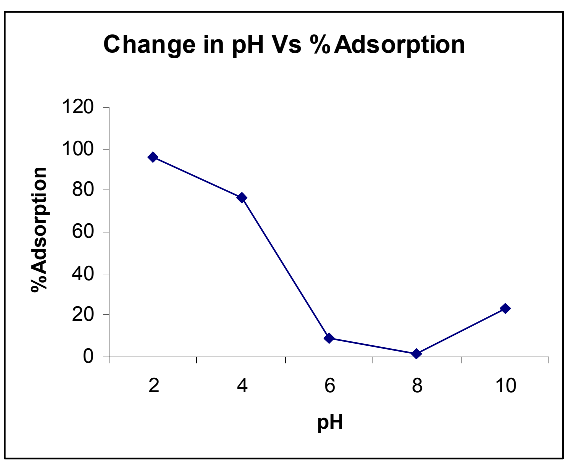

Fig. 7: Effect of pH on percentage adsorption of Brilliant Vital Red dye.

The effect of variation in the stirring speed on the biosorption process was studied. The results are shown in Fig. 8. It was observed that adsorption yield increased with decrease in stirring speed. The minimum adsorption was 63 % for a speed of 400 rpm and maximum adsorption was 73 % for speed of 300 rpm, with 25 ppm initial concentration of the dye solution. By increasing the speed further, there was no further increase in adsorption. This is because all binding sites have been utilized and no binding sites were available for further adsorption. This is also supported by literature. An increasing agitation rate may reduce the film boundary layer, surrounding the sorbent particles, thus increasing the external film diffusion rate and the uptake rate [31].

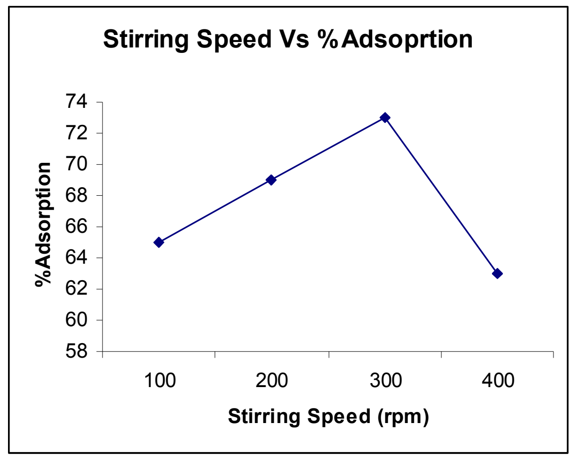

Fig. 8: Effect of stirring speed on percentage adsorption of Brilliant Vital Red dye.

Temperature is a critical parameter for biosorption processes. The percentage adsorption was studied at various temperatures. The results are shown in Fig. 9. It was observed that adsorption yield decreased with increase in temperature. The minimum adsorption was 52 % at 50 $^{\circ}$C and maximum adsorption was 74 % at 30 $^{\circ}$C for 25 ppm initial concentration of the dye solution. It was observed that the percentage of adsorption decreased at higher temperatures. The decrease in adsorption might happen due to the fact that at high temperature, the dye molecules move with greater speed and less time of interaction was available for adsorbate with biosorbent material.

The Langmuir isotherm was shown in Fig. 10 and the corresponding parameters are given in Table-4. 'Q_{max}' value was 10.06. Value of 'R^2' i.e. 0.8356 is showing correlation or linear relationship. R^2 (correlation coefficient) value approaching to one, clearly suggested that Langmuir isotherm holds good to explain adsorption of Brilliant Vital Red on rice husk. 'b' (an adsorption equilibrium constant related to apparent energy of biosorption) for Brilliant Vital Red dye is 0.269 L g^{-1}. The biosorption mechanism for the removal of dyes may be supposed to involve the following three steps:

- Diffusion of the dye through the boundary layer,
- Adsorption of the dye on the biosorbent surface and
- Intra-particle diffusion.

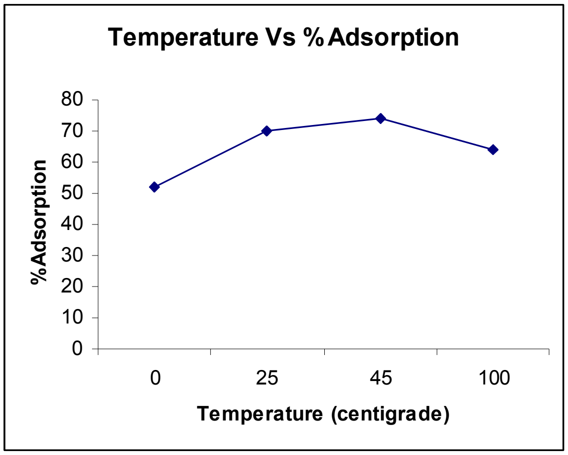

Fig. 9: Effect of temperature on percentage adsorption of Brilliant Vital Red dye.

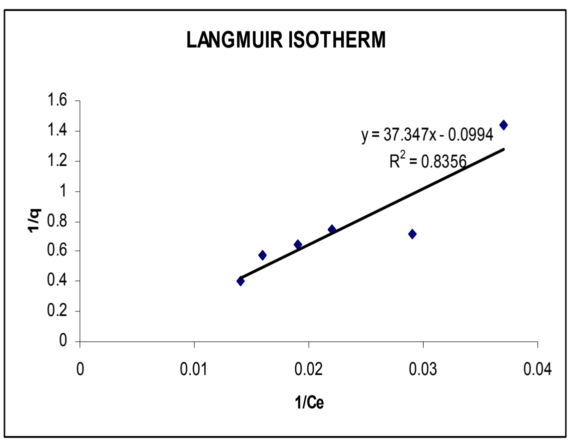

Fig. 10: Langmuir isotherm for adsorption of Brilliant Vital Red dye on rice husk.

Table-4: Langmuir Isotherm parameters.

Slope	Intercept	R^2	Q_{max}	B
37.347	0.0994	0.8356	10.06	0.269

The boundary layer resistance will be affected by the rate of biosorption and increase in contact time, which will reduce the resistance and increase the mobility of dye during biosorption. Since the uptake of dye at the active sites of rice husk is a rapid process due to less contact time between adsorbate and biosorbent requirement and more removing efficiency, the rate of biosorption is mainly governed by liquid phase mass transfer rate, diffusion through the boundary layer or intra-particle mass transfer rate [32].

Experimental Work

Chemicals

All chemicals used during experimental work were of Anal R grade and were used as such without further purification. Brilliant Vital Red (Fluka, λmax = 500 nm, Mol. Wt = 284.19 g/mol, reddish purple), HCl (Merck, 11.6 M), NaOH (Merck, Mol. Wt = 40g/mol). Double distilled water was used for the preparation of all types of solutions and dilutions where ever required.

Instrumentation

Balance ER-120A (AND), Electric grinder (KenWood), pH meter (HANNA pH 211), UV/VIS spectrophotometer (Labomed, Inc. Spectro UV-Vis double beam UVD= 3500).

Standard Solutions

1.0 g of Brilliant Vital Red was taken in 1000 mL measuring flask and dissolved in double distilled water, making volume up to the mark. This was 1000 ppm stock solution of the dye. Standard solutions of dye were prepared by successive dilution of the stock solution.

Adsorption Experiments

The adsorption experiments to study the effects of various parameters were carried out at 25 ± 1°C. pH of the solution was adjusted with 0.1 M HCl and 0.1 M NaOH. Rice husk i.e. biosorbent was ground to fine powder and dried in oven at 70°C for 45 minutes. A known amount of rice husk powder was added to the sample and sufficient time was allowed for adsorption equilibrium. The solutions were then filtered. The dye concentration was determined in the filtrate using (Spectro UV-Vis Double Beam UVD-3500, Labomed spectrophotometer at 500 nm (λ_{max}).

A suitable conventional, indigenous and easily available biosorbent for removing Brilliant Vital Red dye is selected for the following study by comparing percentage adsorption of dye by bagasse, wheat husk and rice husk. These biosorbents were washed, dried, ground by using electrical grinder and screened out for uniform particle size of 60-80 microns. 25 mL of dye solution of 25 ppm were taken in three different conical flasks. 01 g of different biosorbents was added in each of them separately. These flasks were agitated at 100 rpm for 20 minutes. After that, the solutions were filtered and the dye concentration was determined in the filtrate. The percentage adsorption was calculated using formula;

$$\%age \quad Adsorption = \frac{C_o - C_e}{C_o} \times 100 \qquad \text{(Eq.1)}$$

where, C_o and C_e, are the concentrations of dye at initial and at equilibrium respectively. Rice husk has greater adsorption power. Various operating conditions which can influence biosorption process were further studied using rice husk as an adsorbent. Thepercentage adsorption is maximum (72 %) in case of rice husk as a biosorbent. So it was selected for further biosorption study.

The effects of various parameters on the rate of biosorption process were observed by varying the mesh size (20-100), to study particle size of adsorbent (20-100 microns), contact time, t (15-60 min), initial concentration of dye C_o (5-30 ppm), biosorbent amount (0.1-0.6 g), initial pH of the solution (2-10), stirring speed (100-500 rpm) and temperature (20-50 $^{\circ}$C). The solution volume (V) was kept constant (25 mL). The dye adsorption (percentage) at equilibrium was determined by using equation 1. To increase the accuracy of the data, each experiment was repeated three times and the average values were taken [33].

Study of Adsorption Isotherm

Six solutions with concentrations 30, 40, 50, 60, 70 and 80 ppm were made by proper dilution of Stock solution of Brilliant Vital Red dye. pH was adjusted to 2.0 by using 0.1 M HCl . 0.2 g of biosorbent was added to 50 mL of each dye solution and was agitated for 15 minutes. At the end, suspensions were filtered off and filtrates were analyzed for remaining dye concentration by using (Spectro UV-Vis Double Beam UVD-3500, Labomed spectrophotometer at 500 nm (λ_{max}).

Data Evaluation

Langmuir isotherm was plotted by using standard straight-line equation and corresponding two parameters for Brilliant Vital Red dye were calculated from its graph.

$$\frac{1}{q_e} = \frac{1}{bq_m C_e} + \frac{1}{q_m} \qquad \text{(Eq.2)}$$

where q_e (mg g^{-1}) is the amount of dye adsorbed and C_e (ppm) is concentration of dye at equilibrium. q_m (mg g^{-1}) (or Q_{max}) and b (L g^{-1}) are Langmuir isotherm parameters [33-35].

Conclusion

From this study, it is concluded that the rice husk is a good choice among conventional, indigenous and easily available biosorbents for the removal of Brilliant Vital Red dye from aqueous media. Optimum conditions for the removal of Brilliant Vital Red dye using rice husk were: 0.2 g of biosorbent, 25 ppm initial dye concentration, 30^{o}C temperature, 15 minutes contact time, 300 rpm stirring speed and 2.0 pH. Q_{max} value was 15.06 which indicated that rice husk can effectively be used for the removal of Brilliant Vital Red dye from wastewater using the optimized operational conditions.

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