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Continuous fixed bed removal of Novacron Orange P-2R using sugarcane bagasse: prediction of breakthrough curves

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ABSTRACT

A continuous fixed-bed study was carried out using polyethylenimine (PEI)-modified sugarcane bagasse as low-cost biosorbent for the removal of Novacron Orange P-2R reactive dye. The effect of different process parameters viz. bed height (1–3) cm, flow rate (3.6–7.2) mL/min, and initial dye concentration (25–75) mg/L on the biosorption capacity of PEI-modified sugarcane bagasse was investigated. The optimum bed height, flow rate, and initial dye concentration were found to be 3 cm, 3.6 mL/min, and 75 mg/L, respectively. The optimum biosorption capacities were observed to be 20.25 and 23.62 mg/g. The results suggested that the biosorption capacity and breakthrough curves were depended on process parameters. Data obtained from dynamic study were evaluated using the Thomas and Bed Depth Service Time models. Both of these models showed the good fitness and close agreement with experimental results at all experimental conditions, which indicated that both were well fitted for PEI-modified sugarcane bagasse. The results showed that the PEI-modified sugarcane bagasse could be used as a low-cost and efficient fixed-bed biosorbent for the elimination of the reactive dye from aqueous solution in column mode**.** The novelty of this work is the good efficiency of this PEI-treated agro waste for removal of this widely used reactive dye in continuous mode.

Keywords: Continuous; PEI-modified sugarcane bagasse; Reactive dye; Fixed bed; Thomas; BDST

1. Introduction

Water is a valuable resource and its minute volume on earth comprises fresh water which is used for population growth and by industries [1]. The need of fresh water is high than its availability. In last few decades, the fear of aquatic pollution has been enhanced. The industries, especially textile industries play a significant part in economy of the world and in our everyday life, but it discharges huge volumes of colored wastewater which pollutes the environment as well as water resources such as rivers, lakes, etc [2]. These colored textile effluents have untreated dyes and their

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derivatives which not only contaminate the ecosystem but also destroy human and aquatic lives [3].

Dyes have a complicated molecular structure which shows their stability toward biodegradation [4]. Synthetic dyes which are used in textile industries can be classified into three major types: cationic (basic), anionic (direct, acidic, and reactive), and nonionic (disperse and vat) [5]. Among anionic dyes, the usage of reactive dyes has enhanced rapidly because these show good affinity for cellulosic fibers whose utilization is increasing constantly. Reactive dyes are attached with cellulosic fibers by making covalent bonds which differentiate them from all other dyes [6]. Reactive dyes are more soluble in water and difficult to biodegrade. These dyes form a layer on the water surface and reduce the penetration of light into water which hinders the biota growth, slows down photosynthetic activity, and also chelates heavy metal ions which cause micro toxicity to aquatic organisms [7]. These dyes are toxic, cancer-causing and mutagenic in nature. So their removal from wastewater is very necessary before their discharge into water bodies to reduce their hazardous effects on human and marine lives [8].

Nowadays various physical, chemical, and biological methods have been developed for the removal of dyes and other pollutants. Mostly, these methods do not show good results as they show incomplete removal of dyes, require high operational cost, and also produce secondary products which are also hard to dispose off [9]. Among all physicochemical and biological methods, adsorption has been considered an efficient and attractive technology for the removal of dyes from wastewater. The advantage of adsorption is its cost-effectiveness, easy handling, and less production of byproducts [10]. Cost is a major factor which is considered in the selection of an adsorbent. Several biological waste materials such as peanut husk, corn cobs, rice bran, wheat straw, and PEI-modified sugarcane bagasse have been explored for taking away dyes from colored industrial wastewater [11]. Biosorption is generally a very rapid technology and utilizes inexpensive resources such as agro and industrial wastes which exist in plenty. These resources are very economical and can be used after little processing [12].

Sugarcane bagasse consists of cellulose, lignin, and hemicellulose. Several functional groups such as amino, hydroxyl, and carboxyl exist on the surface of this waste biomaterial which has the capability to attach with dye anions and can help in their removal from aqueous solution [13]. So biosorption is an ultimate technique which decreases the quantity of dyes in large volumes of colored industrial wastewater to minute quantities. However, the investigation for the best and effective biosorbent is under consideration [14]. Biosorption in column is an effective method for water purification. It has been investigated that the biosorption capacity of biosorbent can be enhanced using the fixed-bed biosorption technique [15].

Novacron Orange P-2R reactive dye behaves as a pollutant because it is a widely used dye in industries for coloring cellulosic fibers because of its bright coloration, easy application procedure, and water fastness, while the other dyes show limitations. So the wastewater discharge from different industries contains high amounts of this reactive dye due to low fixation rate. This dye has more solubility in water and is difficult to biodegrade, so wastewater after giving wide treatments may still contain this reactive dye.

In this study, reactive dye Novacron Orange P-2R has been removed using PEI-modified sugarcane bagasse in continuous mode. Different process parameters such as bed height, flow rate, and initial dye concentration have been optimized to check the effectiveness of this study on industrial scale for the elimination of dye from huge volumes of wastewater. Different kinetic models like Bed Depth Service time (BDST) and Thomas have been applied on the experimental data.

2. Materials and methods

2.1. Selection and preparation of biosorbent

PEI-modified sugarcane bagasse was made by treating the sugarcane bagasse with polyethyleneimine [13]. Then it was washed with distilled water and dried at 60°C for 24 h in an oven. After converting it into powder form, it was sieved using Octagon siever (OCT-DIGITAL 4527-Ol) of 300-μ particle size. The biosorbent of 300-μ particle size was saved in air tight jars for further use.

2.2. Preparation of stock solution of the dye

Novacron Orange P-2R reactive dye was gifted from commercial market of Faisalabad city, Pakistan. The λ_{max} of dye was 486 nm and C.I was reactive orange −13. The dye was 60–70% pure because it was a commercial dye and was available in the form of sodium salt (Na_2 SO_4). Standard solution of the dye was prepared by dissolving 1 g dye in 1,000 mL distilled water. The stock solution was shook well and then preserved in air tight bottles for further use.

2.3. Column study

The Pyrex glass columns (internal diameter: 1.2 and 2.2 cm and height: 43 cm) were used for conducting

continuous flow biosorption experiments. Three columns were used in the setup for performing experiments, fed by flow rate in the range of 1.8–7.2 mL/min using multi-channel peristaltic pump. A glass wool was placed on the stainless steel that was attached at the end of the column. Polytetrafluoroethylene (PTFE) was utilized for making all fittings and inters connected tubes. All experiments were performed at a constant 293 K temperature. The effect of pH (range 2–9) was studied on biosorption of Novacron Orange P-2R using PEI-treated sugarcane bagasse. The optimum pH was found to be 2. Increase in biosorption capacity at low pH might be due to the creation of large number of cationic sites on the biosorbent's surface that resulted in more electrostatic attractions between dye anions and the biosorbent surface and hence more dye removal [13]. Known amount of biosorbent was packed in the column to attain the bed height in the range of 1–3 cm. 0.1-M NaOH and HCl solutions were used for adjusting the pH. The solution of dye of known concentrations in the range of 25–75 mg/L was pumped into the column at a desired flow rate (3.6 to 7.2 mL/min) at constant pH 2. After regular time intervals, samples were collected in test tubes for analysis that was carried out using double beam UV–visible spectrophotometer (Shimadzu Brand UV-4000). It measured the remaining dye concentration after biosorption at λ_{max} = 486 nm [16]. Series of experiments were performed to study the effect of different process parameters such as bed height, flow rate, and initial dye concentration on the biosorption process.

3. Results and discussion

3.1. Fixed-bed column study of Novacron Orange P-2R

The removal of Novacron Orange P-2R in a glass column (having diameter 2.2 and 43 cm in length) was determined for three different bed heights, flow rates, and initial dye concentrations using Eq. (1) and all these values are presented in Table 1.

$$\text{Break through capacity}(Q_{50\%}) = \frac{\text{Break through time (at 50\%)} \times \text{flow rate} \times \text{initial dye conc.}}{\text{Mass of biosorbent in the bed}} \quad (1)$$

3.2. Effect of bed height

The breakthrough curves attained for the biosorption of Novacron Orange P-2R for three varying heights 1, 2, and 3 cm (0.8, 1.6, and 2.4 g, respectively) of modified-bagasse bed at the constant inlet concentration 25 mg/L of Novacron Orange P-2R solution, flow rate 3.6 mL/min, and the breakthrough curves were plotted between time and ratio of outlet (final) and inlet (initial) Novacron Orange P-2R concentrations (C_{out}/C_{in}). The results are shown in Fig. 1. An increase in the bed height increased both the time of breakthrough and the saturation/exhaustion time. When the height of the adsorption bed is increased, the time of breakthrough also increased because the zone of mass transfer had to travel more distance from the entering point of the bed to the exit point [15]. An increase in the bed height provides greater number of fixation sites for binding, by increasing the specific surface area of the modified bagasse, and thus causing more biosorption of the dye resulting in the higher removal of Novacron Orange P-2R. The mass of the biosorbent also increased due to the increase in the bed height which offered more surface area for the biosorption process, and thereby increasing the volume of the treated solution. The reduction in the bed height causes the predominance of phenomenon of axial dispersion rather than mass transfer; therefore, the solute had no good time for diffusion into the whole bed of the biosorbent, and thus reducing solute diffusion [17]. The biosorption capacities of three bed heights i.e. 1, 2, and 3 cm were found to be 13.5, 18.56, and 20.25 mg/g, respectively (Table 1). The maximum biosorption capacity was found at 3 cm by keeping the flow rate constant at 3.6 mL/min and initial dye concentration as 25 mg/L. This 3-cm bed height was then selected as the optimum bed height for further experiments. It showed that the biosorption capacity of pretreated sugarcane bagasse for Novacron Orange P-2R increased by increasing the bed height because at higher bed height, the biosorbent molecules had more time to contact with dye molecules. So the quantity of dye molecules observed in aqueous solution at higher bed height is less. Reduction in the slope of breakthrough curve was observed using a large quantity of biosorbent dose which caused the broadened mass transfer zone. Similar trend was observed in batch and fixed-bed column adsorption of crystal violet using jackfruit. It was observed that the

Table 1
Column adsorption capacities ($Q_{50\%}$) of Novacron Orange P-2R at different experimental conditions of flow rate (mL/min), bed height (cm), and initial dye concentration (mg/L)

Inlet conc. (mg/L)	Break point (50%) (min)	Flow rate (mL/min)	Bed height (cm)	Adsorption capacity (mg/g)
25	120	3.6	1	13.5
25	330	3.6	2	18.56
25	540	3.6	3	20.25
25	210	5.4	3	11.81
25	180	7.2	3	13.50
50	300	3.6	3	22.50
75	210	3.6	3	23.62

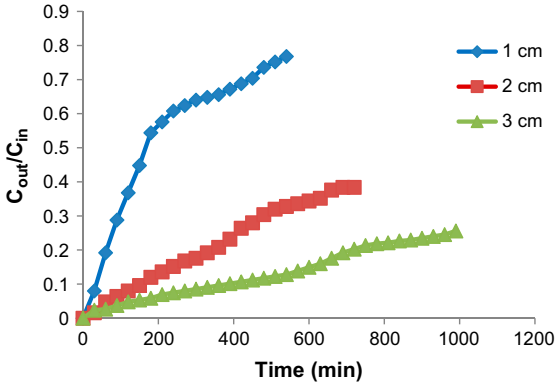

Fig. 1. Breakthrough curve for bed height in continuous mode study.

biosorption capacity enhanced by increasing the bed height from 3 to 12 cm and breakthrough time was also enhanced from 350 to 1,000 min [18].

A symmetrical S-shaped curve is associated with microporosity. More often than not, the breakthrough curves for sugarcane bagasse are not a symmetrical S shape but are skewed, being steeper at the beginning of curve. The reason for it is the heterogeneity within the bed, both on micro and macro scales. Within breakthrough experimental systems, the solute being adsorbed is located initially in the porosity of smallest dimensions which have the highest of retentivity. As the narrowest of microporosity is progressively filled toward the wider pores, the retentivity decreases and this manifests itself as a decrease in gradient of the breakthrough curve. Within the bed, transition from the mixture to the pure component occurs within a finite volume element and it is the shape of this volume element which influences the shape of the breakthrough curve. Similar results were found in the removal of methylene blue by peanut husk in continuous mode. The maximum removal of methylene dye was observed at higher bed height [19]. Al-Degs et al. [16] reported the same trend in biosorption of reactive dyes using activated carbon in continuous study.

3.3. Effect of flow rate

Breakthrough curves were attained for Novacron Orange P-2R on modified bagasse for three flow rates 3.6, 5.4, and 7.2 mL/min while keeping the initial concentration 25 mg/L constant and using the optimized bed height 3 cm. The results are given in Fig. 2. It was observed that with higher flow rate, the occurrence of breakthrough was faster [9]. At lower flow rate, more time was required for the time of breakthrough to reach exhaustion/saturation. The variability of the capacity of biosorption and breakthrough curve slope can be described on the principles of mass transfer. Higher flow rate caused saturation of bagasse more rapidly because there was an increase in mass transfer rate, and thus causing the quick saturation of biomass [20]. At the start of the column experiment and at the lowest flow rate 3.6 mL/min, greater removal of Novacron Orange P-2R on modified bagasse was observed. However, by the continuous flow of dye solution through the column, the outlet concentration

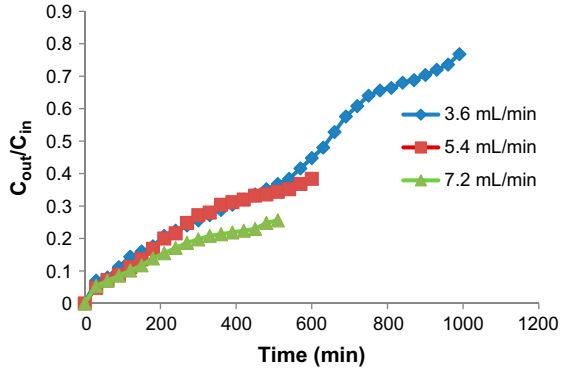

Fig. 2. Breakthrough curve for flow rate in continuous mode study.

of dye rapidly increased and the biosorption bed became exhausted rapidly with dye and the effluent concentration increased to the initial concentration of Novacron Orange P-2R. At higher flow rates, breakthrough curves became much sharper. An increase in the flow rate also decreased the time of breakthrough point and total amount of Novacron Orange P-2R biosorbed onto modified bagasse. It can be attributed to the fact that the biosorption of Novacron Orange P-2R onto modified bagasse is affected by less time of residence of the dye solution in the column, less number of sites for binding and insufficient diffusion of the dye solution in the pores of modified bagasse, and the dye exits the column before the occurrence of equilibrium. Similar trend has also been reported by Aksu and Gonen in fixed-bed experiments for biosorption of phenol using immobilized activated sludge. It was observed that the maximum biosorption capacity was achieved at lowest flow rate 0.8 mL/min [21]. The biosorption capacities of three flow rates 3.6, 5.4, and 7.2 mL/min were found to be 20.25, 11.81, and 13.5 mg/g, respectively, and were presented in Table 1. The maximum capacity of biosorption was found for flow rate 3.6 mL/min, at 3 cm and 25 mg/L initial dye concentration. This 3.6 mL/min flow rate was then selected and was used as the optimum flow rate for further experiments. Han et al. [22] found the higher removal of methylene blue by phoenix tree leaf powder in fixed-bed column at lower flow rate. They observed that at low flow rate, methylene blue showed large interaction with the biosorbent particles due to high residence time which resulted in maximum biosorption of dye molecules from aqueous solution in continuous mode. The significant effect of lowest flow rate 5 mL/min was also observed in removal of acid blue 15 dye by fresh water macroalga *Azolla filiculoides* in column study at constant bed height 25 cm and initial dye concentration 100 mg/L. This trend might be because of the availability of insufficient time for interaction of dye molecules with biosorbent at higher flow rates [23].

3.4. Effect of initial dye concentration

The effect of different initial dye concentrations was investigated using Novacron Orange P-2R solution of 25, 50, and 75 mg/L keeping the bed height 3 cm and flow rate 3.6 mL/min constant. The breakthrough curves were plotted between C_{out}/C_{in} against time (t). The results are presented in Fig. 3. An increase in the initial concentration of Novacron Orange P-2R resulted in less service time for the bed and sharpness of the breakthrough curves. The modified bagasse fixed-bed

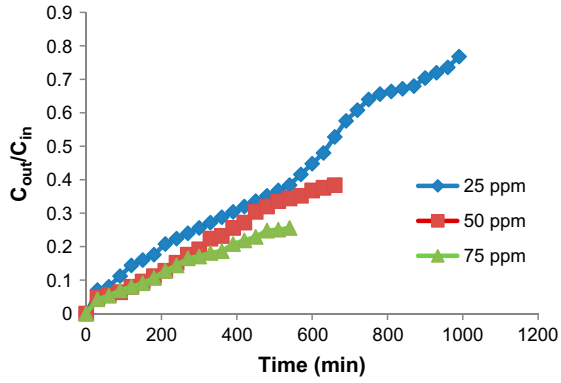

Fig. 3. Breakthrough curve for initial dye concentration in continuous mode study.

column was saturated more rapidly at 75 mg/L which resulted in less time for both the breakthrough point and saturation point. The performance of the column was affected by the change in the initial solution of Novacron Orange P-2R. With an increase in the inlet concentration from 25 to 75 mg/L, both the total removal of Novacron Orange P-2R and treated effluent volume decreased. However, the capacity of the biosorption of the bed at the breakthrough point and saturation were found to increase from 20.25 to 23.625 mg/g at 3 cm bed height and 3.6 mL/min flow rate. The biosorption capacities of three different initial dye concentrations 25, 50, and 75 mg/L were found to be 20.25, 22.5, and 23.62 mg/g, respectively, at 3.6 mL/min flow rate and 3-cm bed height and are presented in Table 1. The maximum biosorption capacity of modified bagasse was found to be 23.62 mg/g for 75 mg/L. The reason for biosorption is the difference in concentration between the dye present in the solution and the amount of dye on the bagasse and this high difference in concentration gives more driving force for the biosorption [24]. Tan et al. [17] investigated the effect of 50–150 mg/L of initial methylene blue concentration at constant bed height 6 cm and flow rate 20 mL/min. It was found that at 150 mg/L dye concentration, the biosorbent bed was exhausted in less time which caused earliest breakthrough. Similar trend has also been observed in the removal of methylene blue from aqueous solution in fixed-bed column study [24].

3.5. Kinetic modeling of experimental data

For the description of packed-bed column experiments and to make it usable on industrial scale, two kinetic models, Thomas and BDST, were applied to the experimental data of the column.

3.5.1. BDST model

The model of BDST describes that there is a linear relationship between the service time (t) and the bed height (z). The equation of BDST is expressed as:

$$t = \frac{N_0 Z}{C_0 U} - \frac{1}{K_a C_0} \ln\left(\frac{C_0}{C_b} - 1\right) \quad (2)$$

where C_b is the concentration (mg/L) of the dye solution at breakthrough point, initial concentration is C_i, V (cm/min) is the linear velocity, N_0 (mg/L) is the capacity of biosorption, and the rate constant is K_a (L/mg min). The plot of t-Z at the 0.2, 0.4, and 0.6 C_b/C_{in} values at the 3.6 mL/min flow rate and 25 mg/L initial concentration, (with $R^2 = 0.96$, 1 and 0.99) respectively, shows the very good validation of model of BDST for Novacron Orange P-2R. By keeping C_i and V as constant values, the slope of the BDST line gave the capacity of sorption of bed N_0, and k_a was calculated from the value of the intercept. The K_a, constant of the rate of reaction, describes the rate of transfer of the dye from the liquid solution to the solid surface of the adsorbant [22]. It was observed that with an increase in the values of C_b/C_{in} from 0.2 to 0.6 at 3.6 mL/min flow rate and 25 mg/L C_i, there was an increase in the value of N_0, while the value of K_a decreased. The capacity of sorption of bed N_0 (mg/L), K_a (L/mg min), together with their R^2 values at C_b/C_i values of 0.2, 0.4, and 0.6 are represented in Table 2.

3.5.2. Thomas model

This model is suitably used for the determination of concentration (q_0) of solid phase of the sorbate and the rate constant (K_{th}) of the sorbate using the linear form of this model given below:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{K_{th} \times q_0 \times W}{Q} - K_{th} \times C_0 \times t \quad (3)$$

Data of the column experiments of Novacron Orange P-2R at different heights of biosorption bed, flow rates, and initial concentrations of Novacron Orange P-2R were fitted to this model and q_0 and K_{th} were determined. The values of q_0 and K_{th} were determined from the plot of t vs. $\ln(C_{in}/C_t - 1)$ and coefficient (R^2) of linear correlation was attained for Novacron Orange P-2R. Table 3 shows the comparison of q_0 predicted by model of Thomas and experimentally determined q_0 values give a summarized form of the parameters of model of Thomas attained at varying heights of the adsorption bed, inlet concentration of Novacron Orange P-2R, and flow rates. The q_0 values were found to increase from 13.50 to 20.25 mg/g with an increase in bed height from 1 to 3 cm and 13.50–23.62 mg/g with increase in initial dye concentration

Table 2
The calculated BDST model's constants for the adsorption of Novacron Orange P-2R on bagasse (V = 3.6 mL/min and C_i = 25 mg/L)

C_b/C_{in}	a (min/cm)	b (min)	N_0 (mg/L)	$K_a \times 10^{-4}$ (L/mg min)	R^2
0.20	45	−20	21.11	2.11	0.96
0.40	150	−60	28.77	2.7	1
0.60	225	−70	31.44	−2.31	0.99

Table 3
Parameters of Thomas model at different experimental conditions for Novacron Orange P-2R

Bed height (cm)	Flow rate (mL/min)	Initial dye conc. (mg/L)	$q_{0\ exp}$ (mg/g)	$q_{0\ cal}$ (mg/g)	K_{th} (L/mg min)	R^2
1	3.6	25	13.50	11.20	−0.0022	0.96
2	3.6	25	18.56	15.10	−0.0043	0.98
3	3.6	25	20.25	21.11	−0.0072	0.99
3	5.4	25	11.81	10.42	−0.0026	0.97
3	7.2	25	13.50	12.17	−0.0031	0.96
3	3.6	50	22.50	20.11	−0.0083	0.98
3	3.6	75	23.62	23.12	−0.0114	0.97

from 25 to 75 mg/L, but a decrease was observed in the value of k_{th} in the same manner as observed in fixed-bed biosorption of crystal violet [18].

3.6. Characterization of the biosorbent (FTIR and SEM)

FTIR spectrum gives the interaction of anions of the dye with the biosorbent's functional groups. The spectrum contains large number of absorption bands that show the complicated nature of the biosorbent. The broad absorption band at 3,334.62 cm^{-1} is due to the presence of −OH and −NH groups on the sugarcane bagasse surface. The complex network of bands appearing in the range 1,650.66–1,457.65 cm^{-1} indicates the overlapping of different bands. This might be due to the overlapping of bands of aromatic ring and double bond (C=C) vibrations with bands of C=O stretching and −OH vibrations. At 1,457.65 cm^{-1}, the peak appeared due to the C–N vibrations. The existence of peak at 1,650.66 cm^{-1} indicated the presence of carboxylic group (–C=O) stretching vibration. The peak at 2,923.77 cm^{-1} may be due to the presence of the aliphatic groups that show the symmetric and asymmetric C–H stretching. All above-identified peaks give the confirmation about the lignin structure of the sugarcane bagasse. So the FTIR spectrum shows the functional groups and the binding sites by which biosorption takes place [13].

The features and morphological properties of the biosorbent surface were determined by doing scanning electron microscopic studies. It gives information about the shape of biosorbent particles as well as the porous structure of the biomass. Greater the number of pores on the biosorbent surface, greater the biosorption of dye will take place. Typical SEM photographs of native biomass and dye-loaded biomass are represented in Fig. 4((a) and (b)). These photographs represented that the texture of the biosorbent was porous and fibrous in nature having high heterogeneity that contributed to the biosorption process.

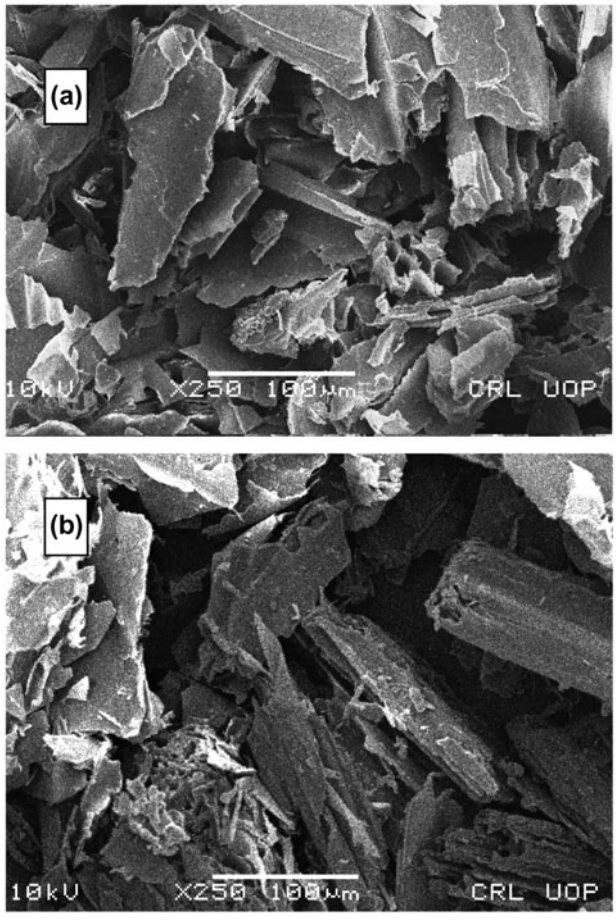

Fig. 4. SEM analysis of (a) native biomass and (b) dye-loaded biomass.

4. Conclusion

The biosorption capacity of PEI-modified sugarcane bagasse was determined for Novacron Orange P-2R reactive dye in continuous mode by optimizing different experimental factors such as bed height, flow rate, and initial dye concentration. It was found that the maximum removal was obtained at higher bed height 3 cm, minimum flow rate 3.6 mL/min, and high initial dye concentration 75 mg/L. Thomas and BDST models both showed the good fitness on the experimental data. On the whole, it can be concluded that the PEI-modified sugarcane bagasse possessed good capability for the removal of Novacron Orange P-2R from aqueous solution with additional qualities of low cost and easy availability.

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