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Removal of Indosol Turquoise FBL dye from aqueous solution by bagasse, a low cost agricultural waste: batch and column study

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ABSTRACT

This study involves the remediation of dye containing synthetic wastewater using bagasse, a low cost agricultural waste by batch and column methods. The simulated wastewater was prepared using Indosol Turquoise FBL, commonly used dye in the textile industry. Sugarcane bagasse was used in native, HCl-treated and Na-alginate-immobilized forms. The effect of different process parameters such as medium pH, biosorbent dose, contact time, initial dye concentration and temperature on the biosorption capacity of bagasse was investigated in batch study. Maximum dye removal (65.09 mg/g) was obtained with HCl-treated bagasse. Pseudo-second-order kinetic model was better fitted to the experimental data. The equilibrium data were best described by Langmuir adsorption isotherm model. The thermodynamic study indicated the thermodynamic nature of biosorption process. Effect of surfactants, heavy metal ions and salt concentration was also explored. Breakthrough capacities were also investigated in column mode study. Effect of bed height, flow rate and initial dye concentration were investigated in column study. Maximum dye removal in continuous mode study was 28.8 mg/g. The experimental data was subjected to Thomas Model and bed depth service time models. Surface analysis of sugarcane bagasse was carried out using Fourier transform infrared (FTIR) spectrometer and scanning electron microscopy (SEM). FTIR analysis of unloaded and Indosol Turquoise FBL loaded bagasse showed the involvement of hydroxyl and carboxylic groups in the biosorption process. The results indicated that bagasse could be used to treat dye containing effluents.

Keywords: Remediation; Kinetics; Thermodynamics; Breakthrough capacity; Adsorption

1. Introduction

Over the years, there is a rapid proliferation in world's giant factories and manufacturing industries enhancing the waste generation [1]. Pollution control is one of the leading issues of society today. Dyes are among the major pollutants that are widely present in industrial waste streams [2]. More than 10,000 dyes are extensively used in many industrial processes such as textile, paper and plastics, leather, pharmaceuticals, food, cosmetics, etc. [3]. Resultantly, considerable amount of colored wastewater is generated which has intensified adverse effects on the several ecosystems and a serious threat for the human health and its environment. A very small amount of dye in water is highly visible [4]. Colored waste water obstructs the light penetration and oxygen

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transfer through water bodies which puts negative effects on aquatic life. These dyes become bioaccumulated in wildlife and also show mutagenic and carcinogenic effects [5]. The release of these dyes effluents in the environment is problematic for both toxicological and esthetical reasons [6]. Therefore, an increased interest has been focused on removing of such dyes from the wastewater. Dyes are recalcitrant organic molecules, resistant to aerobic digestion and are stable to light, heat, and oxidizing agents due to their complex molecular structure and size [7]. Various technologies including chemical oxidation, biological treatment, coagulation–flocculation, and membrane processes are currently used for reducing dye concentrations in wastewater [8]. However, these treatment processes are costly and cannot effectively be used to treat a wide range of dye containing wastewater. Due to the low biodegradability of dyes, a conventional biological wastewater treatment process is not very efficient. So dye wastewater is usually treated by physical- or chemical-treatment processes [9]. The simplicity in operation, economic viability, and environment friendly nature of adsorption process has made it more superior and reliable to other techniques for the treatment of heavily polluted dyes entities [10–12]. Agro wastes are currently receiving stern considerations as raw materials for water pollution control because of their availability and low cost [13]. The feasibility of using agricultural waste materials could be beneficial not only to the environment in solving the solid waste disposal problem, but also to the economy [14]. These agricultural waste materials are the best option for the wastewater treatment. The efficiency of agricultural waste materials can be enhanced by physical and chemical pretreatments of the biomass. The mechanical strength of the biosorbents can be enhanced by their entrapment in the polymeric matrix for the scale up study [15]. In the present study, different low-cost agricultural wastes (peanut husk, sugarcane bagasse, corncobs, cotton sticks, and sunflower) were used to select best biosorbent for the removal of Indosol Turquoise FBL dye from aqueous solutions. Batch study was carried out with native, HCl-treated and Na-alginate-immobilized biosorbent. Continuous mode study was conducted with native biomass to optimize different parameters.

2. Materials and methods

2.1. Chemicals

All the analytical grade chemicals were taken from Sigma–Aldrich (USA) and Merck (Germany).

2.2. Preparation of biosorbents

Different agricultural wastes (peanut husk, sugarcane bagasse, corncobs, cotton sticks and sunflower) were collected from different areas of Pakistan. The biomasses were cut into small pieces and rinsed several times with distilled water to remove dust and foreign particles. The cleaned biomasses were dried in sunlight and oven-dried overnight at 60°C. The dried biomasses were ground with a food processor (Moulinex, France) and sieved using Octagon sieve (OCT-DIGITAL 4527-01) to a 300 μm mesh size and stored in air-tight bottle.

2.3. Preparation of aqueous dye solutions

Indosol Turquoise FBL dye was obtained from Clariant Pakistan Limited, Pakistan and was used without further purification. Stock solution of dye was prepared by dissolving 1 g of dye in 1,000 mL of double distilled water. The experimental solutions of different concentrations ranging from 10 to 200 mg/L were made by further dilutions. Standard curve was developed through the measurement of the dye solution absorbance by UV/Visible Spectrophotometer (Schimadzu, Japan). Indosol Turquoise FBL dye was anionic in nature and its λ_{max} was 606 nm.

2.4. Batch experimental design

Optimization of important process parameters such as pH, contact time, biosorbent dose, initial dye concentration, and temperature for the removal of Indosol Turquoise FBL was carried out by 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 120 rpm. Blank solutions were run under same conditions except the addition of biosorbent. pH of the solution was adjusted using 0.1 M HCl and NaOH solutions. Effect of the presence of different salts (NaCl, KNO_3, $CaCl_2$, $MgSO_4$ and $AlCl_3$) on the biosorption of Indosol Turquoise FBL also investigated at different concentrations (0.1, 0.2, 0.3, 0.4 and 0.5 M) of these salts in 50 mg/L dye solution. Effect of the presence of heavy metals ions (Cd, Pb, Cr, Co and Cu) at different concentrations (50, 100, 150, 200, and 250 mg/L) was also studied on the removal of Indosol Turquoise FBL by sugarcane bagasse. Moreover, effect of surfactants was also investigated using 1% of different surfactants Triton X-100, CTAB, SDS and two commercial surfactants, Arial and Excel. All the experiments were performed in triplicate and reported values are mean ± SD. After certain time, the samples

were taken out and centrifugation was performed at 5,000 rpm for 20 min, and concentration of remaining dye solution was determined by using UV–vis spectrophotometer (Schimadzu, Japan).

2.5. Immobilization of biomass

Sodium-alginate (2.0 g) was dissolved in 100 mL of water by heating, and then the solution was cooled down. Sugarcane bagasse (1 g/100 mL) was added to each of above mixture and mixed until to form a homogeneous mixture. Then, the mixture was dropped into a solution of 0.1 M $CaCl_2$ to form uniform beads of immobilized biomass. The beads were washed with distilled water and stored at 4°C in 0.05 M $CaCl_2$ solution [16].

2.6. Pretreatment of sugarcane bagasse

Sugarcane bagasse was pretreated physically and chemically. During physical treatments autoclaving (biomass was autoclaved at 121°C for 15 min) and boiling (5 g of biomass/100 mL of H_2O and boiled for 30 min) was carried out. In chemical modifications, 1 g of the biosorbent was treated with 5% of different acids (HCl, H_2SO_4 and HNO_3 and CH_3COOH), alkali (NaOH), Surfactants (CTAB, SDS, Triton X-100), chelating agents (PEI, EDTA, and glutaraldehyde) and organic solvents (benzene and methanol). Then all the modified biomass were washed with double distilled water and filtered. The modified biosorbents were dried in an oven at 60°C for 24 h and ground it [17]. The dried ground treated biomasses were stored in air-tight bottles.

2.7. 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) on 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 as described before. The kinetic data were analyzed using pseudo-first-order [18], pseudo-second-order [19] and intraparticle diffusion [20] kinetic models.

2.8. Biosorption equilibrium studies

Equilibrium experiments were carried out by taking 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 [21], Freundlich [22], Temkin [23] and Doubinin–Radushkevich (D–R) [24].

2.9. Biosorption thermodynamics

Biosorption of Indosol Turquoise FBL was investigated at different temperatures (303–333 K) in the orbital shaking incubator under preoptimized 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 biosorption process.

2.10. Column studies

Biosorption performance of biosorbents in continuous system is important factor in accessing the feasibility of biosorbent in real applications. Continuous biosorption experiments in a fixed-bed column were conducted in a glass column (20 mm ID and 43 cm height), packed with a known quantity of sugarcane bagasse. At the bottom of the column, a stainless sieve was attached followed by a layer of glass wool. A known quantity of the sugarcane bagasse was packed in the column to yield the desired bed height of the adsorbent (1, 2, and 3 cm). Indosol Turquoise FBL dye solution of known concentrations (50, 75, and 100 mg/L) at pH 3 was pumped upward through the column at a desired flow rate (1.8, 3.6, and 5.4 mL/min) controlled by a peristaltic pump (Prominent, Heidelberg, Germany). The dye solutions at the outlet of the column were collected at regular time intervals, and the concentration was measured using a double-beam UV–visible spectrophotometer (Shimadzu, Japan) at 606 nm. All the experiments were carried out at room temperature (28 ± 1°C).

2.11. FTIR and SEM 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 discs. The surface structure of sugarcane bagasse biomass was analyzed by JEOL JMT 300 scanning electron microscope (SEM).

3. Result and discussion

3.1. Screening study

Screening study was performed to select the best biosorbent among different biosorbents (peanut husk, sugarcane bagasse, corncobs, cotton sticks, and

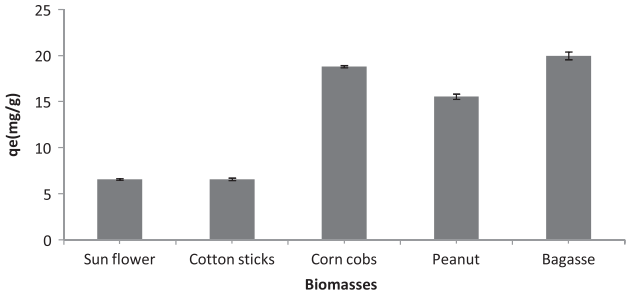

Fig. 1. Screening of different agricultural wastes for Indosol Turquoise FBL: dye concentration 50 mg/L, temperature 30 °C, shaking speed 120 rpm.

sunflower) having maximum biosorption capacity for Indosol Turquoise FBL dye. The results are presented in Fig. 1 which demonstrated that sugarcane bagasse was the best biosorbent with high removal efficiency for the Indosol Turquoise FBL dye. Sugarcane bagasse was selected to use as biosorbent in the further study.

3.2. Effect of pretreatments

To enhance the biosorption capacity of sugarcane bagasse, different physical and chemical treatments were given to the biomass. Chemical pretreatments included the treatment of biomass with different acids (HCl, H_2SO_4, HNO_3 and CH_3COOH), alkali (NaOH), surfactants (CTAB, SDS, Triton X-100), chelating agents (PEI, EDTA and glutaraldehyde) and organic solvents (benzene and methanol). The physical treatments of biosorbent included its boiling and autoclaving. The results are presented in Fig. 2. Overall results demonstrated an increase in biosorption efficiency of bagasse by the pretreatment with HCl, CH_3COOH, Triton X-100 and organic solvents. Boiling and autoclaving also enhanced biosorption efficiency of bagasse. The maximum biosorption capacity of sugarcane bagasse was achieved with its treatment with HCl. The treatment of biosorbent with acid removes the impurities and ions present on its surface and enhanced the porosity by exposing more active sites [25], and hence, acids may improve sorption capacity of biosorbent by amplifying the surface area [26].

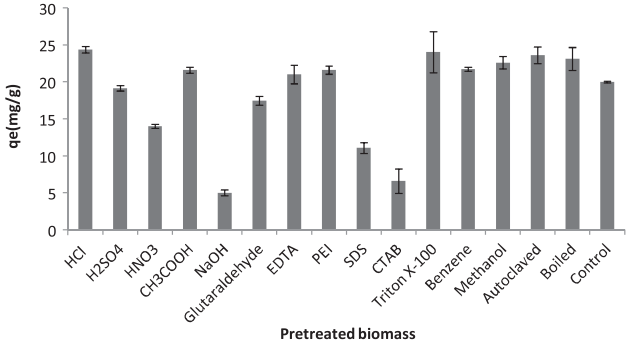

Fig. 2. Chemical and physical pretreatments of bagasse: dye conc. 50 mg/L, temperature 30 °C, shaking speed 120 rpm.

3.3. Effect of pH

The solution pH influences on the surface properties of the biosorbent and ionization/dissociation of the dye molecules. The effect of pH on biosorption of Indosol Turquoise FBL was studied in the range of 3–9 which is presented in Fig. 3. The amount of dye biosorbed decreased with the increase in pH from 3 to 9 keeping the biosorbent dose and initial dye concentration constant (0.01 g/50 mL and 50 mg/L, respectively). The lowest dye biosorption occurred at pH 9 and the maximum biosorption occurred at pH 3.0. At the acidic pH, the number of positively charged sites on the surface of biosorbent increased which favored the biosorption of dye anions due to electrostatic attraction. Moreover, the decrease in the biosorption of Indosol Turquoise FBL with increase of pH value was also due to the competition between anionic dye and excess OH^- ions in the solution which may be due to the fact that the high concentration and high mobility OH^- ions were preferentially adsorbed as compared with dye anions. The most effective pH was 3, and it was used in further studies. Similar trend was observed for the biosorption of direct dyes on activated carbon prepared from saw dust and orange peel [27,28]. Dawood and Sen [29] also observed the highest removal of Congo Red dye by adsorption onto pine biomass at acidic range of pH (3.55).

3.4. Effect of contact time

The relation between biosorption of Indosol Turquoise FBL and contact time was investigated to

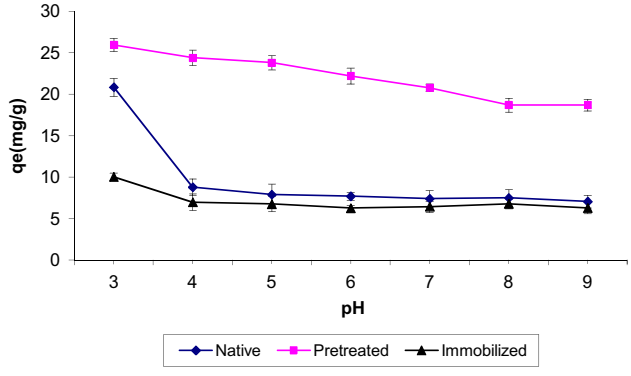

Fig. 3. Effect of pH on the removal of Indosol Turquoise FBL: temperature, 30 °C, shaking speed 120 rpm.

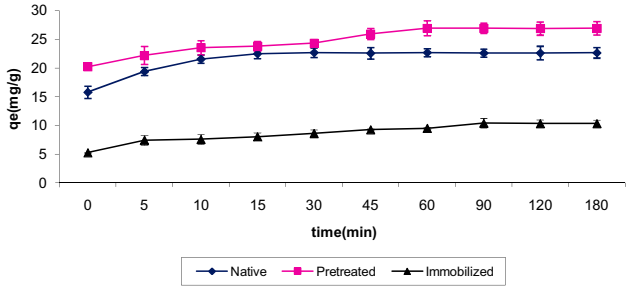

Fig. 4. Effect of contact time on the removal of Indosol Turquoise FBL: temperature, 30℃, shaking speed 120 rpm.

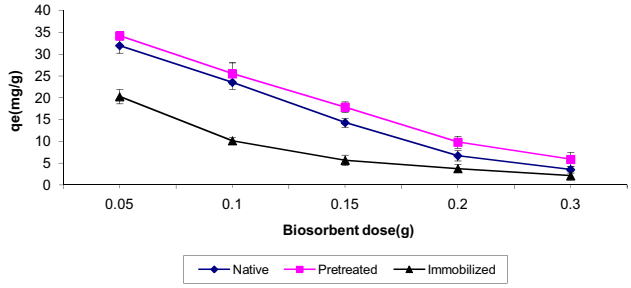

Fig. 5. Effect of biosorbent doseonr the removal of Indosol Turquoise FBL: temperature, 30℃, shaking speed 120 rpm.

identify the rate of dye removal. The effect of contact time for the biosorption of dye was studied for a period of 3 h for initial dye concentration of 50 mg/L at optimum pH (3). The results are presented in Fig. 4 which showed that the biosorption of anionic dye by native and pretreated biomass was very fast in the first 15 min, and then gradually decreased with the prolongation of contact time. After 30 min of contact, no obvious variation in dye biosorbed was examined. The rapid biosorption of dye during the first 15 min was probably due to the abundant availability of active sites on the bagasse surface, but with the gradual occupancy of these sites, the biosorption became less efficient. Equilibrium was achieved after 1 h of contact time with immobilized biomass. This is due to the fact that in case of immobilized biomass, the biosorbent is present inside the matrix and its active sites are not freely exposed so more contact time is requires for the attainment of equilibrium. Based on these results, 30 min was taken as the equilibrium time for pretreated and native biomass and 1 h contact time was selected for immobilized biomass. Similar result was reported by [30]. Jain et al. [31] observed that 20 min retention time was enough to get equilibrium for the removal of naphthol yellow S dye by using activated carbon as adsorbent. Errias et al. [32] also worked on the adsorption of anionic dye RR120 onto clay and found the trend of rapid adsorption.

3.5. Effect of biosorbent dose

Biosorbent dose seems to have a great influence on biosorption process. The effect of biosorbent dose on the biosorption of Indosol Turquoise FBL was studied in the range of 0.05–0.3 g/50 mL keeping the initial dye concentration of 50 mg/L and results indicated that there is a continuous decrease in biosorption capacity with the inncrease in biosorbent dose (Fig. 5). This might be due to the fact that increase in biosorbent dose at constant dye concentration and volume would lead to saturation of biosorption sites and this can be due to particulate interaction such as aggregation resulting from high-sorbent dose [33]. Such aggregation would lead to a decrease in total surface area of the biosorbent and increase in diffusional path length. Similar results were also reported by other researchers [34–36].

3.6. Effect of initial dye concentration

The initial concentration of the dyes provides an important driving force to overcome the mass transfer resistance of all molecules between the aqueous and solid phases. The effect of initial concentration of Indosol Turquoise FBL on the biosorption capacity of bagasse was determined in the range of 10–200 mg/L. The results indicated that with the increase in initial dye concentration from 10 to 200 mg/L, the biosorption capacity of bagasse increased (Fig. 6). Initially the rapid biosorption rate of dye was due to biosorption of dye molecules on the external surface of biosorbent. After the saturation of external surface, the dye molecules get biosorbed in the porous structure of bagasse. Safa and Bhatti [35] also observed an increase in biosorption capacity of rice husk by increase in initial dye concentration [35]. Similar results are also reported by Mittal et al. [37] for the removal of methyl violet dye by using waste materials as adsorbent.

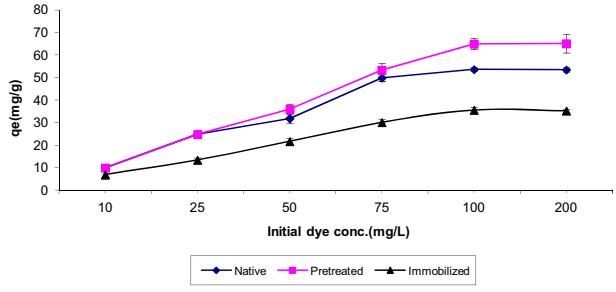

Fig. 6. Effect of initial dye concentration on the removal of Indosol Turquoise FBL: temperature, 30℃, shaking speed 120 rpm.

3.7. Effect of temperature

Various textile dye effluents are produced at relatively high temperature; therefore, temperature can be an important factor for the real application of the adsorption process for dye removal. The effect of temperature on the equilibrium biosorption capacity of the sugarcane bagasse was studied in the temperature range of 30–60 ℃ at an initial dye concentration of 50 mg/L. The results indicated that the biosorption of Indosol Turquoise FBL dye on bagasse decreased as the solution temperature increased. This indicated the exothermic nature of biosorption process. This can be explained by the fact that by the weakening of bonds between dye molecules and binding sites of biosorbent at high temperatures, the biosorption capacity reduced at higher temperatures [27]. Similar trend was observed for the adsorption of direct dye on various adsorbents [38].

3.8. Biosorption kinetics

Kinetic studies are necessary to optimize different operating conditions for the biosorption process. Various kinetic models have been suggested for explaining the order of reaction. The kinetics of Indosol Turquoise FBL onto sugarcane bagasse was analyzed using pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models. The applicability of these kinetic models was determined by measuring the correlation coefficients (R^2). When the value of R^2 is high, the model is best applicable to data.

3.8.1. Pseudo-first-order model

The integral form of the pseudo-first-order model generally expressed as [39,40].

$$\log(q_e - q_t) = \log q_e - K_1 \frac{t}{2.303} \quad (1)$$

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) and t is the contact time (min). The biosorption rate constant K_1 was calculated from the plot of $\log(q_e - q_t)$ against t. The values of rate constant K_1, q_e calculated, q_e experimental and R^2 of Indosol Turquoise FBL are presented in Table 1. By Lagergren pseudo-first-order model, a plot of $\log(q_e - q_t)$ vs. t gives a straight line with very poor correlation coefficient (R^2). Moreover, pseudo-first-order kinetic model predicted a significantly lower value of the equilibrium biosorption capacity (q_e) than the experimental value. So results indicate inapplicability of pseudo-first-order kinetic model to the kinetic data of Indosol Turquoise FBL. Mostly, the pseudo-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 [41].

Table 1
Application of different kinetic models

Kinetic models	Free	Treated	Na-alginate immobilized
Pseudo-first-order			
K_1 (L/min)	0.025	0.039	0.024
q_e experimental (mg/g)	22.7	26.95	10.4
q_e calculated (mg/g)	1.587	5.33	3.78
R^2	0.6519	0.8474	0.8927
Pseudo-second-order			
K_2 (g/mg min)	0.156	0.024	0.024
q_e experimental (mg/g)	22.7	26.95	10.4
q_e calculated (mg/g)	22.72	27.17	10.54
R^2	1	0.9997	0.9984
Intraparticle diffusion			
K_{pi} (mg/g min$^{1/2}$)	0.3835	0.518	0.369
C_i	19.10	21.52	6.347

3.8.2. Pseudo-second-order kinetic model

The biosorption mechanism over a complete range of the contact time is explained by the pseudo-second-order kinetic model. The linear form of pseudo-second-order kinetic model can be written as:

$$\left(\frac{t}{q_t}\right) = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

A plot between t/q_t vs. t gives the value of the constants K_2 (g/mg h), and also q_e (mg/g) can be calculated. The pseudo-second-order parameters K_2, q_e calculated, q_e experimental and R^2 of Indosol Turquoise FBL are shown in Table 1. The higher values of correlation coefficient with native, pretreated and immobilized biomass indicated the fitness of this model on the experimental data. The experimental q_e values are in close agreement with the predicted q_e values which also confirms the best fitness of pseudo-second-order kinetic model. The results showed that the pseudo-second-order kinetic model is more appropriate and effective than pseudo-first-order kinetic model. These results are in agreement with the reported results of other researchers [42,43].

3.8.3. Intraparticle diffusion model

Different steps are involved in the movement of dye molecules from aqueous solution to the biosorbent

surface. The biosorption mechanism may be controlled by single step or combination of many steps. In the batch experiment system which involves fast and continuous stirring, film diffusion, intraparticle diffusion or a mixture of both mechanisms may be the rate determining or rate controlling step. The intraparticle diffusion equation is written as follows:

$$q_t = K_{pi}t^{1/2} + C_i \quad (3)$$

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 Indosol Turquoise FBL are given in Table 1. Intraparticle diffusion played important role in the biosorption process [44]. The poor value of correlation coefficient (R^2) indicates that the biosorption process of Indosol Turquoise FBL onto the bagasse is not only depended on intraparticle diffusion but other mechanisms might be involved. Therefore, the data is not fitted well to the intraparticle diffusion model.

3.9. Biosorption isotherms

The biosorption isotherm is important for the description of how the biosorbate will interact with the biosorbent and gives an idea of the biosorption capacity of the biosorbent [45]. To simulate the biosorption isotherm, different models (Freundlich, Langmuir, Temkin, and Doubinin–Radushkevich (D–R)) were selected to explicate dye bagasse interaction.

3.9.1. Freundlich isotherm

The biosorbent surface may be considered as a monolayer or multilayer. The Freundlich isotherm model is valid for multilayer biosorption and is derived by assuming a heterogeneous surface with interaction between adsorbed molecules with a nonuniform distribution of heat of sorption over the surface [46]. Mathematically, it can be expressed as

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (4)$$

where q_e is the amount of dye biosorbed per unit of biosorbent at equilibrium time (mg/g), C_e is equilibrium concentration of dye in solution (mg/L). K_F and n are isotherm constants where K_F indicate the biosorption capacity and n is a measure of deviation from linearity and used to verify types of biosorption [47]. It is suggested that if n is equal to unity, the biosorption is linear. Further, n below unity indicates that biosorption is a chemical process; whereas, n above unity is associated with a favorable biosorption and a physical process [39]. The values of R^2, K_F and n are presented in Table 2. Values of correlation coefficients were high which shows a good linearity. The results indicate that value of n was greater than unity which shows that dye molecules were favorably adsorbed onto bagasse biomass.

3.9.2. Langmuir isotherm

The Langmuir isotherm is valid for the biosorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites [48].

The linear form of Langmuir can be written as [49]

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (5)$$

The Langmuir constants, q_m (maximum biosorption capacity) (mg/g) and b (values for Langmuir constant related to the energy of biosorption (L/mg)) are predicted from the plot between C_e/q_e vs. C_e. The results are presented in Table 2. Higher values of R^2 and close values of experimental and calculated biosorption capacities indicate good fitness of this model on the equilibrium data of Indosol Turquoise FBL.

Table 2
Application of different equilibrium models

Isotherm models	Native	Treated	Na-alginate immobilized
Langmuir			
q_m calculated (mg/g)	55.55	66.67	39.52
q_m experimental (mg/g)	53.96	65.09	35.5
b	0.225	0.259	0.058
R_L	0.02	0.018	0.078
R^2	0.992	0.992	0.989
Freundlich			
K_F	17.69	23.32	4.549
n	3.9	4.23	2.21
R^2	0.949	0.855	0.934
Temkin			
A	23.32	51.3	0.65
B	370.27	339.9	307.39
R^2	0.882	0.879	0.92
D–R			
q_m (mg/g)	43.34	34.39	18.46
$K \times 10^4$ (mol^2 KJ^{-2})	3	0.8	0.6
E (KJ mol^{-1})	40.82	79.05	91.28
R^2	0.832	0.484	0.199

The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor for equilibrium parameter, $R_{L,}$ which can be calculated as:

$$R_L = \frac{1}{1 + bC_o} \quad (6)$$

where C_o is the initial dye concentration and b is the Langmuir constant. The values of R_L indicate the type of isotherm to be favorable ($0 = R_L = 1$), unfavorable ($R_L = 1$), irreversible ($R_L = 0$) or linear ($R_L = 1$). Value of R_L in the present study was in the range of 0–1 which shows that biosorption of Indosol Turquoise FBL onto bagasse was a favorable process. This was a great agreement with the findings regarding to the value of n (Freundlich isotherm constant).

3.9.3. Temkin isotherm

The Temkin isotherm model [23] suggests an equal distribution of binding energies over the number of the exchanging sites on the surface. The distribution of these energies depends on the number of functional groups on the dye molecule and the adsorbent surface.

The linear form of Temkin isotherm can be written as

$$q_e = B\ln A + B\ln C_e \quad (7)$$

where $B = RT/b$, T is the absolute temperature in Kelvin, b is Temkin constant and R is the universal gas constant ($8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$). A is the equilibrium binding constant and B is corresponding to the heat of sorption. These constants and R^2 values can be calculated by plotting graph between q_e and $\ln C_e$. The value of R^2 and other constants are presented in Table 2. R^2. Low values of R^2 suggest that the experimental data were not fitted better to the Temkin isotherm model.

3.9.4. D–R isotherm

The D–R isotherm model is more generalized model as compared with Langmuir isotherm. This model is based on the fact that there is no homogeneous surface or constant biosorption potential [50]. It is used for estimation of the porosity apparent free energy.

The linear form of (D–R) isotherm model [24] can be seen below

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (8)$$

where β is a constant corresponding to the adsorption energy, q_m the theoretical saturation capacity and ε is the Polanyi potential which is calculated from equation below:

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

where R ($\mathrm{Jmol^{-1}\,K^{-1}}$) 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 one mole of ion is transferred from infinity in solution to the adsorbent. E was calculated from the β value by the following relation [51]

$$E = 1/(2\beta)^{1/2} \quad (10)$$

Poor values of correlation coefficients indicate low fitness of D–R model to the experimental data. The value of E demonstrated the involvement of chemical adsorption mechanism in the biosorption of Indosol Turquoise FBL onto bagasse biomass.

3.10. Thermodynamic studies

The thermodynamic parameters such as standard Gibbs free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated from the temperature data obtained from the biosorption of Indosol Turquoise FBL onto bagasse.

The thermodynamic parameters can be calculated using the following equations:

$$\Delta G^\circ = -RT\ln K_d \quad (11)$$

where $K_d = \frac{q_e}{C_e}$, R is the gas constant ($8.314\,\mathrm{J/mol\,K}$) and T is the absolute temperature.

According to Van't Hoff equation

$$\Delta G^\circ = \Delta H - T\Delta S^\circ \quad (12)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (13)$$

The values of ΔH° and ΔS° were determined from the slope and intercept of Van't Hoff graph. The values of ΔG°, ΔH° and ΔS° are presented in Table 3. The biosorption of Indosol Turquoise FBL dye onto sugarcane bagasse biomass in native, pretreated and immobilized form was an exothermic reaction which was also confirmed by negative values of ΔH°. The negative values of ΔS° suggested the decrease in

Table 3
Thermodynamic study

Temperature (K)	Native			Pretreated			Immobilized		
	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° ($J\,mol^{-1}\,K^{-1}$)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° ($J\,mol^{-1}\,K^{-1}$)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° ($J\,mol^{-1}\,K^{-1}$)
303	−2.4	−50.76	−162	−3.18	−55.01	−172	0.65	−58.43	−194
308	−0.53			−1.53			1.86		
313	0.90			−0.12			2.78		
318	1.69			0.92			3.82		
323	1.95			1.47			4.90		
333	2.36			1.72			6.26		

randomness at the solid/solution interface during the biosorption of Indosol Turquoise FBL onto sugarcane bagasse. The negative values of ΔG° implied the spontaneous nature of the biosorption process. Similar results are also reported in the literature by other researchers [40,52].

3.11. Effect of electrolytes

Excess amount of salts are used during dying process so textile effluents also contain different electrolytes and the presence of these electrolytes also effects the biosorptive removal of dyes from these effluents. Effect of the presence of different salts (NaCl, KNO_3, $CaCl_2$, $MgSO_4$ and $AlCl_3$) was investigated during this study. The results showed that presence of salts increased the biosorption capacity of bagasse for the Indosol Turquoise FBL. Effect of ionic strength of these electrolytes was also investigated by varying the electrolyte concentration from 0.1 to 0.5 M and it was observed that by increasing the concentration of these salts, the removal of Indosol Turquoise also increased. The reason behind this increase in biosorption of anionic dye at higher salt concentrations might be the salting out phenomena which resulted in reduction of dye solubility in water which leads to the adsorption of dye molecules on the biosorbent [53]. Same trend was observed for the removal of Solar Red BA by barely husk biomass [36].

3.12. Effect of heavy metal ions

The presence of heavy metal ions in dye solution also affects the biosorption process of dye molecules onto biosorbent. Biosorption process was studied in the presence of different heavy metal ions (Cd, Pb, Cr, Co and Cu) at different concentrations varying from 50 to 250 mg/L. Results showed that the presence of heavy metal ions in dye solution increased the biosorption capacity of bagasse for the removal of Indosol Turquoise FBL dye. By increase in concentration of metal ions, the biosorption capacity increased in case of Cd, Pb, and Co, while opposite trend was observed in case of Cr and Cu metal ion concentration. Increase in biosorption capacity can be justified as metal ions could interact with dye molecules to form precipitates or aggregates and thus reduce their solubility and increase in biosorption potential [54]. This trend was in agreement with the reported results [36]. While the decrease in biosorption of dye in the presence of Cr and Cu ions can be explained due to the fact that these ions can occupy some of the binding sites of the biomass, and ultimately biosorption capacity decreases [55].

3.13. Effect of surfactants

The biosorption of Indosol Turquoise FBL onto bagasse was also studied in the presence of various surfactants (Triton X-100, SDS, CTAB, Arial, and Surf Excel), and results indicated that in the presence of surfactants, the biosorptive removal of dye appreciably decreased. This is due to the fact that surfactants compete with the dye molecules for the preferential adsorption onto the biomass active sites [56].

3.14. Column study

The results of Indosol Turquoise FBL biosorption onto bagasse using a continuous system were presented in the form of breakthrough curves which showed the loading behavior of Indosol Turquoise FBL from the solution expressed in terms of normalized concentration defined as the ratio of the outlet Indosol Turquoise FBL concentration to the inlet Indosol Turquoise FBL concentration as a function of time (C_t/C_o vs. t). Effluent volume (V_{eff}) can be calculated as

$$V_{eff} = Ft_{total} \tag{14}$$

where t_{total} and F are the total flow time (min) and volumetric flow rate (mL/min). Breakthrough capacity ($Q_{0.5}$) (at 50% or $C_t/C_o = 0.5$) expressed in mg of dye adsorbed per gram of biosorbent was calculated by the following equation:

$$\begin{aligned}&\text{Breakthrough capacity}(Q_{0.5})\\&= \text{dye adsorbed on biosorbent bed (mg)}/\\&\quad \text{mass of biosorbent in bed (g)}\\&= \text{breakthrough time (at 50\%)}\\&\quad \times \text{flow rate} \times \text{feed concentration}/\\&\quad \text{mass of biosorbent in bed (g)}\end{aligned} \tag{15}$$

3.14.1. Effect of bed height

The breakthrough curves obtained for Indosol Turquoise FBL biosorption onto bagasse at different bed heights (1, 2, and 3 cm), at a constant flow rate of 1.8 mL/min and at initial dye concentration of 50 mg/L are shown in Fig. 7. The results obtained are presented in Table 4 which indicated that when the bed height increased from 1 to 3 cm, an increase in the volume of solution treated (V_{eff}) was observed from 864 to 1,800 mL. This can be attributed to the fact that when there was an increase in bed height, the axial dispersion got decreased in the mass transfer and as a result the diffusion of the dye molecules into the sorbent got increased. Thus, the solute got enough time to get diffused into the whole of the sorbent mass, staying for more time into the column and treating more volume of effluent [14]. The experimental results showed that by increasing the bed height, the adsorption capacity of bagasse also increased. Maximum adsorption capacity (27 mg/g) was obtained at the bed height of 3 cm. The increase in adsorption capacity with the increase in bed height was due to higher adsorbent doses at higher bed depths which provided more adsorption sites for the biosorption of dye molecules. Breakthrough time and exhaustion time also increased with increase in bed height [57,58]. Since breakthrough time is the determining parameter of the process, the larger it is, the better the intraparticulate phenomenon and the bed sorption capacity are.

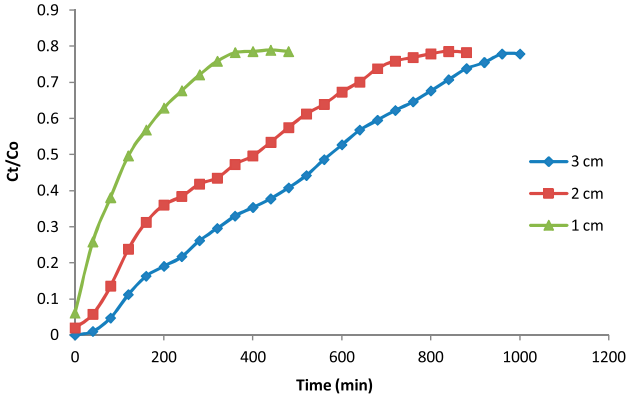

Fig. 7. Effect of bed height in on the removal of Indosol Turquoise FBL in continuous mode.

3.14.2. Effect of solution flow rate

Flow rate is found to be an important parameter affecting the performance of a biosorbent in continuous mode study. The effect of flow rate on the removal of Indosol Turquoise FBL was investigated at different flow rates (1.8, 3.6 and 5.4 mL/min) keeping constant bed height of 3 cm and 50 mg/L initial dye concentration. The experimental results are presented in Fig. 8 which shows that the breakthrough time decreased with an increase in the flow rate. The breakthrough point was achieved in 50 min as compare to 600 min when flow rate increased from 1.8 to 5.4 mL/min. The earlier breakthrough point at higher flow rates was

Table 4
Column data and parameters with different bed height, flow rate and inlet concentration

Inlet concentration (mg/L)	Bed height (cm)	Flow rate (mL/min)	Treated volume (mL)	Breakthrough point (50%) (min)	Biosorption capacity (mg/g)
50	1	1.8	864	120	10.8
50	2	1.8	1,584	400	24
50	3	1.8	1,800	600	27
50	3	3.6	1,872	160	14.4
50	3	5.4	1,944	50	6.75
75	3	1.8	1,440	420	28.35
100	3	1.8	1,224	320	28.8

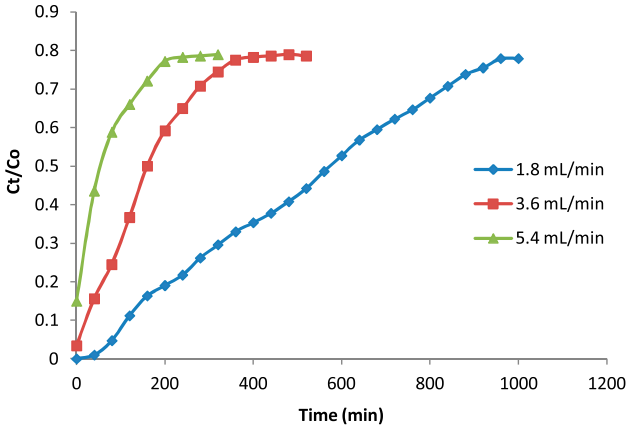

Fig. 8. Effect of flow rate on the removal of Indosol Turquoise FBL in continuous mode.

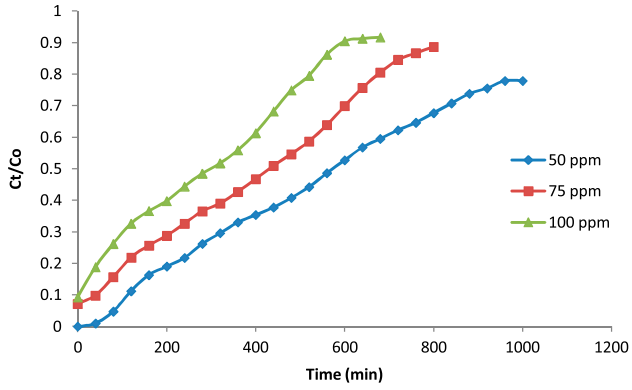

Fig. 9. Effect of initial dye concentration on the removal of Indosol Turquoise FBL in continuous mode.

due to reduced contact time between dye molecules and adsorbent. The reason was that at higher flow rates, the rate of mass transfer increased, that is, the amount of dye adsorbed onto unit bed height (mass transfer zone) increased with increasing flow rate leading to faster saturation at higher flow rate [59]. The volume of dye treated (V_{eff}) increased at higher flow rates. As the flow rate increased from 1.8 to 5.4 mL/min, the volume of treated solution increased from 1,800 to 1,944 mL/min. It was observed that better column performance was achieved at lower flow rates. As the flow rate of dye solution increased the biosorption capacity of bagasse decreased. This might be due to insufficient residence time of dye solution at higher flow rate. This result was in agreement with the findings of other researchers in the literature [14,60].

3.14.3. Effect of initial dye concentration

The effect of initial dye concentration was investigated by varying the concentration of Indosol Turquoise FBL from 50 to 100 mg/L at constant bed height of 3 cm and flow rate of 1.8 mL/min. The experimental results are presented in Fig. 9. The results indicated that the time to attain 50% breakthrough capacity decreased as the initial dye concentration increased. This may be explained by the fact that a lower concentration gradient caused a slower transport due to a decreased diffusion coefficient or decreased mass transfer coefficient [61,62]. The maximum C_t/C_o ratio was observed as 0.77, 0.88, and 0.91 for initial dye concentrations of 50, 75, and 100 mg/L. The adsorption capacity of bagasse increased from 27 to 28.8 mg/g with the increase in initial dye concentration. As the influent concentration increased, dye-loading rate increased and the driving force increased for mass transfer [58]. At higher concentrations, the volume of treated dye solution (V_{eff}) decreased. The results are in agreement with the work of previous researchers [14].

3.14.4. Application of Thomas model

Thomas model [63], assumes the Langmuir kinetics of adsorption–desorption and no axial dispersion, and is derived from the adsorption that the rate driving force obeys pseudo-second-order reversible reaction kinetics. This model also assumes a constant separation factor but it is applicable to either favorable or unfavorable isotherms. The primary weakness of the Thomas model is that its derivation is based on pseudo-second-order reaction kinetics. Sorption is usually not limited by chemical reaction kinetics but is often controlled by interphase mass transfer. This model is suitable for biosorption processes where the external and internal diffusion limitations are absent. This discrepancy can lead to some error when this method is used to model adsorption process [64,65].

The linearized form of Thomas model can be expressed as follows (Eq. (16)):

$$\ln\left(\frac{C_o}{C_t}-1\right)=\frac{K_{Th}\times q_o\times W}{Q}-K_{Th}\times C_o\times t \tag{16}$$

where K_{Th} (mL/min mg) is the Thomas rate constant; q_o (mg/g) is the equilibrium Indosol Turquoise FBL uptake per g of the biosorbent; C_o (mg/L) is the inlet dye concentration; C_t (mg/L) is the outlet concentration at time t; W (g) the mass of adsorbent, Q (mL/min) the flow rate and t_{total} (min) stands for flow time. A linear plot of $\ln[(C_o/C_t) - 1]$ against time (t) was employed determine values of K_{Th} and q_o from the intercept and slope of the plot.

The column data were fitted to the Thomas model to determine the Thomas rate constant (K_{Th}) and

maximum solid-phase concentration (q_o). The determined coefficients and relative constants were obtained using linear regression analysis according to Eq. (17) and the results are listed in Table 5. From Table 5, it is seen that values of determined coefficients (R^2) range from 0.95 to 0.995. Results indicate that as the bed heights increased, the value of q_o increased significantly but the value of K_{Th} decreased with the increase in bed height and opposite trend was seen in case of flow rate. With the increase in flow rate, the value of q_o decreased but the value of K_{Th} increased. As the inlet concentration increased the value of q_o increased but the value of K_{Th} decreased. The reason is that the driving force for adsorption is the concentration difference between the dye on the adsorbent and the dye in the solution [66]. These results indicated that higher bed height, lower flow rate and higher initial dye concentration are favorable for higher adsorption of Indosol Turquoise FBL onto bagasse in continuous mode study.

3.14.5. Application of bed depth service time (BDST) model

Among various design approaches, bed depth service time (BDST) approach based on Bohart and Adams equation is widely used [67]. This approach, herein after be referred as the BDST approach, is based on surface reaction rate theory, gives an idea of the efficiency of the column under constant operating conditions for achieving a desired breakthrough level. In the fixed-bed systems, the main design criterion is to predict how long the adsorbent material would be able to sustain removing a specified amount of impurity from solution before regeneration is needed. This period of time is called the service time of the bed. BDST is a simple model for predicting the relationship between bed height (Z) and service time (t) in terms of process concentrations and adsorption parameters. Hutchins proposed a linear relationship between bed height and service time given by equation:

$$t = \frac{NoZ}{CoU} - \frac{1}{K_a} C_o \ln\left(\frac{C_o}{C_b} - 1\right) \tag{17}$$

where C_o is the initial dye concentration (mg/L), C_b is the breakthrough dye concentration (mg/L), U is the linear velocity (cm/min), No is the sorption capacity of bed (mg/L), K_a is the rate constant in BDST model (L/mg/min), t is the time (min) and Z is the bed height (cm) of the column. Eq. (18) can be re written in the form of a straight line.

$$t = aZ - b \tag{18}$$

where

$$a = \text{slope} = \frac{No}{C_o U}$$

and

$$a = \text{intercept} = \frac{1}{K_a C_o} \ln\left(\frac{C_o}{C_b} - 1\right)$$

The results of BDST model are presented in Table 6 which showed that at different C_t/C_o ratios, the values of correlation coefficient were high which showed good agreement of experimental data with BDST model.

Table 6
BDST parameters

C_t/C_o	a	b	K_a (L mg^{-1} min^{-1}) 10^4	No ($\times 10^{-4}$) mg L^{-1}	R^2
0.2	105	83.33	3.32	30.09	0.981
0.4	220	156.6	0.517	63.05	0.983
0.6	265	60	−0.135	75.95	0.9905

Table 5
Thomas model parameters

Inlet conc. (mg/L)	Bed height (cm)	Flow rate (mL/min)	K_{Th} (mL/min mg) $\times 10^3$	q_o (mg/g)	R^2
50	1	1.8	0.15	9.47	0.955
50	2	1.8	0.07	23.22	0.995
50	3	1.8	0.068	26.49	0.996
50	3	3.6	0.142	15.15	0.958
50	3	5.4	0.154	5.25	0.950
75	3	1.8	0.060	26.85	0.968
100	3	1.8	0.052	26.01	0.982

3.15. FTIR and SEM analyses

FTIR analysis was performed to elucidate the active sites present on the biosorbent to check out the pattern of biosorption of Indosol Turquoise FBL onto bagasse. A broad band at 3346.50 cm^{-1} indicated the presence of O-H group (carboxylic acids, phenols, and alcohols) on the surface of biosorbent as in cellulose, pectin, and lignin. The presence of peak at 2904.8 cm^{-1} indicated the asymmetric and symmetric vibrations of C–H of aliphatic acids. The peak present at 1732.08 cm^{-1} was because of stretching vibration of C=O bond which is due to presence of nonionic carboxylic groups which might be assigned to carboxylic acids and their esters. The peak at 1062.78 cm^{-1} was assigned to the stretching vibrations of C–OH of carboxylic acids and alcoholic groups. Due to specific interaction between biosorbent and dye molecules, change in the spectra was observed due to vanishing and broadening of some peaks. The –OH stretching peaks in dye loaded biosorbent disappeared or absorbed at lower frequency which confirmed the involvement of hydroxyl groups in the biosorption mechanism. The FTIR spectra indicated the exchanging sites and functional groups on which biosorption takes place [41].

The surface features and morphological characteristics of the biosorbent can be studied by using SEM. It is used to determine the particle shape and porous structure of biomass. Greater the number of pores, greater will be the biosorption of dye onto the biosorbent surface. The photographs indicated the porous and fibrous texture of the biosorbent with high heterogeneity that could contribute to the biosorption of the dyes.

4. Conclusion

This study highlighted the potential of bagasse for the removal of Indosol Turquoise FBL from aqueous solution. Batch experiment results indicated that maximum dye removal was achieved at pH 3 using 0.05 g bagasse at 303 K. The biosorption capacity (mg/g) of bagasse decreased with increase in biosorbent dose and temperature. The equilibrium data fitted well to the Langmuir adsorption isotherm and pseudo-second-kinetic model. The thermodynamic parameters indicated the feasibility of reaction. Continuous study results indicated that increase in bed height increased the breakthrough time and biosorption capacity while increase in flow rate and initial dye concentration decreased the breakthrough time. The column data fitted well to Thomas model and BDST model. Overall results indicated that bagasse could be used as an efficient biosorbent for the removal of Indosol Turquoise FBL from aqueous solution.

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