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Removal of anionic dyes by rice milling waste from synthetic effluents: equilibrium and thermodynamic studies

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ABSTRACT

This study describes the removal of Everdirect Orange-3GL and Direct Blue-67 by low cost rice milling waste in a batch mode. The effect of various process parameters like solution pH, particle size, biosorbent dose, initial dyes concentration, contact time and temperature on the removal of anionic dyes was investigated. Maximum biosorption capacity of rice milling waste was observed at pH 1 and 3 for Everdirect Orange-3GL and Direct Blue-67, respectively. The results showed that the biosorption capacity of rice milling waste decreased with increase in biosorbent dose and increased with increase in initial dyes concentration and temperature. A maximum biosorption capacity of 31.44 and 52.63 mg/g was observed for Everdirect Orange-3GL and Direct Blue-67, respectively. Analysis of equilibrium data was done by commonly used isotherms. The experimental data followed the Langmuir, Freundlich and Temkin isotherm models very well. Adsorption data of both dyes was better described by the pseudo-second-order kinetic model. Thermodynamic study revealed that the process was feasible and spontaneous at higher temperatures. Positive value of $\Delta H°$ (13.31 and 40.64 kJ/mol) showed that the process was endothermic in nature. FT-IR spectrum was also taken to investigate the functional groups involved in the biosorption of anionic dyes. The results suggested the applicability of rice milling waste in industrial processes for remediation of industrial effluents.

Keywords: Everdirect Orange-3GL; Direct Blue-67; Biosorption; Thermodynamics; Kinetics; Equilibrium models

1. Introduction

Dyes are extensively used in textile, paper, leather, plastics, cosmetics, pharmaceuticals and food industries to color various substances [1]. Textile sector is one of the largest consumers of synthetic dyes. The amount of textile dyes discharging into the aquatic streams is approximately 1000 tones per annum [2]. Discharging of wastewater containing dyes into the aqueous streams is hazardous to aquatic life. The polluted water is also harmful to human beings and animals and their metabolites are highly toxic [3,4]. Even a minute amount of dye (1 ppm) is highly visible and shows color in water stream. This color is undesirable from a ecological point of view as the photosynthetic activity is disturbed by blocking the penetration of sunlight [5].

A number of conventional treatment methods like coagulation, chemical precipitation, membrane filtration, solvent extraction, chemical oxidation, photolysis, reverse osmosis and flocculation have been used for the treatment of dye containing wastewaters [6]. However, these methods are generally ineffective in color

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removal and expensive for the treatment of dyes containing wastewaters. Adsorption has been observed to be an effective process for color removal from industrial effluents. Adsorption has been distinguished as the most popular treatment method for the removal of dyes from aqueous solution showing advantages of high efficiency, simple operation, easy recovery and reuse of adsorbent [7,8].

Recently a number of studies have been focused on low cost biomaterials that are capable of removing dyes from wastewaters. Some low cost biosorbents such as deolied soya [6], barley husk [9], citrus waste [10,11], hen feathers [12], sunflower seed hull [13], coconut husk [14], raw date pits [15], etc. have been used by various workers. However, these low-cost adsorbents have generally low adsorption capacities and require large amounts of adsorbents. Therefore, there is a need to find new, economical, easily available and effective adsorbents.

Milling of rice crop produces rice husk as agriculture waste material having no commercial significance. The rice milling waste contains about 20% silica and other organic substances such as cellulose, hemicellulose and lignin. The main aim of the present research study was to investigate the potential of this lignocellulosic waste material for the removal of anionic direct dyes, Everdirect Orange-2GL and Direct Blue-67 from aqueous solutions in batch system.

2. Materials and methods

2.1. Preparation of rice milling waste

Fresh rice milling waste was procured from local rice mills. The biomass was washed several times with distilled water to remove dust and other foreign particles. The cleaned biomass was first dried in sunlight and then in an oven at 70 °C for 12 h. The washed materials was ground with food processor (Moulinex, France) and sieved using Octagon sieve (OCT-DIGITAL 4527-01) to various mesh sizes: < 0.250, 0.250–0.355, 0.355–0.500, 0.500–0.710 and 0.710–1.000 mm.

2.2. Preparation of aqueous dye solutions

In the present investigation, two anionic dyes, Everdirect Orange-3GL (C.I. no, Orange-39) and Direct Blue-67 (C.I. no, 27925) were used. These dyes were gifted by Sandal Dye Stuff Industry, Faisalabad, Pakistan. Stock solutions of both dyes were prepared by dissolving 1.0 g of each dye in 1000 mL of double distilled water. The experimental solutions of different concentrations ranging from 25 to 150 mg/L for Everdirect Orange-2GL and from 25 to 300 mg/L for Direct Blue-67 were made by further dilutions. Standard curves were developed at λ_{max} 415 and 570 nm for Everdirect Orange-3GL and Direct Blue-67, respectively through the measurement of the dye solution absorbance by UV/Visible spectrophotometer (Hitachi U-2001).

2.3. Batch biosorption experimental studies

Optimization of various process parameters such as pH, biosorbent dose, particle size, initial dye concentration, contact time and temperature was carried out using classical approach. The 250-mL conical flasks containing 50 mL of dyes solution of known pH, concentration and biosorbent dose were shaken in orbital shaking incubator (PA250/25H) at 100 rpm. Blank solutions were also run under the same conditions except the addition of biosorbent material. To study the effect of pH, various pHs (1–8 for Everdirect Orange-3GL and 3–8 for Direct Blue-67) were adjusted using 0.1 M HCl and NaOH solutions. After certain time, the samples were taken out and centrifugation was performed at 2000 rpm for 20 min.

The amount of biosorbed dye per unit mass was calculated using following equation:-

$$q = (C_0 - C_e)V / W \tag{1}$$

where q is the amount of dye biosorbed on the biosorbent (mg/g), C_0 and C_e are the initial and equilibrium concentration of dye solution, respectively. V is the volume of dye solution (L) and W is the amount of the rice milling waste (g).

All the experiments were conducted in triplicate and results are reported as mean ± SD.

2.4. Adsorption equilibrium studies

Adsorption equilibrium provides fundamental physiochemical data for evaluating the applicability of sorption process as a unit operation. In this study, five most common adsorption isotherm models were employed viz., the Langmuir [16], Freundlich [17], Temkin [18], Doubinin–Radushkevich [19] and Harkins–Jura isotherm models.

2.5. Adsorption kinetics studies

Information on adsorption kinetics is required for selecting optimum operating conditions for full scale batch process. The biosorption kinetics of Everdirect Orange-3GL and Direct Blue-67 onto rice milling waste was determined by pseudo-first order [20], pseudo-second order [21] and intraparticle diffusion [22] kinetic models.

2.6. Thermodynamics studies

Various thermodynamics parameters such as enthalpy changes ($\Delta H°$), entropy changes ($\Delta S°$) and Gibbs free energy changes (ΔG°) were used to determine the spontaneity of biosorption process. The Gibbs free energy (ΔG°) for the biosorption of dyes by rice milling waste biomass was calculated using following equation:

$$\Delta G^{\circ} = -RT \ln K_c \qquad (2)$$

where K_c is the equilibrium constant (q/C_e), R is gas constant (8.314 kJ mol^{-1} K^{-1}), and T is the solution temperature (K).

3. Results and discussion

3.1. Effect of pH

The effect of pH on the biosorption of direct dyes was investigated over a pH range 1.0–8.0 for Everdirect Orange-3GL and 3–8 for Direct Blue-67, respectively. The pH less than 3.0 was not studied due to color change by the dye solution and hence its structural characteristics [23]. The results showed the maximum biosorption was recorded at pH 1.0 and 3.0 for Everdirect Orange-3GL and Direct Blue-67, respectively (Fig. 1). At higher pH value, the biosorption of both anionic dyes was not effective. A maximum biosorption capacity of 19.92 and 16.27 mg/g was observed for Everdirect Orange-3GL and Direct Blue-67, respectively, at the optimum pH. The percentage removal efficiency decreased from 52.54% at pH 1.0 to 18.68% at pH 8.0 for Everdirect Orange-3GL and from 59.07% at pH 3.0 to 3.89% at pH 8.0 for Direct Blue-67. The pH value of the dye solution is a most important controlling factor that should not be neglected during the biosorption process [24]. The exchanging sites of biosorbents and ionization/dissociation process of dye molecules are strongly affected by pH changes. An increase in H$^+$ ion concentration occurs at low pH and the surface of the rice milling waste gets positive charge by taking H$^+$ ions. A strong electrostatic interaction develops between positively charged biomass surface and negatively charged dye molecule. At high pH value, electrostatic repulsion appears due to number of negatively charged sites on the biosorbent [25,26]. Adsorption also decreases due to excess of OH$^-$ ions which show competition with dye anions for the binding sites [27]. A similar behavior was observed for the adsorption of anionic dyes by the hybrid material prepared from octadecyl dimethyl hydroxyethyl quaternary ammonium (SN) and magnesium silicate. This hybrid contained a large number of positive charges which attracted the anionic dyes [28].

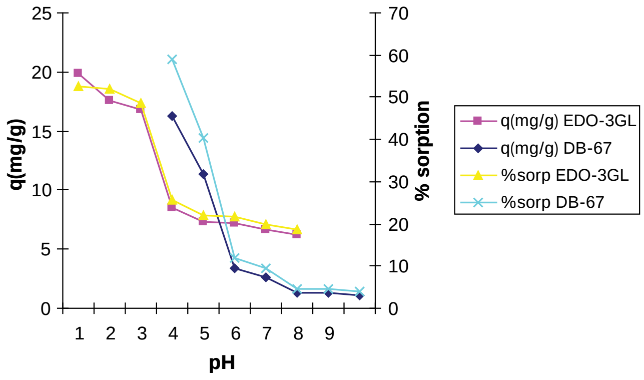

Fig. 1. Effect of pH on the biosorption of Everdirect Orange-3GL and Direct Blue-67 dyes (biosorbent dose: 0.09 g/50 mL for Everdirect Orange-3GL and 0.1 g/50 mL for Direct Blue-67, Co: 50 mg/L, Temp: 30 °C, shaking speed: 100 rpm, contact time: 3 h and 4 h for Everdirect Orange-3GL and Direct Blue-67 dyes, respectively, particle size: 0.255 mm).

3.2. Effect of biosorbent dose

The effect of biosorbent dose on the biosorption of Everdirect Orange-3GL and Direct Blue-67 on rice milling waste was evaluated by varying the biosorbent doses and results are reported in Fig. 2. The quantity of dye biosorbed decreased from 23.33 to 6.87 mg/g for Everdirect Orange-3GL and 17.42 to 3.98 mg/g for Direct Blue-67, while the percent dye removal increased from 32.24% to 97.92% for Everdirect Orange-3GL and from 39.07% to 74.44% for Direct Blue-67, respectively. Maximum biosorption capacity (mg/g) was observed at 0.05 and 0.1 g of biosorbent dose for Everdirect Orange-3GL and Direct Blue-67, respectively. The increase in biosorption capacity with small dose is due to large surface area of mesopores and an increase in the number of available binding sites [27]. The dye removal capacity of biomass decreased due to the saturation of the binding sites at large amount of biosorbent doses. Bulut et al. [29] reported that the biosorption of Direct Blue 71 by wheat shells from aqueous solution occurred at low

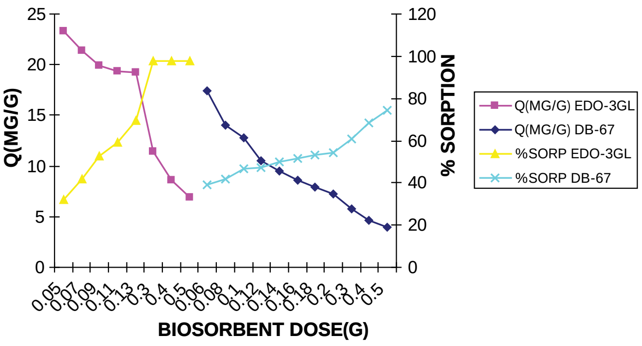

Fig. 2. Effect of biosorbent dose on the biosorption of Everdirect Orange-3GL and Direct Blue-67 dyes (pH: 1, Co: 50 mg/L, Temp: 30 °C, shaking speed: 100 rpm, contact time: 3 h and 4 h for Everdirect Orange-3GL and Direct Blue-67 dyes, respectively, particle size: 0.255 mm).

biosorbent doses. Similar behavior regarding the biosorption of anionic dye on peanut hull was observed by Gong et al. [30].

3.3. *Effect of biosorbent particle size*

The effect of biosorbent size on the biosorption of Everdirect Orange-3GL and Direct Blue-67 is represented in Fig. 3. The particle size of biosorbent decreased the time necessary for the passage of dye molecules into the pores of the exchanging sites. The results show that biosorption capacity decreased with increase in the particle size for both the dyes. The maximum biosorption capacity (14.00 mg/g for Everdirect Orange-3GL and 16.27 mg/g for Direct Blue-67) was recorded with the smallest particle size (0.255 mm mesh size). The smallest particle size (0.255 mm) of the biomass was subsequently used to study other process parameters for both the dyes. The smallest size of the particles provides large surface area and more binding sites for the adsorbate [31,32]. Gong et al. [30] also investigated the removal of anionic dyes by powdered peanut hull biomass which increased with decrease in the biosorbent particle size.

3.4. *Effect of initial dye concentration*

The effect of initial concentration of Everdirect Orange-3GL and Direct Blue-67 onto the biosorption capacity of rice milling waste was investigated by varying the initial concentrations of Everdirect Orange-3GL (25–150 mg/L) and Direct Blue-67 (25–200 mg/L) at different biosorbent dosages (0.05, 0.1 g/50 mL for Everdirect Orange-3GL and (0.1, 0.2 g/50 mL) for Direct Blue-67). The biosorption capacity of biomass increased from 14.16 to 27.72 mg/g and 12.95 to 25.59 mg/g for Everdirect Orange-3GL and 6.18 to 37.16 mg/g and 3.92 to 23.21 mg/g for of Direct Blue-67 with increase in the initial dye concentration. However, the percent dye removal decreased with increase in the dye concentration. This effect is illustrated in Figs. 4 and 5. The amount of dye biosorbed increased because the dye ions adsorbed on the outer surface of the biomass and then finally began to adsorb internally [33,34]. The percentage removal decreased with increase in the dye concentration due to accumulation of dye ion at higher concentrations. Such accumulation decreased the availability of the total surface area of the biosorbent particle for biosorption [30]. Tunc et al. [35] also reported a decrease in percentage removal of Ramazol Black B reactive dye due to saturation of exchanging sites at higher dye concentration using cotton plant waste.

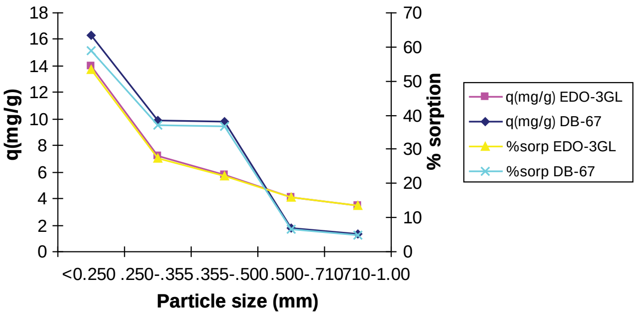

Fig. 3. Effect of particle size on the biosorption of Everdirect Orange-3GL and Direct Blue-67 dyes (biosorbent dose: 0.09 g/50 mL for Everdirect Orange-3GL and 0.1 g/50 mL for Direct Blue-67, Co: 50 mg/L, Temp: 30 °C, shaking speed: 100 rpm, contact time: 3 h and 4 h for Everdirect Orange-3GL and Direct Blue-67 dyes, respectively, pH: 1).

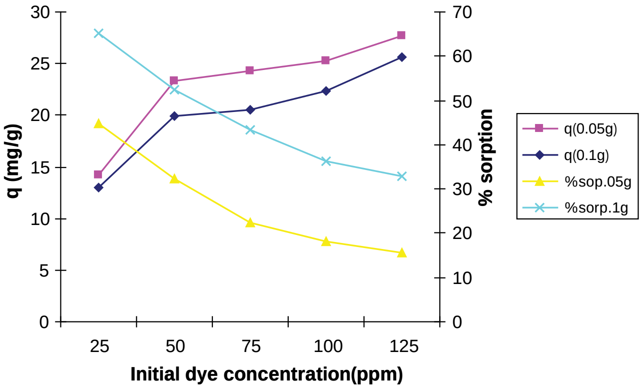

Fig. 4. Effect of initial dye concentration on the biosorption of Everdirect Orange-3GL dye at different biosorbent doses, 0.05 g and 0.1 g/50 mL (Co: 25, 50, 75, 100 and 125 mg/L, Temp: 30 °C, shaking speed: 100 rpm, contact time: 3 h, particle size: 0.255 mm, pH: 1).

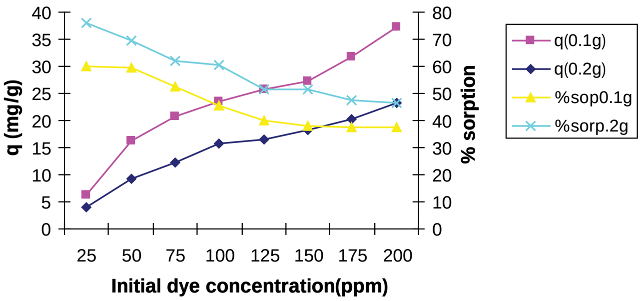

Fig. 5. Effect of initial dye concentrations on the biosorption of Direct Blue-67 dye at different biosorbent doses, 0.1 g and 0.2 g/50 mL (Co: 25, 50, 75,100, 125, 150, 175 and 200 mg/L, Temp: 30 °C, shaking speed: 100 rpm, contact time: 4 h, particle size: 0.255 mm, pH 3).

3.5. *Effect of contact time*

The biosorption capacity of rice milling waste for Everdirect Orange-3GL and Direct Blue-67 was evaluated as a function of time and results are depicted in Figs. 6 and 7. The amount of dye biosorbed (mg/g) by the biosorbent increased rapidly with the increase in contact time. When the agitation time was further increased, there was no drastic increase in the biosorption capacity of the biosorbent. The equilibrium time for the Everdirect Orange-3GL and Direct Blue-67 was 180 and 240 min, respectively, although the results were recorded after for 300 min. After the establishment of equilibrium, an even, flattened saturation curve was obtained for each dye. The amount of dye biosorbed at equilibrium was 12.95 mg/g (at 25 mg/L), 19.92 (at 50 mg/L) and 6.18 (at 25 mg/L), 16.27 (at 50 mg/L for Everdirect Orange-3GL and Direct Blue-67, respectively). It was generally observed that the biosorption capacity increased with time and after certain time reached to equilibrium. In the beginning, the fast biosorption might be attributed to presence of positive charged on the rice milling waste surface which developed an interaction with negatively charged dye molecules. Then the biosorption began to slow down due to slow movement of dye molecule into the interior of bulk of the biosorbent [27]. Another reason was large number of exchanging sites helped the biosorption process and then saturation occurred [36]. Waranusantigul et al. [37] reported that rate of biosorption of basic dye (methylene blue) biosorption by giant duckweed increased with increase in the agitation time. In another study, Akar et al. [38] observed that the amount of Acid Blue 40 dye biosorbed (mg/g) by cone biomass *Thuja orientalis* increased with increase in the contact time.

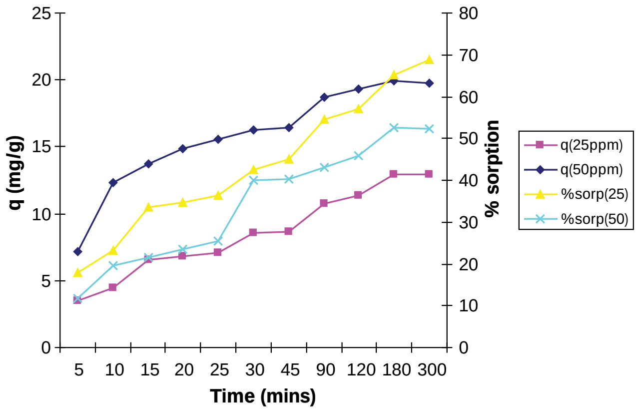

Fig. 6. Effect of contact time on the biosorption of Everdirect Orange-3GL dye at different initial dye conc., 25 mg and 50 mg/L (biosorbent dose 0.09 g/50 mL, Temp: 30 °C, shaking speed: 100 rpm, contact time: 3 h, particle size: 0.255 mm, pH: 1).

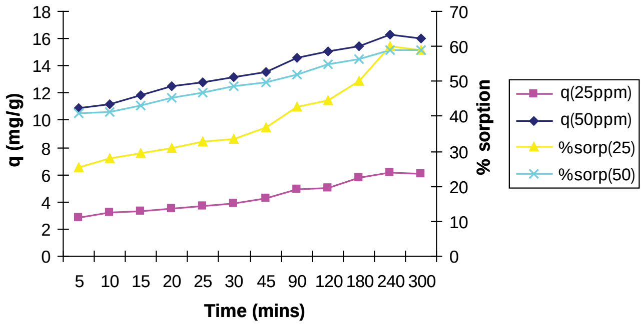

Fig. 7. Effect of contact time on the biosorption of Direct Blue-67dye at different initial dye conc., 25 mg and 50 mg/L (biosorbent dose 0.1 g/50 mL, Temp: 30 °C, shaking speed: 100 rpm, contact time: 4 h, particle size: 0.255 mm, pH: 3).

3.6. Effect of temperature

The results regarding the effect of temperature on the biosorption of Everdirect Orange-3GL and Direct Blue-67 onto rice milling waste are shown in Fig. 8. The results indicated that with an increase in temperature from 30 to 70 °C the amount of dyes biosorbed (mg/g) increased. The biosorption capacity of the biomass for Everdirect Orange-3GL was found to be 19.92 mg/g at 30 °C and 39.27 mg/g at 70 °C. Similarly for Direct Blue-67, the amount of dye biosorbed was 16.27 and 25.82 mg/g at 30 °C and 70 °C, respectively. The biosorption of both dyes was favorable at high temperatures indicating the endothermic nature of the process. This might be due to increase in the number of molecules attaining sufficient energy to undergo chemical reaction with the biosorbent [28]. Another reason was the increase in the number of pores on the biomass surface at high temperature. The elevated temperature reduced the thickness of outer surface of the biosorbent and increased the kinetic energy of dye molecules, as a result the dye molecules biosorbed easily into the surface of the bio-

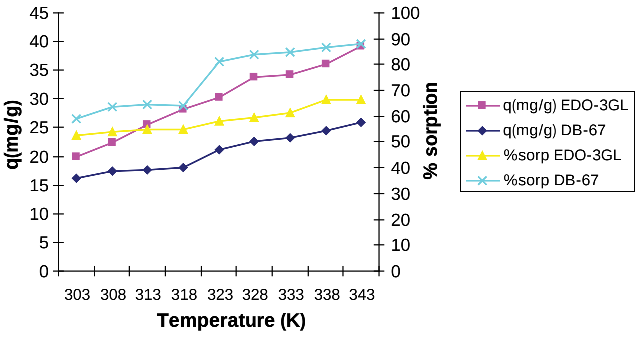

Fig. 8. Effect of temperature on the biosorption of Everdirect Orange-3GL and Direct Blue-67 dyes (pH:1, biosorbent dose: 0.09 g/50 mL for Everdirect Orange-3GL and 0.1 g/50 mL for Direct Blue-67, Co: 50 mg/L, shaking speed: 100 rpm, contact time: 3 h and 4 h for Everdirect Orange-3GL and Direct Blue-67 dyes, respectively, particle size: 0.255 mm).

mass [39]. Aksu and Tezer [40] investigated that the rate of biosorption of reactive dyes on the green algae *Chlorella vulgaris* increased with increase in the temperature. Similar trend in the increase of biosorption of Ramazol Black B by *R. arrhizus* with increase in temperature was reported by Aksu and Tezer [41].

3.7. Biosorption equilibrium modeling

Equilibrium data commonly known as biosorption isotherm are basic requirements for the design of adsorption systems. Analysis of results obtained from the equilibrium isotherm studies is fundamental to evaluate the affinity of biosorbent for a particular sorbate. Five different models like Langmuir, Freundlich, Temkin, Doubinin–Radushevich (D–R), and Harkins–Jura isotherm were used to test or estimate the equilibrium data obtained in this research work. The comparison of the coefficients of determination (R^2) of all models suggests whether the isotherm equation is applicable or not.

3.7.1. Langmuir isoth erm

The monolayer coverage of the sorbate on a sorbent surface at constant temperature is represented by Langmuir isotherm, the biosorption of solute from aqueous solution onto the biosorbent surface is occurred as monolayer biosorption on the homogeneous number of exchanging sites. The linear Langmuir isotherm equation can be presented in the following equation:

$$C_e / q_e = C_e / q_m + 1 / K_a q_m \tag{3}$$

where q_e is the amount of dye biosorbed on the biosorbent (mg/g) at equilibrium, C_e is the equilibrium concentration of dye solution, q_m is the maximum biosorption capacity describing a complete monolayer adsorption (mg/g) and K_a is adsorption equilibrium constant (L/mg) that is related to the free energy of biosorption. The values of various Langmuir constants are described in Table 1. The values of coefficient of determination were high for Everdirect Orange-3GL and Direct Blue-67. The results showed that the Langmuir model was the best fitted model for both the dyes. The important features of the Langmuir isotherm model can be defined by the dimensionless constant separation factor R_L which is expressed by the following equation [42]:

$$R_L = 1 / (1 + K_a C_0) \tag{4}$$

C_0 is the initial dye concentration (mg/L) and K_a is the Langmuir constant (L/mg). R_L shows the nature of biosorption mechanism.

The value of R_L obtained in the present study was in the range of 0–1, describing that the biosorption process was favorable for the both direct dyes.

3.7.2. Freundlich isotherm

The Freundlich isotherm is regarded as an empirical isotherm and it is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface of the sorbent. The linear equation is expressed as follows:

$$\ln q_e = \ln K_F + 1/n \ln C_e \tag{5}$$

where K_F is the Freundlich isotherm constant (mg/g) related to the bonding energy. K_F is defined as the distribution coefficient and suggests the amount of dye biosorbed on the biosorbent for unit equilibrium concentration. The value of n indicates whether the biosorption process is favorable or not. The value of n for favorable adsorption should be greater than 1 [43].

The value of K_F, correlation coefficient and n of both dyes are presented in Table 1. The R^2 values for Everdirect Orange-3GL and Direct Blue-67 showed that the experimental data also fitted well to Freundlich isotherm at higher doses. The values of n are greater than 1 representing that the biosorption of Everdirect Orange-3GL and Direct Blue-67 onto rice milling waste is a favorable physical process [44].

3.7.3. Temkin isotherm

According to Temkin isotherm model there is a linear decrease in the heat of biosorption of the molecules in the layer. This decline is due to adsorbate–adsorbate interactions. And there is equal distribution of maximum binding energy during the biosorption process [45]. In contrast with the Freundlich isotherm; the decrease in the heat of adsorption is linear but not logarithmic. The linear form of Temkin isotherm can be written as

$$q_e = B \ln A + B \ln C_e \tag{6}$$

where $B = RT/b$, T is the absolute temperature in Kelvin and R is the universal gas constant (8.314 J mol^{-1} K^{-1}), A is the equilibrium binding constant and B is corresponding to the heat of sorption. The results of the isotherm parameters/constants are also displayed in Table 1. The coefficient of determinations ($R^2 = 0.951$) for Everdirect Orange-3GL and Direct Blue-67 ($R^2 = 0.964$) were high and showed good linearity. Thus the Temkin isotherm fit well to the data provided by the biosorption of both dyes onto the rice milling waste. The values of Tempkin constant, B obtained from the plot showed that the biosorption process was endothermic in nature. The good linear fitting of the Tempkin isotherm to experimental data is an indication of the strong interaction between the dyes and rice milling waste.

Table 1
Biosorption isotherm constants for the biosorption of Everdirect Orange-3GL and Direct Blue-67 on rice milling waste

Isotherm models	Everdirect Orange-3GL		Direct Blue-67	
	0.05 g	0.01 g	0.1 g	0.2 g
Langmuir				
q_m (mg/g)	30.58	28.41	50.00	29.412
K_a (L/mg)	0.052	0.061	0.018	0.027
R_L	0.098	0.095	0.223	0.157
R^2	0.994	0.986	0.937	0.969
Freundlich				
K_F	6.50	6.41	2.09	1.79
N	3.39	3.37	1.69	1.81
R^2	0.910	0.940	0.952	0.981
Temkin				
A (1/g)	0.754	0.949	0.208	0.326
B	5.88	5.40	10.11	5.96
R^2	0.939	0.951	0.952	0.964
Doubinin–Radushkevich				
q_m (mg/g)	26.05	22.89	32.59	21.39
$K{\cdot}10^4$(mol^2 KJ^{-2})	3.0	2.0	12.0	9.0
E (kJ mol^{-1})	0.408	0.5	0.204	0.236
R^2	0.973	0.916	0.714	0.865
Harkins–Jura				
A	263.16	222.22	333.33	90.909
B	2.39	2.29	2.67	2.18
R^2	0.852	0.881	0.962	0.919

3.7.4. Doubinin–Radushkevich (D–R) isotherm

Another isotherm model Doubinin–Radushkevich (D–R) isotherm was used to analyze the experimental data. The (D–R) isotherm model is more generalized model as compared to Langmuir isotherm. This model is based on the fact that there is no homogeneous surface or constant adsorption potential. It is used for estimation of the porosity apparent free energy. The linear form of (D–R) isotherm model [19] can be seen below:

$$\ln q_e = \ln Q_m - K\varepsilon^2 \quad (7)$$

where K is a constant corresponding to the biosorption energy, Q_m the theoretical saturation capacity and ε is the Polanyi potential which is calculated from equation below:

$$\varepsilon = RT\ln\left(1 + 1/C_e\right) \quad (8)$$

where R (kJ mol^{-1} K^{-1}) is the gas constant and T (K) is the absolute temperature. The mean free energy of biosorption (E) can be defined as the free energy change when 1 mol of ion is transferred from infinity in solution to the biosorbent. E was calculated from the K value by the following relation [46]:

$$E = 1/(2K)^{1/2} \quad (9)$$

The calculated values of D–R parameters for the biosorption of Everdirect Orange-3GL and Direct Blue-67 are given in Table 1. The value of coefficient of determination for Everdirect Orange-3GL ($R^2 = 0.973$) suggests that the D–R model is also fitted very well to the data. On the other hand, the equilibrium data did not fit well for Direct Blue-67 ($R^2 = 0.865$). The values of (E) shown in Table 1 indicated that the physico-chemisorption mechanism plays an important role in the biosorption of both direct dyes onto rice milling waste.

3.7.5. Harkins–Jura isotherm model

The Harkins–Jura isotherm model can be written as:

$$1/q_e = (B/A) - (1/A)\log C_e \tag{10}$$

This isotherm account for multilayer adsorption and can be explained with the existence of heterogeneous pore distribution. The values of various constants are shown in Table 1. The value of coefficient of determination of Everdirect Orange-3GL ($R^2 = 0.881$) is low so data did fit well for this dye. But for Direct Blue-67 R^2 value is comparatively high ($R^2 = 0.962$) showing that the model is well fitted to data.

3.8. Biosorption kinetic studies

Kinetics model are used to examine the rate of adsorption process and potential rate controlling step. In the present work, the kinetic data obtained from batch studies have been analyzed by pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models. The applicability of these kinetic models was determined by measuring the coefficient of determination (R^2) and the experimental q_e.

3.8.1. Pseudo-first-order kinetic model

The Lagergren pseudo-first-order kinetic model is generally expressed as

$$dq_t / dt = k_1(q_e - q_t) \tag{11}$$

where q_e and q_t are the biosorption capacity (mg/g) at equilibrium and time t, respectively, k_1 is the rate constant (L min^{-1}) of pseudo-first-order kinetic model.

After integrating the above equation and applying boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ the equation becomes:

$$\log(q_e / q_e - q_t) = k_1 / 2.303t \tag{12}$$

By rearranging the above equation, following linear form is obtained.

$$\log(q_e - q_t) = \log(q_e) - k_1 / 2.303t \tag{13}$$

The values of rate constant k_1, q_e calculated, q_e experimental and R^2 of Everdirect Orange-3GL and Direct Blue-67 are presented in Table 2. The values of q_e experimental did not show well agreement with the q_e calculated in both dyes, although the values of R^2 are satisfactory. Mostly the first-order kinetic model is not fitted well for whole data range of contact time and can be applied for preliminary stage of biosorption mechanism [42,47]. This indicated that the first-order kinetic model could not be applicable to the biosorption of Everdirect Orange-3GL and Direct Blue-67 dyes onto rice milling waste. The biosorption of methylene blue onto the L cylindrical fibers also followed pseudo-first-order kinetics [48].

3.8.2. Pseudo-second order kinetic model

The pseudo-second order kinetic model equation is generally given as:

$$dq_t / dt = k_2(q_e - q_t)^2 \tag{14}$$

where k_2 (g/mg min) is the second-order rate constant of biosorption process.

By integrating and applying boundary conditions $t = 0 - t$ and $q_t = 0 - q_t$, the above equation can be written in linear form as follows:

$$(t/q_t) = 1/k_2 q_e^2 + 1/q_e(t) \tag{15}$$

The second-order parameters k_2, q_e calculated, q_e experimental and R^2 of Everdirect Orange-3GL and Direct Blue-67 are shown in Table 2. The q_e calculated and q_e experimental for both direct dyes are very close to each other which suggested the applicability of data to pseudo-second-order kinetic model. The coefficient of determination (R^2 =0.999 for Everdirect Orange-3GL) and (R^2 =0.999 for Direct Blue-67) are also very high. Ncibi et al. [24] and Acemioglu [49] reported that the removal of textile metal-complexed dye by *Posidonia oceanica* (L) leaf sheaths and uptake of Congo red from aqueous solution by calcium rich fly ash followed pseudo-second order kinetics.

3.8.3. Intraparticle diffusion model

The movement of dye molecules (adsorbate) from aqueous solution to the biosorbent surface takes place through various steps. In the first step called bulk diffusion, the transportation of dye molecules to the solid

Table 2
Comparative study of kinetic parameters for the biosorption of Everdirect Orange-3GL and Direct Blue-67 on rice milling waste

Kinetic models	Everdirect Orange-3GL		Direct Blue-67	
	25 mg/L	50 mg/L	25 mg/L	50 mg/L
Pseudo-first order				
K_1 (L min^{-1})	17.50×10^3	13.13×10^3	9.212×10^3	9.21×10^3
q_e experimental (mg/g)	12.95	19.92	6.18	16.27
q_e calculated (mg/g)	2.69	2.29	1.67	1.94
R^2	0.952	0.925	0.847	0.924
Pseudo-second order				
K_2 (g/mg min)10^4	0.00347	0.00628	0.00923	0.0089
q_e calculated (mg/g)	13.831	20.408	6.365	16.37
R^2	0.997	0.999	0.994	0.999
Intraparticle diffusion				
K_{pi} (mg/g min$^{1/2}$)	0.6304	0.665	0.226	0.354
C_i	3.797	10.868	2.554	10.724
R^2	0.882	0.690	0.976	0.929

biosorbent phase takes place. Second step involves the boundary layer diffusion of adsorbate molecules on the biosorbent surface which is called film diffusion. In the third step called pore or intraparticle diffusion, the dye molecules move from outer surface of biosorbent into the internal pores. The fourth step involves a chemical reaction in which the dye is adsorbed onto the active binding sites of the biosorbent material. The biosorption mechanism may be controlled by single step or combination of many steps.

In batch experiment system which involves fast and continuous stirring, the intraparticle diffusion is only the rate determining or rate controlling step [50]. The intraparticle diffusion equation is written as follows:

$$q_t = K_{pi} \cdot t^{1/2} + C_i \tag{16}$$

where C_i is the intercept which describes the boundary layer thickness and K_{pi} (mg/g min$^{1/2}$) is the rate constant of intraparticle diffusion. The values of K_{pi} and C_i for Everdirect Orange-3GL and Direct Blue-67 are also given in Table 2. According to Ho et al. [51], the intraparticle diffusion played important role in the biosorption process, if the plot of q_t vs $t^{1/2}$ passes through the origin. But the lines were not passed through the origin and values of correlation coefficient from are also low. Thus the results showed that the biosorption of direct dyes on rice milling waste did not only depend on intraparticle diffusion but many other mechanisms might be involved. Therefore, the data is not fitted well to the intraparticle diffusion model. The value of intercept C_i increased with increase in the dye concentration showing the increase in boundary layer thickness.

3.9. Thermodynamic model of biosorption

Various thermodynamic parameters including Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated from the temperature data obtained from the biosorption of Everdirect Orange-3GL and Direct Blue-67 onto rice milling waste. Different temperature ranges (303–343 K) were used. According to van׳t Hoff equation:-

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S \tag{17}$$

$$\begin{aligned} \log(q / C_{\square}) &= -\Delta G / 2.303RT \\ &= -\Delta H / 2.303RT + \Delta S / 2.303RT \end{aligned} \tag{18}$$

The values of ΔG and ΔH for both dyes were determined from the slope and intercept of van׳t Hoff graph. The results indicated that the value of ΔG decreases with an increase in the temperature. This means that biosorption of both dyes increase with increase in temperature and process was spontaneous at higher temperature. The results also show that the biosorption of Everdirect Orange-3GL was spontaneous at 65 and 70 °C, whereas for Direct Blue-67 process was spontaneous above 50 °C. The positive value of ΔH indicated that the biosorption of Everdirect Orange-3GL and Direct Blue-67 on the rice milling waste was endothermic in nature. The biosorption capacity increased with increase in temperature. This might be due to increase in diffusion of direct dyes into the pores of the biosorbent surface and formation of new binding sites at higher temperature [52]. The positive value of entropy (ΔS) shows the increase in randomness at the solid/liquid interface and reflects a good affinity of biomass towards both direct dyes [53]. Namasivayam and Yamuna [54] described that the removal of Direct Red 12B by biogas residual slurry was endothermic process.

3.10. Infra-red study

The FT-IR spectrum indicates the exchanging sites and functional groups on which biosorption of adsorbate takes place. The FT-IR spectrum of rice milling waste was studied in the range of 400–4000 cm^{-1}. FT-IR spectrum of unloaded biomass showed that the peak at 2924.09 cm^{-1} was due of C–H stretching and indicated the presence of –CH and =CH groups present in the lignin structure of rice milling waste. The band at 1728.22 cm^{-1} could be assigned to C=O stretching vibrations. The peaks at 3062.96 cm^{-1} denote the vibrations of –OH functional groups. The peaks appear due to C=O and –OH vibrations attribute the presence of carboxyl group on the surface of biomass. The existence of peak at 1676.14 cm^{-1} and bifurcated peak at 3651.25 cm^{-1} and 3637.75 cm^{-1} might be due to occurrence of amide group on the surface [55]. Due to specific interaction of biomass with dyes, changes in the spectra were observed due to vanishing and broadening of some peaks. The –OH stretching peaks in dyes loaded biomass disappear or absorb at lower frequency which confirmed the involvement of hydroxyl and carboxyl functional groups in the biosorption mechanism. The intensity of –NH peak at 1676.14 cm^{-1} decreased and disappearance of bifurcation at higher frequency suggested that amide group also participate in the biosorption of dyes.

4. Conclusions

Rice milling waste exhibited good biosorption capacity to remove anionic direct dyes from aqueous solution. Maximum biosorption capacity has been observed at low pH and with small particle size of the biosorbent. Biosorption capacity increased with increase the initial dye concentration. The biosorption capacity also increased with increase in the temperature. The experimental data followed the Langmuir, Freundlich, Temkin isotherm models very well. Moreover, the kinetic data fitted well to pseudo-second-order kinetic model. Thermodynamic investigation showed that the biosorption process was spontaneous at high temperature and endothermic in nature. This study described that rice milling waste could be used efficiently to clean the environment.

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