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Equilibrium and kinetic modeling for the removal of Turquoise Blue PG dye from aqueous solution by a low-cost agro waste

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ABSTRACT

The present study deals with the evaluation of cost-effective and abundantly available biomass of sugarcane bagasse for the removal of Turquoise Blue PG dye from aqueous solutions. The biosorbent was utilized in its native, modified, and immobilized forms. For the modification of biomass, it was treated with different acids, alkali, chelating agents, surfactants, and organic solvents. The experiments were conducted to assess the effects of process variables such as medium pH (5–9), biosorbent dose (0.05–0.30 g), contact time (0–180 min), initial dye concentration (10–200 mg/L), and temperature (30–60 °C). H_2SO_4-treated biomass was selected as potential-modified biosorbent for the removal of Turquoise Blue PG dye as it showed maximum biosorption capacity (69.73 mg/g). Biosorption process was favorable at pH 5 using low biosorbent dosage. Equilibrium was achieved in 120 min. The kinetic analysis showed that the pseudo-second-order model had the best fit to the experimental data. The Langmuir model provided the best fit for the experimental data of the equilibrium biosorption of Turquoise Blue PG onto sugarcane bagasse. Biosorption process was found to be endothermic in nature. The thermodynamic evaluation of Turquoise Blue PG biosorption on sugarcane bagasse revealed that the biosorption phenomenon under the selected conditions was a spontaneous physical process. Fourier transform infrared analyses demonstrated the involvement of different functional groups, mainly hydroxyl, carboxyl, and amine groups. Consequently, sugarcane bagasse was proved to be a very proficient, low-cost biosorbent, and a promising alternative for eliminating dyes from industrial effluents.

Keywords: Biosorption; Turquoise Blue PG; Sugarcane bagasse; Kinetic studies; Thermodynamics

1. Introduction

At present, 10,000 of different dyes and pigments are used by industries and more than 0.7 million tons of synthetic dyes are being produced worldwide [1]. Dyeing effluents from textile, dye, and related industries cause serious environmental hazards. Many of the dyes are toxic, carcinogenic, and mutagenic for human and other organisms [2]. In addition, environment quality is being strongly influenced as these effluents show an impact on the color of wastewater and photosynthetic activity of flora in the biosphere [3]. Besides dyes, such effluents also contain a number of other contaminants such as acids, alkalis, heavy metal ions, electrolytes, dissolved, and other

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suspended solids. [4]. Therefore, wastewater treatment becomes the severe problem for the industrial zone [5]. Various treatment approaches involving biological, physiochemical, advanced oxidation, and membrane filtration [6] have been investigated in order to treat dye containing wastewater. However, performance of these treatments is constrained due to their operations, cost, and production of sludge [7]. Currently, attention is being paid to develop low-cost and highly efficient alternative technologies for wastewater treatment. Biosorption has emerged as a viable alternative for the treatment of such colored effluents due to its ease of operation and performance [8]. Biosorption is an interaction of solute molecules with the active surface of the biomass, fixing them in the free sites owing to the action of physical processes (physisorption) and chemical bonds (chemisorption) [9]. The major advantages of adsorption over conventional treatment methods include: high efficiency, low cost, minimization of biological and/or chemical sludge, regeneration of biosorbent, and the possibility of dye recovery [10]. A number of studies have been made on the use of different adsorbents like activated carbon [11], coir pith [12], peat [13], chitin [14], silica [15], fly ash [16], and many others like hardwood sawdust, bagasse pith, rice husk, rice hull, paddy straw, slag, fenugreek mucilage, and various blends of these [17]. However, search for cost-effective and efficient adsorbent is being made [18]. Biological-based materials such as agricultural-based biomass are of low cost, and easily available in considerably large quantities. These properties make them an attractive alternative adsorbent when compared to commonly used adsorbents such as activated carbon, which is highly expensive and has regeneration problems [19]. The current work describes the biosorptive removal of Turquoise Blue PG by an inexpensive biosorbent i.e. sugarcane bagasse, which is a natural biomaterial and is a capable alternative due to its large quantity and low-price commercial value. However, to the best of our knowledge, the biosorptive removal of Turquoise Blue PG from aqueous solutions by sugarcane bagasse has not been reported in literature. Advantage of using sugarcane bagasse is that it is readily available and do not need regeneration. It is a sugar industry waste byproduct, which is obtainable in large quantities at no cost and can form a good basis for the development of adsorbing materials. Literatures had reported that it could be used successfully for the adsorptive removal of various dyes [20]. Simple pretreatment procedures were used to modify the properties of sugarcane bagasse. The adsorption ability of the modified sorbent was compared with that of the unmodified biosorbent for the biosorption of Turquoise Blue PG. The effects of different factors such as pH, biosorbent dose, initial dye concentration, contact time, and temperature are reported. Equilibrium data were evaluated with different isotherm models. The kinetics and thermodynamics were analyzed by fitting the data to various kinetics models and isotherm equations for the biosorption of Turquoise Blue PG to explain the process feasibility.

2. Materials and methods

2.1. Preparation of biosorbent

Fresh biomass of sugarcane bagasse was purchased from the local market. The biomass was washed several times with tap water. After that it was washed with distilled water to remove dust and other foreign particles. The cleaned biomass was dried in sunlight for 3 d, then for 24 h at 60 °C in an oven. The biomass was ground and then sieved using Octagon sieve (OCT-DIGITAL 4527-01) to a mesh size 0.250 mm. The sieved biomass was stored in plastic bottles for further use [3].

2.2. Pretreatment of biomass

In order to enhance the biosorption capacity, the selected biomass was pretreated chemically and physically. Physical treatment was done by autoclave and boiling. For chemical treatment, the biomass was treated with 5% solution of HCl, HNO_3, H_2SO_4, CH_3COOH, NaOH, KOH, NH_4OH, SDS, CTAB, Triton-X 100, CH_3OH, C_6H_6, PEI, EDTA, and glutaraldehyde. After shaking for 1 h with these solutions, the biosorbents were filtered, washed, and then dried in an oven at 60 °C for 24 h [4].

2.3. Immobilization of biomass

Sodium alginate beads of sugarcane bagasse biosorbent were prepared for the comparison among native, pretreated, and immobilized biosorbents. For this purpose, firstly, aqueous slurry of native screened biosorbent was made with sodium alginate in 1:2 ratio on mass percent basis. Then, a burette (100 mL) was filled with slurry and added drop wise to the 0.10 M $CaCl_2$ solution. When slurry entered into the solution, it changed to the shape of beads. These beads were washed with distilled water. The biosorbent was separated by centrifugation and the supernatants were analyzed spectrophotometrically for determining the remaining dye concentration [21].

2.4. Preparation of aqueous dye solutions

Turquoise Blue PG (gifted by Clariant dye Industry, Faisalabad, Pakistan) was used without further purification. Stock solution of the dye was made by dissolving 1 g of dye in 1,000 mL of distilled water [3]. By diluting the standard solution of dye, various concentrations (10–200 mg/L) were made. Standard curves were developed through the measurement of the dye solution absorbance by UV/visible spectrophotometer (Shimadzu Brand UV-4000). The maximum wavelength λ max for the Turquoise Blue PG was 620 nm.

2.5. Biosorption experiments

The biosorption of Turquoise Blue PG on sugarcane bagasse in liquid–solid system has been studied using a standard batch technique. The biosorption experiments have been carried out in 250 mL conical flasks by mixing a pre-weighed amount of desired biosorbent and 50 mL of aqueous dye solution of fixed concentration. The flasks were then clamped in a horizontal shaker with an intensity of agitation 120 rpm to mix the reaction mixture for the predetermined time interval at constant temperature. The agitation rate was same for all experiments [4]. The parameters such as pH of the medium, adsorbent dosage, time of contact, initial dye concentration, and system temperature were varied during different sets of batch experiments. After adsorption, the samples were filtered out and the solution was centrifuged at high speed to avoid any solid particles in the solution phase. The left-out concentration in the supernatant solution after adsorption process has been analyzed using a double-beam UV–Vis spectrophotometer (Shimadzu Brand UV-4000) by recording the absorbance changes at a wavelength of maximum absorbance (620 nm). All the experiments have been carried out in triplicate. The adsorption data is reported in terms of biosorption capacity (q_{max}) using the following equation:

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

where C_0 and C_e are initial and equilibrium dye concentrations (mg/L), respectively, V is the volume of solution in L, and W is the weight of adsorbent in g.

2.6. Biosorption kinetics

Biosorption kinetics experiments were carried out in 250 mL flasks containing 50 mL of the dye solutions using a known amount of sugarcane bagasse. The flasks were agitated for various time intervals (0–180 min) in an orbital shaker at 120 rpm under constant temperature (30˚C). The samples were taken at different time intervals, centrifuged, and analyzed for remaining dye concentrations. The kinetic data were analyzed using pseudo-first-order [22], pseudo-second-order [23], and intra-particle diffusion [24] kinetic models.

2.7. Biosorption equilibrium

Equilibrium experiments were carried out by taking a known amount of sugarcane bagasse in 250 mL flasks containing 50 mL of the dye solution of different initial dye amounts (10–200 mg/L). The mixture was shaken in an orbital shaker at 120 rpm keeping temperature constant (30˚C). Then most commonly employed biosorption isotherm models were applied in this present investigation viz. the Langmuir [25], Freundlich [26], Temkin [27], Harkins Jura [28], and Dubinin–Radushkevich (DR) [29].

2.8. Biosorption thermodynamics

Biosorption of Turquoise Blue PG was investigated at different temperatures (30–60˚C) in an orbital shaking incubator under pre-optimized conditions. Various thermodynamic parameters such as enthalpy changes (ΔH°), entropy changes (ΔS°), and Gibbs free energy changes (ΔG°) were used to determine the spontaneity of the biosorption process [7].

2.9. FTIR studies

The chemical characteristics of sugarcane bagasse biomass were analyzed and interpreted by Bruker Tensor 27 Fourier transform infrared (FTIR) spectrometer with the samples prepared as KBr disks.

3. Results and discussion

3.1. Pretreatments of biomass

Sugarcane bagasse biomass was treated physically and chemically. The biosorption capacity of biomass increased after giving acidic treatments. H_2SO_4 treatment showed the best results among all the acids used. Treatments with other chemicals did not show any good effect on biosorption. The biosorption capacity was increased noticeably after acidic treatments. This increase might be due to the fact that the surface of biomass becomes protonated thus positively

charged biomass attracts the negatively charged dye molecules more strongly resulting in increased biosorption. Safa and Bhatti [3] also observed that adsorption capacity of agro waste can be enhanced after acidic treatment. Alkali treatments decreased the biosorption capability. Alkali causes deprotonation of the functional groups of biomass, thus, biomass gains net negative charge. As a result of this negative charge, repulsion occurs between dye molecules and the adsorbent surface, thus, adsorption decreases [30]. Methanol treatment lowered the adsorption potential of biomass as a result of ester formation. The carboxylate functional groups present on the surface of biomass form ester with alcohol [31]. Glutaraldehyde also decreased the adsorption ability. It may be due to the effect of cross-linking that occurs between the functional groups of biomass and glutaraldehyde [32].

3.2. Effect of pH

The pH of aqueous solution is considered as one of the most significant parameters which affect the biosorption process. Removal of Turquoise Blue PG from aqueous solution was strongly influenced by pH as indicated in Fig. 1. When experiments were carried out in the pH range 5–9, it was noted that maximum removal of dye took place at pH 5 i.e. 6.62, 18.33, and 6.36 mg/g for native, pretreated, and immobilized biomasses, respectively. pH lower than 5 cannot be used due to the change in dye color, and hence, its structural characteristics. Increase in pH from 5 to 9 decreased the biosorption efficiency. Low pH favors biosorption of dye on bagasse [33]. Solution pH strongly influences the surface charge of the adsorbing material, degree of ionization process of the dye molecules, and also the effluent chemistry. Higher adsorption rate at lower pH was due to the protonation of functional groups which increases the electrostatic interaction between the positively charged adsorbent surface and the negatively charged dye molecules [34]. Similar observation has been reported during the adsorption study of Malachite green onto degreased coffee bean [35].

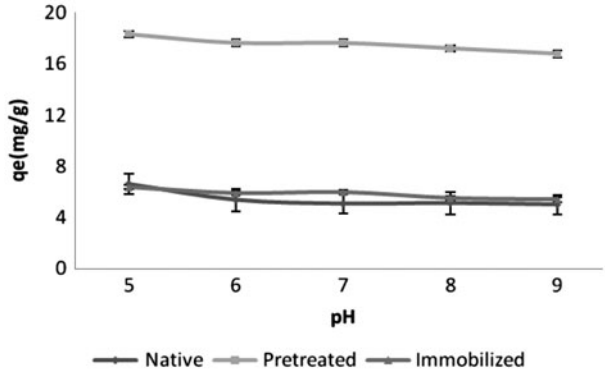

Fig. 1. Effect of pH on the removal of Turquoise Blue PG by sugarcane bagasse: 30˚C, shaking speed 120 rpm.

3.3. Effect of biosorbent dose

Amount of biosorbent is an important parameter as it determines the percentage of decolorization and can also be used to predict the cost of biomass per unit of the dye solution to be treated [36]. The effect of the amount of adsorbent on removal efficiency of Turquoise Blue PG was studied by changing the quantity of adsorbent when the concentration of the dye was chosen to be 50 mg/L at room temperature, pH 5.0, and contact time of 120 min. It was observed that with increase in the amount of adsorbent from 0.05 to 0.3 g, the adsorption capacity of Turquoise Blue PG from aqueous solution decreased. Maximum adsorption capacity was noted at 0.05 g biosorbent dose i.e. 10.06, 25.9, and 11.61 mg/g for native, pretreated, and immobilized biomasses, respectively (Fig. 2). This can be attributed to the increasing surface area of the adsorbent as well as the accessibility of more adsorption sites. At high sorbent dose, the feasible aggregation of biosorbent particles limits the efficiency in the use of reactive groups [37]. Similar trend was noted during the adsorptive study of Safranine by calcinated bones [38].

3.4. Effect of contact time

The time of contact between adsorbate and biosorbent is of great importance in the design of

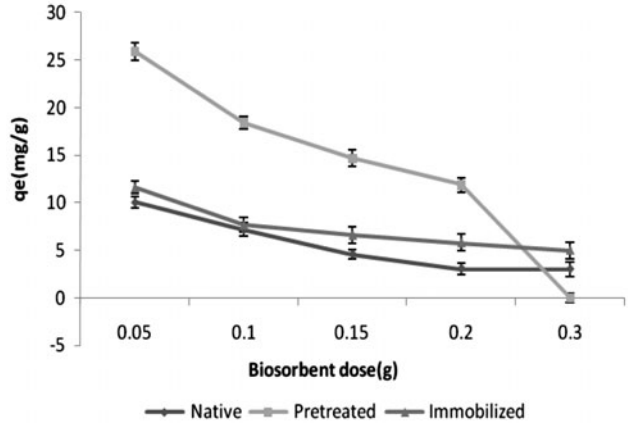

Fig. 2. Effect of biosorbent dose on the removal of Turquoise Blue PG by sugarcane bagasse: 30˚C, shaking speed 120 rpm.

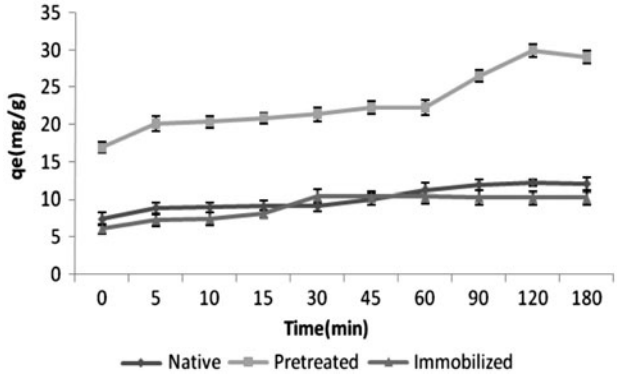

Fig. 3. Effect of contact time on the removal of Turquoise Blue PG by sugarcane bagasse: 30°C, shaking speed 120 rpm.

biosorption system and its large-scale applications. Therefore, time-dependent experiments were conducted in the time range of 0–180 min at room temperature. The results are shown in Fig. 3. An initial rapid biosorption was observed in the first 120 min. After this equilibrium period, the biosorption capacity of Turquoise Blue PG did not change noticeably with time. Therefore, rest of the batch experiments were carried out using equilibrium period to make sure that equilibrium was attained in all experiments.

3.5. Kinetic study

The dynamics and mechanism of sorption process can be understood by evaluating the kinetic data. The adsorbate molecules experience several stages during adsorption process, which include migration of adsorbate molecules to the external surface of adsorbent particles, molecular, and pore diffusion [39]. Any adsorption process of dye molecules may involve either one single step or combinations of these steps depending on various factors [40]. In order to investigate the biosorption processes of Turquoise Blue PG onto the sugarcane biomass, pseudo-first-order, pseudo-second-order, and intra-particle diffusion kinetic models were examined. The pseudo-first-order kinetic equation is commonly expressed as follows:

$$\log\,(q_e - q_t) = \log q_e - K_1\,\frac{t}{2.303} \tag{2}$$

where q_e and q_t (mg/g) are the biosorption capacity at equilibrium and at time t, respectively, as well as K_1 is the rate constant of pseudo-first-order biosorption (L/min). Using the following model, the value of K_1 and q_e were calculated from the slope and intercept of the plot of log $(q_e - q_t)$ vs. t, respectively.

The biosorption kinetics may be described by the pseudo-second-order model, which is generally given by the (Eq. (3)):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where K_2 (g/mg min) is the second-order rate constant of biosorption process.

The plot of t/q_t vs. t explains the whole biosorption process very well by native, pretreated, and immobilized biomasses. Values of K_2 and equilibrium biosorption capacity q_e were calculated from the intercept and slope of the plot of t/q_t vs. t, respectively.

The values of correlation coefficient R^2 were high for all types of adsorbents. This indicates that pseudo-second-order kinetic model fitted well to the biosorption system for the entire sorption period [41]. Vucurovic et al. [42] have reported the validity of pseudo-second-order model which suggests chemisorption as the rate-controlling step. Besides pseudo-second-order model, intra-particle diffusion model was also investigated to search for possible mechanism of biosorption. The model is given as follows:

$$q_t = K_{pi} t^{1/2} + C_i \tag{4}$$

where q_t (mg/g) is the biosorption capacity at any time t, K_{pi} (mg/g min1/2) is the intra-particle diffusion rate constant, and C_i is the boundary layer thickness. The plot for intra-particle diffusion model did not pass through the origin implying that the intra-particle diffusion was not the rate-controlling factor. According to this model, two possible mechanistic phases of adsorption take place. The first phase represents a rapid biosorption due to the mass transfer from the dye solution to the external surface of adsorbent. First phase of speedy diffusion is followed by a slower phase of intra-particle diffusion [43]. Intra-particle diffusion model was not fitted well to the kinetic data of pretreated biomass. The results of application of kinetic models are presented in Table 1. Similar results have been reported in the literature [44].

3.6. Effect of initial dye concentration

In order to attain the effect of initial dye concentration (10–200 mg/L) with 0.05 g of sugarcane bagasse at room temperature and the stirring speed of 120 rpm on the biosorption capacity of Turquoise Blue PG,

Table 1
Comparative study of kinetic parameters for the biosorption of Turquoise Blue PG by sugarcane bagasse waste biomass

Kinetic models	Native	Pretreated	Immobilized
Pseudo-first-order			
K_1 (L/min)	0.064	0.085	0.012
q_e (mg/g)	10.43	15.79	6.38
R^2	0.786	0.797	0.691
Pseudo-second-order			
K_2 (g/mg min)	0.026	0.034	0.021
q_e (mg/g)	12.50	30.30	10.41
R^2	0.996	0.987	0.996
Intra-particle diffusion			
K_{pi} (mg/g min$^{1/2}$)	0.38	0.333	0.638
C_i	7.70	6.974	7.02
R^2	0.812	0.695	0.818

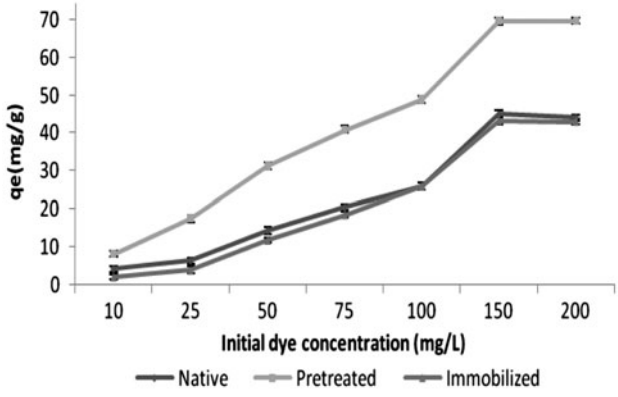

Fig. 4. Effect of initial dye concentration on the removal of Turquoise Blue PG by sugarcane bagasse: 30 °C, shaking speed 120 rpm.

different experiments were carried out. Fig. 4 depicts these results. The increase in initial dye concentration causes an increase in the amount of dye sorbed on the biomass. Bulut et al. [45] observed that the amount of dye sorbed per unit mass of biosorbent increases as initial dye concentration increases. It might be due to unsaturation of binding sites of the biomass which resulted into an increase in the dye removal. Khaled et al. [46] investigated the effect of initial concentration of Direct N Blue-106 on the biosorption of orange peel carbon. The amount of adsorbed dye increased with increase in the dye concentration.

3.7. Biosorption isotherms

Equilibrium data commonly known as biosorption isotherms are basic requirements for the design of biosorption systems. Five different models like Langmuir, Freundlich, Temkin, Harkins–Jura, and DR isotherm were used to test or estimate the equilibrium data obtained in this research work. The comparison of the correlation coefficients (R^2) of all models suggests whether the isotherm equation is applicable or not.

3.7.1. Langmuir model

The Langmuir adsorption model is established on the following hypotheses: (1) uniformly energetic adsorption sites, (2) monolayer coverage, and (3) no lateral interaction between adsorbed molecules. Graphically, a plateau characterizes the Langmuir isotherm. Therefore, at equilibrium, a saturation point is reached where no further biosorption can occur. A basic assumption is that sorption takes place at specific homogeneous sites within the adsorbent. Once a dye molecule occupies a site, no further adsorption can take place at that site. A mathematical expression of the Langmuir isotherm is given by Eq. (5):

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{5}$$

where C_e (mol/L) is the equilibrium concentration of Turquoise Blue PG in the solution, q_e (mg/g) is the

Table 2
Comparison of the isotherm parameters for the biosorption of Turquoise Blue PG by sugarcane bagasse waste biomass

Isotherm models	Native	Pretreated	Immobilized
Freundlich			
K_F	0.812	5.99	0.16
N	1.23	1.86	0.87
R^2	0.762	0.862	0.671
Langmuir			
q_{max} (mg/g)	47.5	54.9	41.08
b	2.46	2.39	2.01
R^2	0.997	0.999	0.991
Temkin			
a (L/g)	103.74	154.2	127.5
b	134.78	157.54	159.13
R^2	0.703	0.723	0.846
Harkins–Jura			
A	412.68	358.92	352.84
B	1.95	1.86	1.92
R^2	0.858	0.749	0.753
Dubinin–Radushkevich			
q_m (mg/g)	23.12	43.81	21.43
β	0.00001	0.000002	0.00003
R^2	0.545	0.688	0.624

amount of Turquoise Blue PG biosorbed at equilibrium. q_{max} (mg/g) is monolayer biosorption capacity of the biosorbent, and b is the binding energy of adsorption. The values of various Langmuir constants for Turquoise Blue PG dye are described in Table 2. The value of correlation coefficient showed that Langmuir model best fitted all types of biomasses.

3.7.2. Freundlich model

The Freundlich isotherm endorses the heterogeneity of the surface and assumes that the biosorption occurs at sites with different biosorption energies. The biosorption energy varies as a function of surface coverage. This equation is also applicable to multilayer adsorption and is expressed by the following equation:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{6}$$

where K_F is the Freundlich constant and n is the heterogeneity factor. The K_F value is related to the adsorption capacity; while $1/n$ value is related to the adsorption intensity. The values of K_F, correlation coefficient, and n of dye are presented in Table 2. For all types of adsorbents, the R^2 value is not so high showing that the experimental data did not fit well to the Freundlich isotherm model.

3.7.3. Temkin model

Temkin and Pyzhev considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms and suggested that because of these interactions; the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The Temkin isotherm has been used in the following form:

$$q_e = B \ln A + B \ln C_e \tag{7}$$

$RT/bT = B$ ($J\,mol^{-1}$), which is the Temkin constant related to heat of sorption, whereas A ($L\,g^{-1}$) is the equilibrium-binding constant corresponding to the maximum binding energy. R ($8.314\,J\,mol^{-1}\,K$) is the universal gas constant and T (K) is the absolute temperature. The results of the isotherm parameters/constants are displayed in Table 2. The value of correlation coefficient was not so good for biosorption.

3.7.4. DR isotherm

The Dubinin–Radushkevich is another important isotherm model which can be used to analyze the obtained data. The DR isotherm model is a more generalized model when compared to the 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 DR isotherm model can be seen below:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{8}$$

q_m is the maximum biosorption capacity, β is the activity coefficient related to mean adsorption energy, and ε is the Polanyi potential which can be calculated from the equation given below:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{9}$$

R ($kJ\,mol^{-1}\,K^{-1}$) stands for gas constant and T (K) shows the absolute temperature. The DR isotherm constants of Turquoise Blue PG are presented in Table 2. The values of correlation coefficients for Turquoise Blue PG by all types of biomasses are low which indicate that this model did not fit well.

3.7.5. Harkins–Jura isotherm model

Multilayer biosorption takes place due to the presence of heterogeneous pore distribution. This process can be explained by the Harkin–Jura isotherm model. The linear form of this model is given as follows:

$$\frac{1}{q_e^2} = \frac{B}{A} - \frac{1}{A}\log C_e \tag{10}$$

The values of Harkin–Jurra isotherm parameters are presented in Table 2. The values of correlation coefficients for Turquoise Blue PG indicate that the model fitted poorly to the obtained data. Thus the model showed that sugarcane bagasse does not possess heterogeneous pore distribution.

3.8. Effect of temperature

The effect of temperature on the adsorption kinetics was investigated at six different temperatures i.e. 30, 35, 40, 45, 50, and 60°C by keeping all other parameters constant such as pH, initial dye concentration, contact time, and adsorbent dosage. The temperature dependence of Turquoise Blue PG adsorption kinetics is shown in Fig. 5. The experimental results

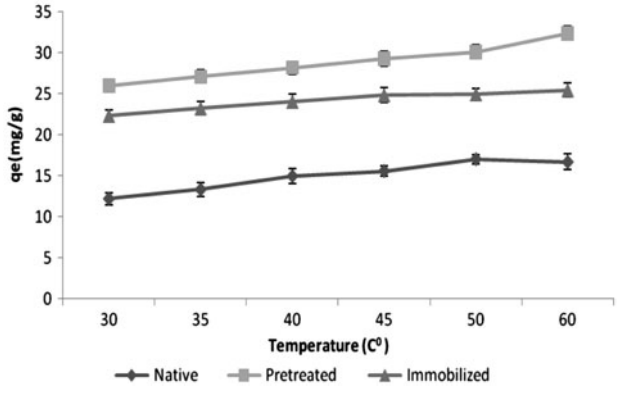

Fig. 5. Effect of temperature on the removal of Turquoise Blue PG by sugarcane bagasse: pH 5, biosorbent dose: 0.05 g/50 mL, initial dye concentration: 50 mg/L, shaking speed 120 rpm.

reveal that the magnitude of adsorption is proportional to the solution temperature. Results show the amount of dye adsorbed increased from 12.20 to 17.02, 25.94 to 32.36, and 22.34 to 25.45 mg/g for native, pretreated, and immobilized biomasses, respectively when the temperature was increased. The biosorption of Turquoise Blue PG was favorable at high temperatures indicating the endothermic nature of the process. This was attributed to the increase in the number of pores on the biomass surface at high temperature. At high temperature, the thickness of outer surface of the biosorbent was reduced and the kinetic energy of dye molecules was increased, as a result, the dye molecules biosorbed easily into the surface of the biomass [47]. Safa and Bhatti [4] investigated that the rate of biosorption of direct dyes onto rice husk increased with increase in the temperature.

3.9. Thermodynamics of biosorption

Thermodynamic parameters associated to the process of biosorption i.e. Gibb's free energy change (ΔG°, kJ mol^{-1}), enthalpy change (ΔH°, kJ mol^{-1}), and entropy change (ΔS°, J mol^{-1} K^{-1}) were determined by the following equations:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{11}$$

$$\Delta G^\circ = -RT \ln K_d \tag{12}$$

where $K_d = q_e/C_e$

The combination of above equations gives:

$$\log\left(\frac{q_e}{C_e}\right) = -\frac{\Delta G^\circ}{2.303\mathrm{RT}} = -\frac{\Delta H^\circ}{2.303\mathrm{RT}} + \frac{\Delta S^\circ}{2.303\mathrm{RT}} \tag{13}$$

where R is the universal gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature (Kelvin), and K_d shows the equilibrium biosorption constants of the isotherm fits. The ΔH° and ΔS° values can be calculated from the slope and intercept of the linear plot of ln (K_d) vs. $1/T$. The thermodynamic results are depicted in Table 3. The nature of interaction can be classified, up to some extent, by the magnitude of change in enthalpy. Enthalpy changes (ΔH°) indicate that the biosorption by native, pretreated, and immobilized biomasses followed endothermic processes. Negative values of ΔG° showed that the Turquoise Blue PG dye biosorption by sugarcane biosorbent was a spontaneous and feasible process at all studied temperatures. The positive values of ΔS° indicated a high preference of dye molecules for the surface of biosorbent and also suggested the option of some kind of structural changes and readjustments in the dye–carbon biosorption complex [48].

3.10. Effect of salt, surfactants, and heavy metals

Various types of salts, surfactants, and heavy metals are used during dyeing process in industries thus

Table 3
Thermodynamic parameters for the biosorption of Turquoise Blue PG by sugarcane bagasse waste biomass

	Native			Pretreated			Immobilized		
Temp (°C)	ΔG°	ΔH°	ΔS°	ΔG°	ΔH°	ΔS°	ΔG°	ΔH°	ΔS°
30	−0.63	243.01	1.27	−2.38	259.23	8.74	−0.45	112.32	1.86
35	−0.63			−2.43			−0.46		
40	−0.64			−2.45			−0.47		
45	−0.65			−2.52			−0.48		
50	−0.65			−2.56			−0.49		
60	−0.66			−2.65			−0.50		

Note: ΔG° = kJ mol^{-1}; ΔH° = kJ mol^{-1}; ΔS° = J mol^{-1} K^{-1}.

a significant amount of salts and surfactants are also present in wastewater which considerably affects the dye biosorption. The effect of ionic strength (0.2–1.0 M) of NaCl on the removal of Turquoise Blue PG was investigated. The results show that the amount of dye adsorbed increased with increase in the concentration of salts. This can be attributed to the fact that occurrence of these ions produced salting-out phenomenon and thus the solubility of dyes into water was reduced and the extent of biosorption onto the biosorbent was significantly increased. Additionally, increase in the ionic concentration enhances the electrostatic interactions among biosorbent sites and the dye molecules which results in an increased dye removal. Same trend was reported by Janos et al. [49] who noted that the biosorption of acidic dye increased when concentration of salts was increased using wood shaving biomass. Concentration of salts also exerts significant effect on the biosorption capacity of biosorbent as more salt concentration leads to more dye removal. These results were in agreement with the work of Grabowska and Gryglewicz [50]. The effect of the presence of heavy metal ions i.e. Pb^{2+} (0.2–1.0 M) on the removal of Turquoise Blue PG was also investigated. The results show that the biosorption capacity increased in the presence of Pb^{2+}. The adsorption capacity was slightly increased by increasing the concentration of Pb^{2+}. Increase in the adsorption capacity of dye with addition of certain Pb^{2+} ions might be due to the complex formation between metal ions and dyes and binding to the biosorbent surface [51]. Textile industries also discharge surfactants along with dyes into the water streams. The effect of presence of surfactants on the Turquoise Blue PG biosorption by sugarcane bagasse was determined using different surfactants i.e. SDS (sodium dodecyl sulfate), Triton X-100, CTAB (cetyltrimethylammonium bromide), Excel, and Ariel. All types of surfactants significantly decreased the biosorption of Turquoise Blue PG. The decrease of biosorption capability might be due to the repulsive interactions between surfactant and anionic dye molecules.

3.11. FTIR studies

In order to understand the possible biosorbent–dye molecule interactions, it is essential to identify the functional groups present on the biomass involved in this process. The main effective binding sites can be identified by FTIR spectral comparison of the dye-loaded biosorbent. FTIR spectrum in the range of 4,000–400 cm^{-1} for the sugarcane bagasse after biosorption of Turquoise Blue PG is shown in Fig. 6. FTIR spectrum shows the complicated nature of biosorption band at 1,650.67 cm^{-1} because aromatic ring bands and double-bond (C–C) vibrations overlap the

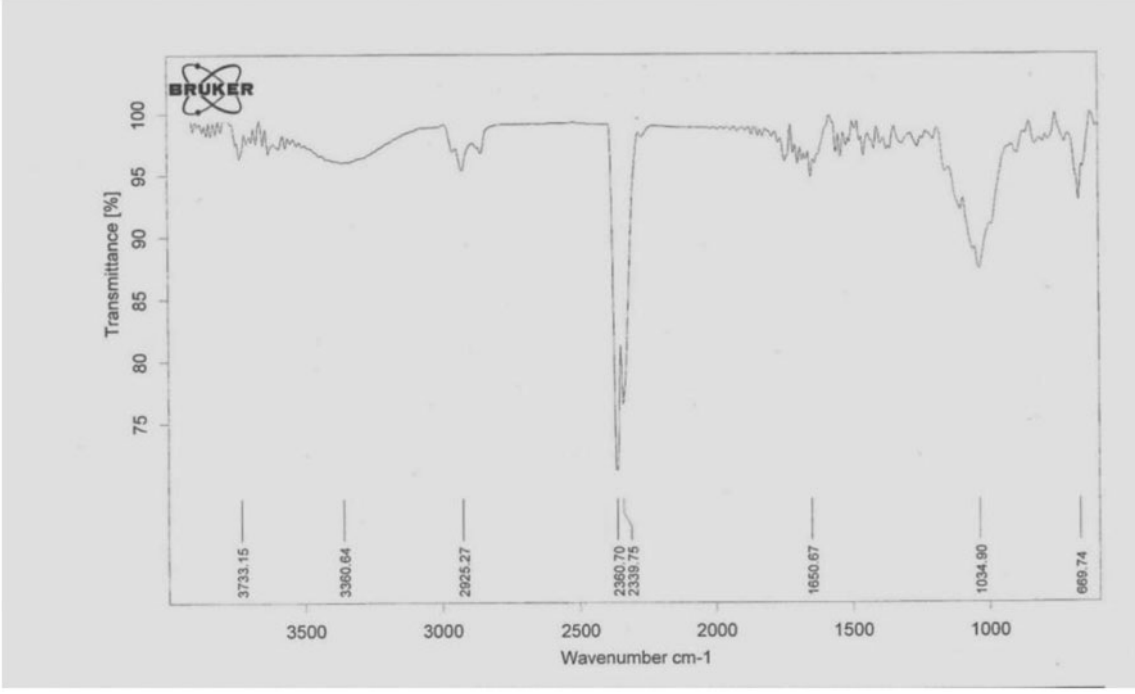

Fig. 6. FTIR spectrum of sugarcane bagasse loaded with Turquoise Blue PG.

aforesaid C=O stretching vibration bands and OH binding vibration bands. The peak appearing at 1,650.67 cm^{-1} arises from C=O stretching in amide groups. The peak at 1,034.90 cm^{-1} corresponds to C–O stretching vibration of alcohols and carboxylic acids. Presence of peak in the range of 2,360.70–2,339.75 cm^{-1} suggests the participation of functional group O–H (carboxylic acid and derivatives) in dye biosorption by sugarcane bagasse. The dye-loaded FT-IR spectrum of sugarcane bagasse biomass indicated that the functional groups like –NH2, –OH, and –C=O are present on the sugarcane bagasse surface and are involved in Turquoise Blue PG biosorption.

Conclusion

In this study, the removal of Turquoise Blue PG from aqueous solutions by biosorption onto sugarcane bagasse as a low-cost and naturally available sorbent was investigated. The results show that the natural biomass of sugarcane bagasse is an excellent biosorbent for the used dye. The biosorption was rapid and increased by the decrease in biosorbent dosage. The pH experiments showed that the significant biosorption took place in acidic range. The equilibrium uptake was increased with increase in the initial concentration of dye in the solution. Experimental data were better described by pseudo-second-order model. The adsorption isotherm data were well explained by Langmuir model. The biosorption capacity increases with an increase in solution temperature. The mechanism of dye biosorption was confirmed by FTIR analysis which showed that biosorption includes mainly electrostatic interactions and complex formation between molecules of dye and functional groups present on the surface of biosorbent. Finally, the agro waste sugarcane bagasse can be used as an effective natural biosorbent for the economic treatment of waste effluents containing synthetic dyes.

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