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Equilibrium modeling for adsorptive removal of Indosol Black NF dye by low-cost agro-industrial waste: batch and continuous study

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ABSTRACT

In the present study, a low-cost agricultural waste, peanut husk, has been used as a potential biosorbent in native, pretreated and sodium-alginate immobilized form for the adsorptive removal of Indosol Black NF dye from aqueous solutions. Pretreatment of peanut husk with a chelating agent, polyethyleneimine, significantly enhanced its biosorption capacity. Different important process parameters like pH, contact time, biosorbent dose, initial dye concentration, and temperature were optimized during the study. The biosorption process was found to be feasible at acidic pH and was exothermic in nature. An agitation time of 15–30 min was sufficient to get equilibrium with native and pretreated biomass while immobilized biomass took 1 h for attainment of equilibrium. Maximum biosorption capacity (89.6 mg/g) was with pretreated biomass. Dye biosorption process followed pseudo-second-order kinetic model and equilibrium data fitted well to Langmuir isotherm model. Thermodynamic study indicated the spontaneity of biosorption process at lower temperatures. Continuous mode study was carried out to optimize the important parameters like bed height, flow rate, and initial dye concentration. Thomas and bed depth service time models were applied to the column study data. Maximum biosorption capacity in continuous mode study was 40.32 mg/g. Surface analysis of peanut husk biomass was carried out using Fourier transform infrared (FTIR) and scanning electron microscopy (SEM). FTIR analysis showed the involvement of hydroxyl, carbonyl, and carboxyl groups in the biosorption process. The results indicated that peanut husk could be used for treatment of wastewater containing dyes.

Keywords: Indosol Black NF; Biosorption; Batch studies; Kinetics; Thermodynamics

1. Introduction

Textile industries are playing a major role in increasing water pollution by releasing dye containing wastewater. It is estimated that in textile industry, total dye consumption is in excess of 10^7 kg per year [1,2] and about 1 million kg per year of dyes is discharged into water bodies [3]. Dye manufacturers and consumers are interested in stability and fastness, and so they are producing the dyestuff that is hard to degrade after use [4,5]. The presence of these dyes in wastewaters can affect photosynthetic activity due to reduced light penetration and may also be toxic to certain forms of aquatic life [6]. The wastewater discharged to natural receiving waters may make them

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unacceptable for public consumption. So it is necessary to eradicate dyes from textile wastewater.

Over the years, techniques like oxidative degradation [7], photo degradation [8], biochemical degradation [9], etc. have been utilized for the removal of pollutants from aqueous solution but these methods prove to be practically infeasible in terms of cost and application [10]. These methods also pose techno-economical limitations for field-scale applications [11]. This initiated researchers to explore newer and cost-effective methods for dye removal. The affinity of dye molecules to adhere to the surfaces could be exploited as a means of removing them through sorption [12]. It is now well established that due to its sludge free and easy operation, the adsorption technique has an edge over other physico-chemical methods of dye removal. Moreover, through biosorption the dyes can be completely removed even from the diluted solutions [13]. It is the procedure of choice and gives the best results among the numerous techniques of dye removal, and can be used to remove different types of coloring materials and other types of pollutants [14,15]. Over the last few decades, there has been an increase in the use of plant waste products for dye removal by biosorption from wastewater [16]. Among different agricultural wastes eucalyptus bark [17], date pits [18], citrus wastes [19], banana peel [20], rice husk [21], and barely husk [22] have been successfully employed for the removal of dyes from aqueous solution. But new economical, locally available and highly effective biosorbents are still under development.

Different agricultural wastes (bagasse, peanut husk, corncobs, cotton sticks, and sunflower) have been tested for the removal of Indosol Black NF dye which is a commonly used dye in textile industries and among these different biosorbents, peanut husk showed best removal potential so it was selected for this study. Peanut is an oil plant and it is extensively cultivated in Pakistan so peanut husk is abundantly available in Pakistan as a cheap agricultural by-product. Most of this agricultural by-product is arbitrarily thrown away or set on fire hence increases the environmental pollution. This agricultural by-product can be effectively used as biosorbent for the treatment of dye containing waste water. Both batch adsorption and fixed-bed adsorption studies are required to obtain key parameters required for the design of fixed-bed adsorber. Peanut husk was exploited in natural, treated, and immobilized form for the removal of Indosol Black NF dye in batch study while column study was performed with raw form of biosorbent.

2. Materials and methods

2.1. Chemicals

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

2.2. Preparation of biomass

Different agricultural waste materials (bagasse, peanut husk, corncobs, cotton sticks, and sunflower) were collected from different areas of Punjab, Pakistan to use as biosorbents in this study. These biomasses were cut into small pieces and were 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.

2.3. Preparation of aqueous dye solutions

Indosol Black NF dye was obtained from Clariant Pakisatn Limited, Faisalabad, 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 Black NF dye was anionic in nature and its λ_{max} was found to be 482 nm.

2.4. Batch experimental program

Screening test was carried out with five agricultural wastes for the selection of best biosorbent to use in the further study. Optimization of important process parameters such as pH, contact time, biosorbent dose, initial dye concentration, and temperature for the removal of Indosol Black NF 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 presence of different salts (NaCl, KNO_3, $CaCl_2$, $MgSO_4$, and $AlCl_3$) on the biosorption of Indosol Black NF was 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 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 for the adsorptive removal of Indosol Black NF by peanut husk biomass. Presence of surfactants was also investigated by using 1% of different surfactants Triton X-100, CTAB and one commercial surfactant, Arial. 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).

The equilibrium adsorption uptake, q_e (mg/g), was calculated using the following relationship:

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

where C_o is the initial dye concentration (mg/L), C_e is the equilibrium dye concentration (mg/L), V is the volume of the solution (L), and w is the mass of the biosorbent (g).

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. Peanut husk biomass (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 [23].

2.6. Pretreatment of peanut husk biomass

Peanut husk biomass was pretreated physically and chemically. During physical treatments, autoclaving (the peanut husk 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, and 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. Then the modified biosorbent were dried in oven at 60°C for 24 h and ground it [24].

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 peanut husk. 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 [25], pseudo-second-order [26], and intraparticle diffusion [27] kinetic models.

2.8. Biosorption equilibrium

Equilibrium experiments were carried out by taking known amount of peanut husk 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 [28], Freundlich [29], Temkin [30], and Dubinin–Radushkevich (D–R) [31].

2.9. Biosorption thermodynamics

Biosorption of Indosol Black NF 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. Fixed bed study

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 peanut husk biomass. At the bottom of the column, a stainless sieve was attached followed by a layer of glass wool. A known quantity of the peanut husk was packed in the column to yield the desired bed height of the adsorbent (2, 3, and 4 cm). Indosol Black NF dye solution of known concentrations (50, 75, and 100 mg/L) at pH 2 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 482 nm. All the experiments were carried out at room temperature (28 ± 1 °C).

2.11. FTIR and SEM studies

The chemical characteristics of peanut husk 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 peanut husk biomass was analyzed by JEOL JMT 300 scanning electron microscope (SEM).

3. Result and discussion

3.1. Screening study

The results of screening study are presented in Fig. 1. The results showed that all the biosorbents have a good potential to adsorb the dye but maximum removal efficiency (20.48 mg/g) was exhibited by peanut husk. Hence, peanut husk was selected for further study.

3.2. Effect of pretreatments

Chemical modification procedures include pretreatment, binding site enhancement, binding site modification, and polymerization. The chemicals used for the pretreatment of peanut husk include different acids (HCl, H_2SO_4, HNO_3, and CH_3COOH), base (NaOH), surfactants (CTAB, SDS, Triton X-100), chelating agents (PEI, EDTA, and glutaraldehyde), and organic solvents (benzene and methanol). Peanut husk was also physically pretreated by autoclaving and boiling. The biosorption capacity of peanut husk was significantly enhanced when it was pretreated with polyethyleneimine (PEI). This might be due to the fact that new functional groups are introduced onto the surface of biosorbent through the grafting of long polymer chains onto the biomass surface via direct grafting or polymerization of a monomer. The results are presented in Fig. 2. Deng and Ting [32] worked extensively with PEI treated biomass, and found that when a large number of primary and secondary amine groups of PEI are cross-linked with biosorbent, it exhibited good biosorption capacities towards different metal ions [32].

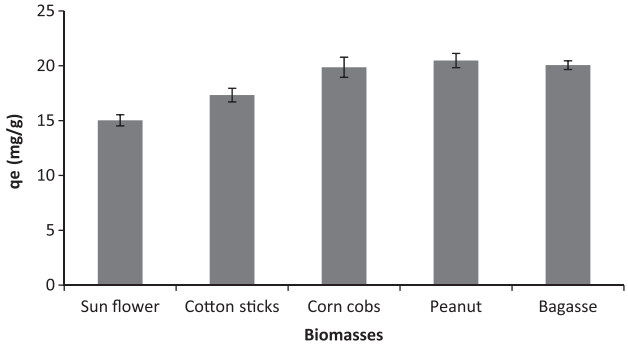

Fig. 1. Screening of different agricultural wastes for removal of Indosol Black NF: Dye concentration 50 mg/L, biosorbent dose 0.1 g/50 mL, temperature 30 °C, shaking speed 120 rpm.

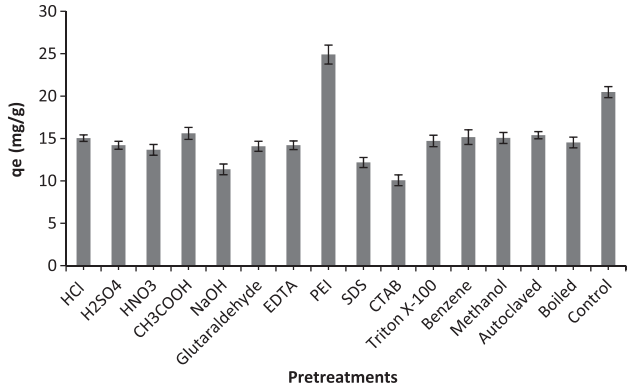

Fig. 2. Chemical and physical pretreatment of peanut husk for removal of Indosol Black NF: Dye concentration. 50 mg/L, biosorbent dose 0.1 g/50 mL, temperature 30 °C, shaking speed 120 rpm.

3.3. Effect of pH

Solution pH plays a very important role in biosorption process. At different pH levels, the electrostatic attraction, the structure of dye molecules, and biosorbent could play significant roles in adsorption of dye molecules onto the biomass surface [33]. Hence, the experiments were conducted to investigate the effect of pH on dye removal. The results indicated that maximum dye removal was achieved at pH 2 in case of native, PEI-treated, and immobilized biomass (Fig. 3). This might be due to the fact that a strong electrostatic interaction is developed between the biomass surface and dye anions due to protonation of functional groups at lower pH. With the increase in pH, the number of negatively charged sites is increased. The negatively charged binding sites on the biomass do not favor the adsorption of anionic dyes due to the electrostatic repulsion [34]. Another possibility of decreased adsorption at high pH is that at alkaline pH presence of excess OH^- ions destabilize

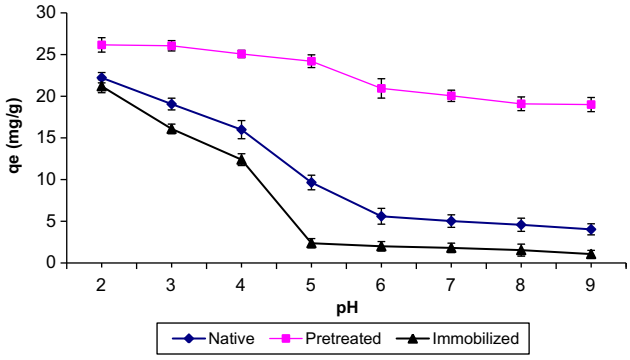

Fig. 3. Effect of pH on the biosorption of Indosol Black NF: Dye concentration 50 mg/L, biosorbent dose 0.1 g/50 mL, temperature 30°C, shaking speed 120 rpm.

the dye anions and compete with the dye anions for the adsorption sites. The effective pH was 2 and it was used in further studies. The biosorption capacity of Na-alginate immobilized biomass is less than free biomass. This may be due to the blocking of binding sites through immobilization and dye molecules become unable to reach the binding sites easily [35].

3.4. Effect of contact time

The biosorption potential of peanut husk was checked as a function of time and results are represented in Fig. 4. According to the results, biosorption seems to be the quick process. About 15–30 min of agitation time was found to be enough to get equilibrium point with native and PEI treated biomass. This might be due to the availability of great number of binding sites on the surface of biomass in the start which become occupied by dye molecules with the passage of time. Afterwards, the biosorption began to slow down due to slow movement of dye molecule into the interior bulk of the biosorbent [36]. Another possibility of later slow rate of dye removal is due to the electrostatic repulsion between the adsorbed negatively charged sorbate species onto the surface of adsorbent and the available anionic sorbate species in solution [37]. The dye removal rate was found to be slower with immobilized biomass and the equilibrium was achieved in 60 min. This is because of the fact that biosorbent existed inside the immobilized biomass; so dye molecules require more time to reach the active sites [21].

3.5. Effect of biosorbent dose

The biosorbent dosage gives an idea about the ability of biosorbent to adsorb the dye from an economical point of view. It was found that with the increase in biosorbent dose from 0.05 to 0.3 g, the dye removal decreased (Fig. 5). The decrease in amount of dye adsorbed, q_e (mg/g) with increasing biosorbent mass is due to the split in concentration gradient between solute concentration in the solution and the solute concentration in the surface of the biomass [38]. Similar results were reported for the removal of Congo red dye by using the pine cone biomass [39]. Thus with increasing biosorbent dosage, the amount of dye adsorbed onto unit weight of biosorbent get reduced which causes a decrease in q_e value with increasing biomass concentration [40].

3.6. Effect of initial dye concentration

Initial dye concentration plays a vital role in biosorption process. The high concentration of dye solution acts as a driving force to transfer dye molecules from bulk solution to the biomass surface and hence it overcome the mass transfer resistance between the aqueous and solid phases [41]. This explanation agrees with our experimental results of

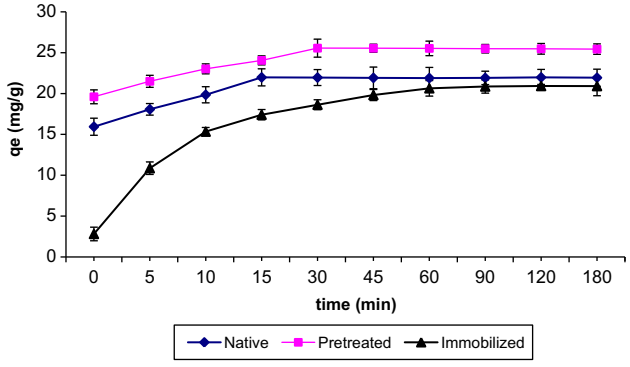

Fig. 4. Effect of contact time on the biosorption of Indosol Black NF: Dye concentration 50 mg/L, biosorbent dose 0.1 g/50 mL, temp 30°C, shaking speed 120 rpm.

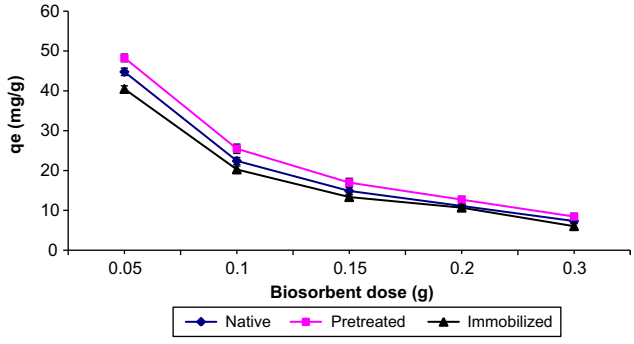

Fig. 5. Effect of biosorbent dose on the biosorption of Indosol Black NF: pH 2, temperature 30°C, shaking speed 120 rpm.

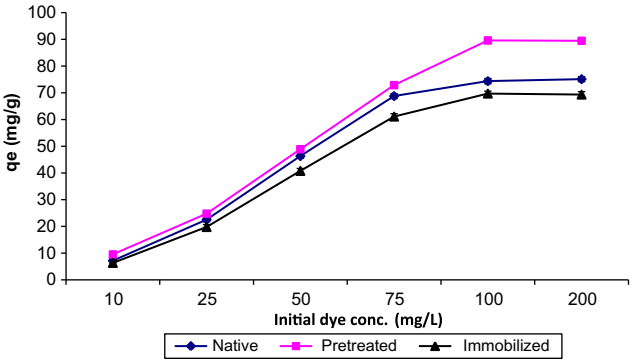

Fig. 6. Effect of initial dye concentration on the biosorption of Indosol Black NF: pH 2, temperature 30°C, shaking speed 120 rpm, biosorbent dose 0.05 g/50 mL.

effect of initial dye concentration (Fig. 6). The results clearly depict an increase in dye adsorption with the increase in initial dye concentration from 10 to 200 mg/L. The maximum dye removal (89.6 mg/g) was attained with PEI-treated biomass. The adsorption potential of immobilized biomass is low as compare to free biomass. Congo red adsorption onto the bentonites followed the trend of increased dye removal with increasing dye concentration [42].

3.7. Effect of temperature

Textile industries release their effluents at relatively high temperatures so temperature can be an important factor in dye removal process. The results demonstrate a slight decrease in dye removal with an increase in temperature (figure not shown). About 303 K was found to be favorable temperature for the dye removal from aqueous solution. This shows that biosorption of dye on peanut husk is an exothermic process and similar trend was previously reported by some other researchers [41,43]. In the process of biosorption, weak interaction forces (Van der Waals forces and hydrogen bonding) are involved and increase in temperature results in breakdown of adsorptive forces which result in decrease in dye removal at higher temperatures.

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 Black NF onto peanut husk biomass 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

Pseudo-first-order kinetic model is based on the fact that, the change in dye concentration with respect to time is proportional to power one. The integral form of the pseudo-first-order model generally expressed as

$$\log(q_e - q_t) = \log q_e - K_1 \times \frac{1}{2.303} \quad (2)$$

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 values of rate constant K_1, q_e calculated, q_e experimental and R^2 for the biosorption of Indosol Black NF using native, pretreated, and immobilized peanut husk biomass 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 significantly lower values of the equilibrium biosorption capacity (q_e) as compare to the experimental values. So results indicate inapplicability of pseudo-first-order kinetic model to the kinetic data of Indosol Black NF. Mostly, the firstorder kinetic model is not fitted well for whole data range of contact time and can be applied for preliminary stage of adsorption mechanism [44].

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 different equation is shown below:

$$\frac{dq_t}{d_t} = K_2(q_e - q_t)^2 \quad (3)$$

where K_2 (g/mg min) is the second-order rate constant of biosorption process.By integrating and applying boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$, the above equation can be written in linear form as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Table 1
Application of various kinetic models for the removal of Indosol Black NF

Kinetic models	Native	PEI treated	Na-alginate immobilized
Pseudo-first-order			
K_1 (L/min)	0.018	0.02	0.03
q_e experimental (mg/g)	21.98	25.56	20.92
q_e calculated (mg/g)	0.912	1.21	7.54
R^2	0.27	0.36	0.79
Pseudo-second-order			
K_2 (g/mg min)	0.110	0.086	0.015
q_e experimental (mg/g)	21.98	25.56	20.92
q_e calculated (mg/g)	22.02	25.57	21.36
R^2	1	0.9999	0.9994
Intraparticle diffusion			
K_{pi} (mg/g min$^{1/2}$)	0.382	0.409	1.158
C_i	18.338	21.549	9.529
R^2	0.559	0.655	0.667

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 second-order parameters K_2, q_e calculated, q_e experimental and R^2 for biosorption of Indosol Black NF are shown in Table 1. Results indicated that the values calculated and experimental q_e values are closer to each other. The correlation coefficient (R^2) is one for native and 0.999 for pretreated and immobilized biomasses which showed that the pseudo-second-order kinetic model well fitted to kinetic data. 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 [1,45].

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:

$$q_t = K_{pi} t^{1/2} + C_i \quad (5)$$

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 Black NF are given in Table 1. The intraparticle diffusion model implies that the plot of q_t vs. $t^{1/2}$ should be linear. If the intraparticle diffusion is involved in the biosorption reaction, then a plot of the amount of the solid adsorbed per unit mass of adsorbent (q_t) against square root of time ($t^{1/2}$) gave a straight line and the particle diffusion would be the controlling step if this line passed through the origin [46]. The poor value of correlation coefficient (R^2) indicates that the biosorption process of Indosol Black NF onto the peanut husk biomass was not depended on intraparticle diffusion only. It may be concluded that surface adsorption and intraparticle diffusion were concurrently operating during the biosorption of Indosol Black NF dye onto peanut husk biomass.

3.9. Biosorption isotherm

The biosorption isotherm is important for the description of how the dye molecules will interact with the biosorbent and gives an idea of the biosorption capacity of the biosorbent [47]. To simulate the biosorption isotherm, different models (Freundlich, Langmuir, Temkin, and (D–R)) were selected to explicate dye biosorbent 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 [29]. Mathematically, it can be expressed as

$$\log q_e = \log K_F = \frac{1}{n} \log C_e \quad (6)$$

where q_e is the amount of dye adsorbed per unit of adsorbent 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 indicates the biosorption capacity and n is a measure of deviation from linearity of the biosorption and used to verify types of biosorption [48]. It is suggested that if n is equal to unity, the biosorption is linear, n below unity indicates that biosorption is a chemical process; whereas, n above unity is associated with a favorable biosorption [47]. The values of R^2, K_F, and n are presented in Table 2. Values of correlation coefficient R^2 for native, pretreated, and immobilized biomass were very low which shows inapplicability of the model and are reported in the literature [49,50].

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 [51].

Table 2
Application of various equilibrium models for the removal of Indosol Black NF

Isotherm models	Native	PEI treated	Na-alginate immobilized
Langmuir			
q_m calculated (mg/g)	76.92	91.74	79.36
q_m experimental (mg/g)	75.11	89.6	69.3
b	0.256	0.297	0.06
R_L	0.019	0.016	0.07
R^2	0.992	0.995	0.923
Freundlich			
K_F	25.28	27.52	7.37
n	3.69	3.52	1.75
R^2	0.273	0.425	0.614
Temkin			
A	32.29	14.87	0.83
B	254.39	194.61	141.41
R^2	0.382	0.61	0.751
Dubinin–Radushkevich			
q_m (mg/g)	88.85	107.69	69.88
$K \times 10^4$ (mol^2 kJ^{-2})	0.009	0.007	0.06
E (KJmol^{-1})	7.453	8.45	2.88
R^2	0.654	0.696	0.996

The linear form of Langmuir can be written as [52].

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (7)$$

The Langmuir constants, q_m (maximum adsorption capacity) (mg/g) and b (values for Langmuir constant related to the energy of adsorption (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 for native, pretreated, and immobilized biomass (0.992, 0.995, and 0,923) and close agreement between experimental and calculated biosorption capacities indicate good fitness of this model to the equilibrium data of Indosol Black NF.

The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor for equilibrium parameter, R_L [53] which can be calculated as:

$$R_L = \frac{1}{1 + bC_o} \quad (8)$$

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 Black NF onto peanut husk was a favorable process. Different researchers found the fitness of Langmuir model to their experimental data [54,55].

3.9.3. Temkin isotherm

The Temkin isotherm model [30] 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:

$$q_e = B\mathrm{In}A + B\mathrm{In}C_e \quad (9)$$

where $B = RT/b$, T is the absolute temperature in Kelvin, b is Temkin constant, 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. 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 values for the data of biosorption of

Indosol Black NF onto native, pretreated, and immobilized biomass are 0.382, 0.61, and 0.751, respectively. Low values of R^2 suggest that the experimental data was 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 to Langmuir isotherm. This model is based on the fact that there is no homogeneous surface or constant biosorption potential. It is used for estimation of the porosity apparent free energy.

The linear form of (D–R) isotherm model [31] can be seen below

$$\mathrm{In}q_e = \mathrm{In}q_m - \beta\varepsilon^2 \tag{10}$$

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

$$\varepsilon = RT\mathrm{In}\left(1+\frac{1}{C_e}\right) \tag{11}$$

where R (8.314 $\mathrm{Jmol^{-1}\,K^{-1}}$) 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 biosorbent. E can be calculated from the β value by the following relation [56].

$$E = 1/(2\beta)^{1/2} \tag{12}$$

The value of this parameter can give information about biosorption mechanism. When one mole of ions is transferred, the value range 1–8 kJ/mol indicates physical adsorption [57], the value of E between 8 and 16 kJ/mol, indicates the adsorption process, followed by ion-exchange mechanism [58], while its value in the range of 20–40 kJ/mol is indicative of chemical adsorption [59]. So here it seems that physical adsorption mechanism is involved in case of native and immobilized biomass while ion exchange mechanism is involved in case of adsorption of dye molecules onto pretreated biomass (Table 2). Values of correlation coefficient ($R^2 = 0.654$, 0.696, and 0.996) for native, pretreated and immobilized biomass indicate low fitness of D–R model to the experimental data.

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 Black NF onto peanut husk biomass.

The thermodynamic parameters can be calculated using the following equations:

$$\Delta G^\circ = -RT\mathrm{In}K_d \tag{13}$$

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

According to Van't Hoff equation

$$\Delta G^\circ = \Delta H^\circ - \Delta H^\circ \tag{14}$$

$$\log(q_e/C_e) = -\Delta G^\circ/2.303RT = -\Delta H^\circ/2.303RT + \Delta S^\circ/2.303RT \tag{15}$$

The values of ΔH° and ΔS° were determined from the slope and intercept of Van't Hoff graph and are presented in Table 3. The biosorption of Indosol Black NF onto native, pretreated, and immobilized peanut husk biomass is an exothermic reaction which is also confirmed by negative values of ΔH°. Toor and Jin

Table 3
Thermodynamic studies for the removal of Indosol Black NF by peanut husk

Temp (K)	Native	Pretreated	Immobilized
	ΔG° (kJ/mol) ΔH° (kJ/mol) ΔS° ($\mathrm{Jmol^{-1}K^{-1}}$)	ΔG° (kJ/mol) ΔH° (kJ/mol) ΔS° ($\mathrm{Jmol^{-1}\,K^{-1}}$)	ΔG° (kJ/mol) ΔH° (kJ/mol) ΔS° ($\mathrm{Jmol^{-1}\,K^{-1}}$)
303	−6.39, −52.07, −151	−8.77, −70.1, −203	−3.51, −26.19, −74.96
308	−4.71	−6.74	−3.16
313	−3.99	−5.86	−2.36
318	−3.93	−4.80	−2.12
323	−2.91	−3.76	−1.85
333	−1.73	−2.85	−1.35

[42] also found similar results for the removal of diazo dye by using modified natural bentonite [42]. The negative values of ΔS° suggest the decrease in randomness at the solid/solution interface during the biosorption of Indosol Black NF onto peanut husk biomass. The negative values of ΔG° imply the spontaneous nature of the biosorption process. Similar results are also reported in literature by other researchers [41,43].

3.11. Effect of salts

Dyeing processes consume large amounts of salt. Hence, the concentration of salt in textile wastewater can be generally high. Experiments were conducted to check out the effect of salt concentration on the removal of Indosol Black NF dye by native peanut husk biomass (figure not shown). The results indicated that by increasing the salts concentration, the capacity of biosorbent to adsorb dye increased. This is due to the fact that increase in the ionic strength increases the positive charge of the surface of biosorbent hence it increases the electrostatic interaction between dye anions and biosorbent which results in increase in biosorption potential of biosorbent. Haq et al. [22] also observed an increase in biosorption capacity of barley husk biomass for the removal of Solar Red BA dye in presence of salt (KCl). The experimental results indicate that peanut husk biomass can be used for the removal of dye from salt containing water.

3.12. Effect of heavy metal ions

Different heavy metals were used for this study and results show that the removal of dye increases in case of Cd, Pb, and Co and a slight decrease in dye removal was observed in case of Cr and Cu (Figure not shown). Interaction between heavy metals and dye molecules results in the precipitation or aggregation of dye which lowers its solubility in the solution and so enhances its biosorption onto the biomass [22,60]. While the decrease in biosorption of dye in 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 [19].

3.13. Effect of surfactants

Surfactants are also used in textile industries to wash out the products and presence of these surfactants exerts a significant effect on the adsorptive removal of dyes. Usually presence of surfactants put a negative effect on the dye removal as surfactants compete with the dye molecules for the preferential adsorption onto the biomass active sites [22,61]. This explanation is in agreement with our experimental results. A slight decrease in the dye removal was observed in case of Triton X-100 and CTAB while a drastic decrease (0.93 mg/g) in dye adsorption was observed in case of a commercial surfactant, Arial (figure not shown).

3.14. Fixed bed study

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

$$V_{\text{eff}} = F \times t_{\text{total}} \tag{16}$$

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 adsorbent was calculated by the following equation:

$$\begin{aligned}&\text{Breakthrough capacity, } Q_{0.5}\\ &\quad = \text{Dye adsorbed on biosorbent bed (mg)/}\\ &\qquad \text{Mass of biosorbent in bed (g)}\\ &\quad = \text{ breakthrough time (at 50\%)} \times \text{flow rate}\\ &\qquad \times \text{ feed concentration/}\\ &\qquad \text{Mass of biosorbent in bed (g)}\end{aligned} \tag{17}$$

3.14.1. Effect of bed height

The breakthrough curves obtained for Indosol Black NF biosorption onto native peanut husk biomass at different bed heights (2, 3, and 4 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 indicate that by increasing the bed height from 2 to 4 cm the dye removal capacity of column increased from 22.8 to 34.56 mg/g. This is due to the fact that more biosorbent is present in case of higher bed heights which provide more binding sites for the attachment dye molecules [45,62]. The volume of treated effluent, breakthrough time, and exhaustion time also increase with the increase in bed height. Since, breakthrough time is the determining parameter of

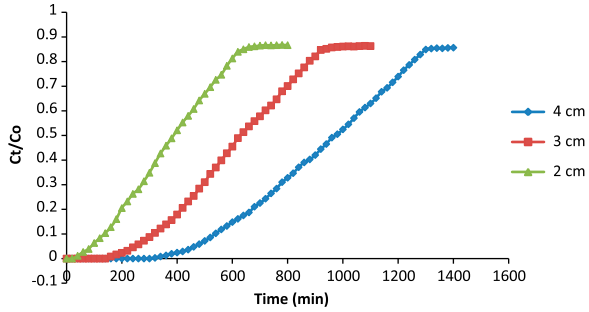

Fig. 7. Effect of bed height on the biosorption of Indosol Black NF by peanut husk.

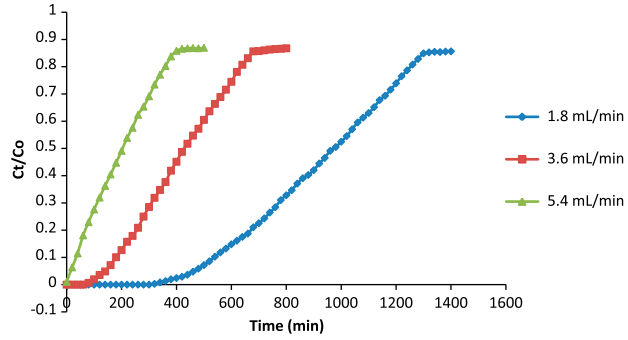

Fig. 8. Effect of flow rate on the biosorption of Indosol Black NF by peanut husk.

the process, the larger the breakthrough time, the better the intraparticulate phenomenon, and higher will be the biosorption capacity of column. 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 biosorbent got increased. Thus, the solute got enough time to get diffuse into the whole of the biosorbent, staying for more time into the column and treating more volume of effluent [63].

3.14.2. Effect of solution flow rate

Flow rate significantly affects the performance of column in continuous mode study. The effect of flow rate on the biosorption of Indosol Black NF onto peanut husk was investigated at different flow rates (1.8, 3.6, and 5.4 mL/min) keeping the bed height and initial dye concentration (4 cm and 50 mg/L) constant. The experimental results are presented in Fig. 8. The results indicate that the breakthrough time decreases at higher flow rates (Table 4). The earlier breakthrough point at higher flow rates was due to reduced contact time between dye molecules and biosorbent. 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 peanut 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 [63,64].

3.14.3. Effect of initial dye concentration

The effect of initial dye concentration was investigated by varying the concentration of Indosol Black NF from 50 to 100 mg/L at constant bed height of 4 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 [65,66]. The biosorption capacity of peanut husk increased from 34.56 to 40.32 mg/g by increasing the initial dye concentration from 50 to 100 mg/L. This is because the driving force for the mass transfer and the dye loading rate increases as the influent concentration increases [67]. The results are in agreement with the work of previous researchers [63]. However, the

Table 4
Column data and parameters with different bed height, flow rate and inlet concentration for the removal of Indosol Black NF

Inlet concentration (mg/L)	Bed height (cm)	Flow rate (mL/min)	Treated volume (L)	Breakthrough point (50%) (min)	Biosorption capacity (mg/g)
50	2	1.8	0.684	380	22.8
50	3	1.8	1.116	620	27.9
50	4	1.8	1.728	960	34.56
50	4	3.6	1.512	420	30.24
50	4	5.4	1.120	200	21.6
75	4	1.8	1.260	700	37.8
100	4	1.8	1.008	560	40.32

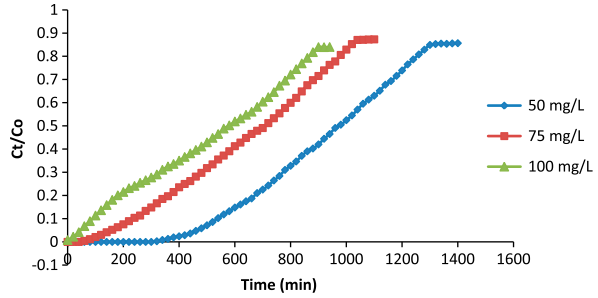

Fig. 9. Effect of initial dye concentration on the biosorption of Indosol Black NF by peanut husk.

biosorption capacity obtained from the column study was lower than that of obtained from the batch study for the same initial dye concentrations used. This might be due to the insufficient contact time between the dye molecules and the biosorbent in the column [68].

3.14.4. Application of Thomas model

Thomas model [69], assumes the Langmuir kinetics of adsorption–desorption and no axial dispersion, and is derived from the assumption that the rate driving force obeys second-order reversible reaction kinetics. This model also assumes a constant separation factor but it is applicable to either favorable or unfavorable isotherms.

The linearized form of Thomas model can be expressed as follows:

$$\ln\left(\frac{C_o}{C_t}-1\right)=\frac{k_{Th}\times q_o\times W}{Q}-K_{Th}\times C_o\times t \quad (18)$$

where k_{Th} (mL/min mg) is the Thomas rate constant; q_o (mg/g) is the equilibrium Indosol Black NF 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 biosorbent, 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 (figure not shown) to 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. (18) and the results are listed in Table 5. From Table 5 and itis seen that values of determined coefficients (R^2) range from 0.97 to 0.99. Results indicate that q_o increased significantly with the increase in bed height and initial dye concentration but the value of k_{Th} decreased 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. The reason is that the concentration difference between the dye on the biosorbent and the dye in the solution is the main driving force [55]. These results indicate that higher bed height, lower flow rate, and higher initial dye concentration are favorable for higher biosorption of Indosol Black NF onto peanut husk biomass in continuous mode study.

3.14.5. Application of bed depth service time model

Bed depth service time (BDST) approach is based on Bohart and Adams equation and it is widely used model [70]. BDST model is based on surface reaction rate theory. It 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 biosorbent will be able to sustain removing a specific 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 biosorption parameters. Hutchins proposed a linear relationship between bed height and service time given by Eq. (19)

Table 5
Thomas model parameters for the removal of Indosol Black NF by peanut husk

Inlet conc. (mg/L)	Bed height (cm)	Flow rate (mL/min)	K_{Th} (mL/min mg) × 10^3	q_0 (mg/g)	R^2
50	2	1.8	0.16	24.08	0.971
50	3	1.8	0.13	29.4	0.979
50	4	1.8	0.10	34.94	0.975
50	4	3.6	0.16	32.01	0.974
50	4	5.4	0.19	22.66	0.99
75	4	1.8	0.067	37.76	0.972
100	4	1.8	0.04	40.15	0.984

Table 6
BDST parameters for removal of Indosol Black NF by peanut husk

Ct/C_o	a	b	Ka (Lmg^{-1} min^{-1}) 10^4	No ($\times10^{-4}$) mg L^{-1}	R^2
0.2	232.5	−275.83	1.005	66.64	0.998
0.4	270	−231.67	0.35	77.39	0.994
0.6	305	−185	0.44	87.42	0.993

$$t = \frac{NoZ}{CoU} - \frac{1}{k_a C_o} \mathrm{In}\left(\frac{C_o}{C_b} - 1\right) \quad (19)$$

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), N_o is the biosorption 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. (20) can be re written in the form of a straight line.

$$t = aZ - b \quad (20)$$

where

$$a = \text{slope} = \frac{No}{CoU} \quad (21)$$

and

$$b = \text{intercept} = \frac{1}{K_a C_o} \mathrm{In}\left(\frac{C_o}{C_b} - 1\right) \quad (22)$$

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

3.15. FTIR and Scanning electron microscopic studies

The FTIR spectra of peanut husk before and after the biosorption of dye were studied in the range of 400–4,000 cm^{-1}. The results of the FTIR spectrum of unloaded biosorbent revealed the presence of peak at 2926.01 cm^{-1} which is due to the C–H stretching and indicates the presence of –CH and CH groups in the structure of peanut husk biomass (Fig. 10). The band at 1735.93 cm^{-1} allocate the C=O stretching vibrations. A broad band at 3309.85 cm^{-1} indicates the presence of –OH group (carboxylic acids, phenols, and alcohols) on the surface of biomasses as in cellulose, pectin, and lignin. Due to specific interaction between biosorbent and dye molecules, change in the spectra was observed due to vanishing and broadening of some peaks (Fig. 11). The –OH stretching peaks in

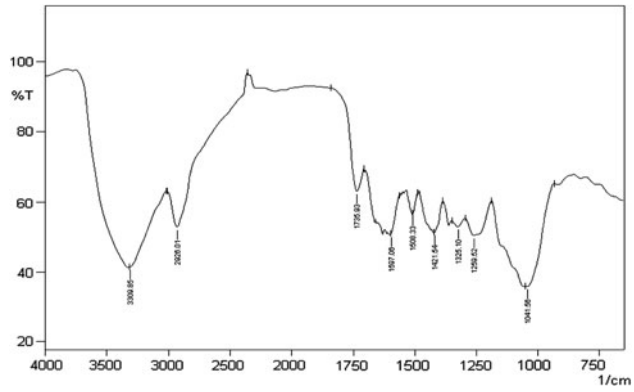

Fig. 10. FT-IR analysis of unloaded peanut husk biomass.

dye loaded biosorbent disappeared or absorbed at lower frequency which confirmed the involvement of hydroxyl groups in the biosorption mechanism. The FTIR spectra indicate the exchanging sites and functional groups on which biosorption takes place [71].

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. Typical SEM photographs of free peanut husk and Indosol Black NF loaded biomass are shown in Figs. 12 and 13. These photographs indicated the porous and fibrous texture of the biosorbent with high heterogeneity that could contribute to the biosorption of the dyes.

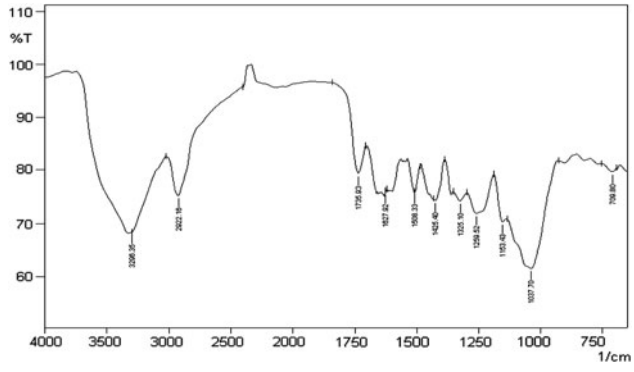

Fig. 11. FT-IR analysis of Indosol Black NF loaded peanut husk biomass.

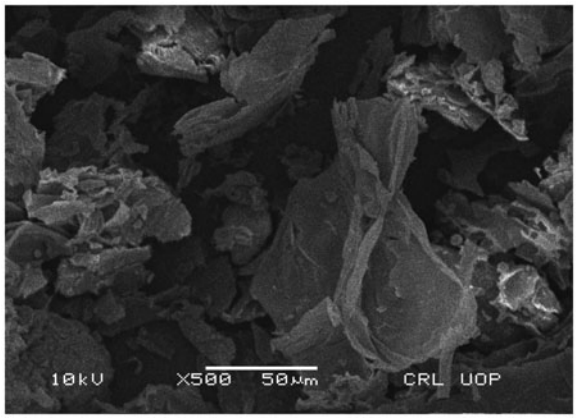

Fig. 12. SEM analysis of native peanut husk biomass.

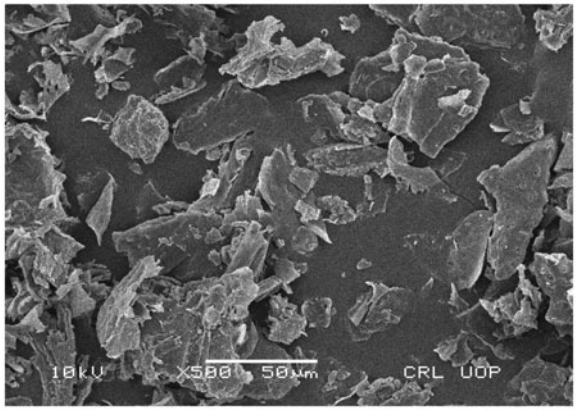

Fig. 13. SEM analysis of peanut husk biomass loaded with Indosol Black NF dye.

4. Conclusion

The biosorption of Indosol Black NF dye from aqueous solution by the native, PEI pretreated and Na-alginate immobilized biomass was studied in a batch system with respect to medium pH, contact time, biosorbent dose, initial dye concentration, and temperature. Peanut husk showed great potential for the removal of Indosol Black NF dye from aqueous solution. The results of the study clearly exhibited that chemical modification methods could be used to maximize the dye biosorption efficiency of the peanut husk biomass. Biosorption of Indosol Black NF dye was strongly pH dependent. The maximum biosorption capacities of the native, pretreated and immobilized biomass were found to be 75.1, 89.6, and 69.7 mg/g respectively. Pseudo-second-order kinetic model and Langmuir adsorption isotherm model were fitted well to the experimental data.

The native peanut husk biomass also showed good potential for the removal of Indosol Black NF dye in continuous mode study. Maximum dye removal in column study was 40.32 mg/g. The difference between the batch and continuous capacity could also be attributed to the fact that effective surface area of the peanut husk biomass packed in the column become lower than that in the stirred batch vessels.

Acknowledgments

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