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Removal of Indigo Carmine and Eosin Y Anionic Dyes from Aqueous Solution by Fixed Bed Chitosan

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Abstract : *The removal of Indigo carmine and Eosin Y from aqueous solutions using natural adsorbent Chitosan in a fixed bed has been investigated. The effect of initial concentration on the breakthrough curve has been examined. The adsorption isotherm of Indigo carmine and Eosin Y from aqueous solution on chitosan in a packed bed at 303.15 K was determined. The break through experimental results are tested with Thomas model, Yoon-Nelson model and Adam-Bohart model by means of non-linear regression analysis.*

Keywords: *Adsorption, Breakthrough Curve, Eosin Y, Fixed Bed, Indigo Carmine*

1. Introduction

Dyes are commonly used in textile, printing, pharmaceutical, paper, leather, and cosmetic industries [1,2]. Out of all, textile industry uses maximum amount dyes in its processing. Textile industries release a considerable amount of dyes along with its effluent [3]. There are several methods to remove dyes from effluents, which may be broadly classified as physical, chemical, and biological methods. To apply suitable treatment method one need to understand more about the dyes such as, what category it is belonging to its chemical nature. Dyes are classified to several categories. The commonly encountered classification is natural and synthetic dye. The another classification is anionic, cationic dyes. It is interesting to note that every dye has its unique chemistry, structure and particular way of bonding.

Effluents from textile industry causes contamination to the water bodies. These dyes pollute natural water bodies and it lead to serious problem. Therefore, treatment of colour effluents is an important subject globally. There are several methods for the removal of dyes from effluents. However, the treatment using adsorbent has proven to be a very efficient and less energy intensive operation [4]. The adsorption studies are usually carryout in batch mode or column mode operations. Each mode of contact has its own advantages. Batch studies are usually carried out to see the effect of concentration, adsorbent dosage, pH and kinetics [5,6]. Column studies are used to establish breakthrough curves and to see effect of dosage, flow rate, pH and concentration [7]. Both the methods are used to establish isotherms. The method of establishing isotherm through break through studies is known as Frontal method.

The information obtained from the break through curve such as break through time, exhaust time and stoichiometric wave front time are used in scale up. Present study aims to remove Indigo carmine and Eosin Y anionic dyes from synthetic waste water by using a natural adsorbent chitosan and to investigate the influence of initial concentration on column adsorption process. The study focuses on establishing breakthrough curve for a fixed bed. The established break through curves are evaluated with popular models suggested by Thomas, Yoon-Nelson, and Adam-Bogart by means of non-linear regression analysis. Further, we have reported adsorption isotherms and some important parameters such as break through time, exhaust time and stoichiometric wave front time.

2. Experimental Procedure

The chitosan was prepared from chitin from the waste of crab and shrimp shells [9]. This waste is available abundantly from local fish market of Cuddalore, Tamil Nadu. These are the marine source of Bay of Bengal, India. The anion dyes indigo carmine (CAS No. 860 – 22 – 0, mass fraction purity 98) was purchased from Loba Chemie (India) and Eosin Y (CAS No. 17372-87-1, mass fraction purity 88) was purchased from Nice (India).

The chitin was deacetylated with 50 % sodium hydroxide solution to get chitosan. The degree of deacetylation of the chitosan sample was found to be 55.44 percent from the Fig.1, FTIR spectrum [4]. The concentration of the dye in the solution at the column outlet was accurately measured by UV spectrophotometer (Jasco UV model V – 630) at 611 nm for indigo carmine and 517 nm for eosin Y respectively. The calibration was done with known concentration of dye solution. The UV response curves and calibration graphs for Indigo carmine and Eosin Y graphs are shown in Fig. 2a , Fig. 2b, Fig. 3a and Fig. 3b respectively.

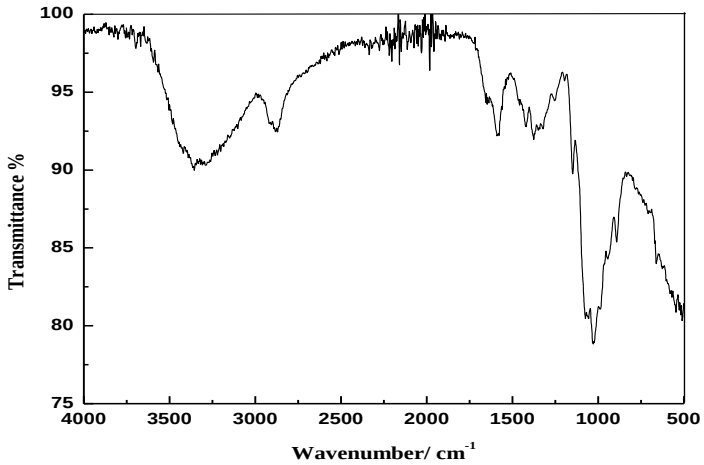

Fig. 1 The FTIR spectrum of chitosan sample.

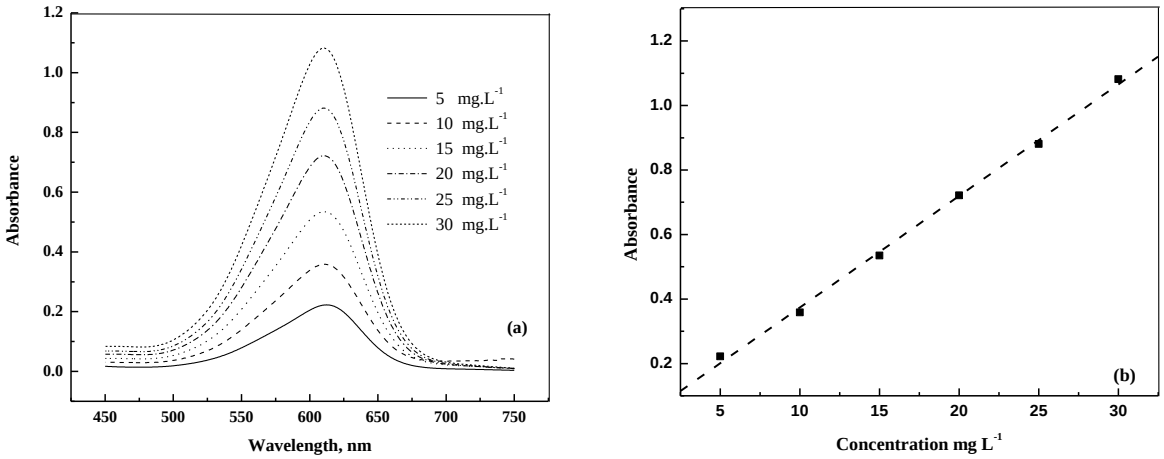

Fig. 2 (a) Absorbance versus wavelength for Indigo carmine (b) absorbance versus concentration for Indigo carmine.

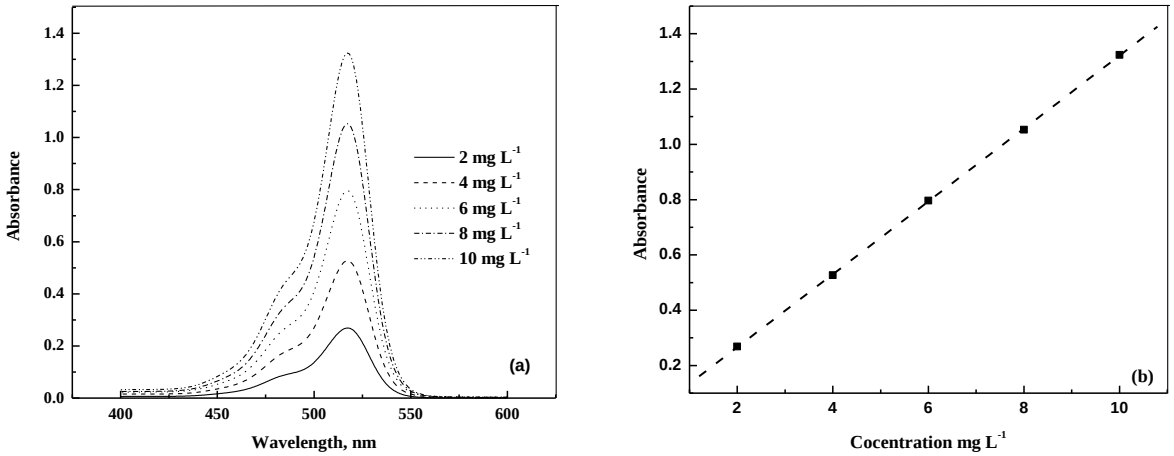

Fig.3 (a) Absorbance versus wavelength for Eosin Y (b) absorbance versus concentration for Eosin Y.

3. Theory

The analysis of packed bed adsorption is generally based on the exit stream concentration (C_t) vs time(t) data, which is a functions of column geometry, operating conditions and equilibrium adsorption data. The C_t vs t curve is known as breakthrough curve. A typical breakthrough curve is given in the Fig.4. From the shaded area behind the breakthrough curve between initial (t_o) and exhaust time (t_u) we can calculate the uptake of adsorbate by the adsorbent, which give the value of adsorbate per unit amount of adsorbent and is known as q and it is calculated with Eq.1 [9] The corresponding equilibrium concentration in liquid (C_e) in liquid phase can be calculated with Eq.2.

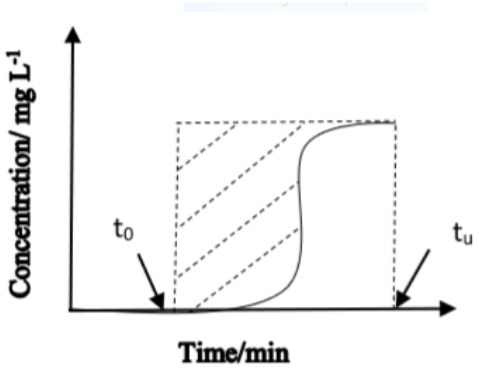

Fig. 4. A typical breakthrough curve

Thus, estimated q_e and C_e give a point on adsorption isotherm. By performing breakthrough test for various inlet concentrations by fixing temperature and the adsorbent dosage, we get various q values and from Eq.2 we get corresponding equilibrium concentrations, which results as an isotherm.

$$q_e = \frac{(shaded\ area)F}{m} \tag{1}$$

Where F is the flow rate and m is the mass of adsorbent.

$$q_e = \frac{(C_o - C_e)V}{m} \tag{2}$$

Where C_o Initial concentration, C_e equilibrium concentration, V is the cumulative volume and m is the mass of adsorbent.

3.1 Breakthrough curves

The performance of a fixed-bed column is described with the help of the breakthrough curve. The time for breakthrough and the shape of the breakthrough curve are important parameters for determining the operation and the dynamic response of an adsorption column. There are several models in the literature to predict break through curves. Some of important models from the literature are briefly presented in the following section.

Thomas model [10] is expressed in a linear form and, is represented with Eq.3. It is used to calculate maximum adsorption capacity of an adsorbent.

$$\ln\left[\frac{C_o}{C_t} - 1\right] = \frac{k_T q_{max} m}{Q} - k_T C_o t \tag{3}$$

Where C_t and m are the packed bed outlet adsorbate concentration at time (mg/L) and mass of adsorbent in the column (g). the k_T and q_{max} represent the Thomas model kinetic coefficient (mL/min mg) and maximum solid phase concentration (mg/g). the value of k_T and q_{max} can be obtained from the plot of $\ln\left(C_o/C_t - 1\right)$ versus t (min). Yoon – Nelson model [11] is expressed in a linear form and is represented with Eq.4. It is based on the assumption that the rate of decrease

in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption as well as the probability of adsorbate breakthrough on the adsorbent. This model is less complicated when compared to the other models, and doesn't requires any information such as characteristics of adsorbate, type of adsorbent, and the physical properties of the adsorption bed.

$$\ln\left(\frac{C_t}{C_o - C_t}\right) = k_{YN}\ t - \tau\ k_{YN} \qquad (4)$$

Where C_t is the packed bed outlet adsorbate concentration at time (mg/L) , k_{YN} and τ represent the Yoon-Nelson model rate constant (min^{-1}) and time required for 50% of adsorbate break through (min). The value of k_{YN} and τ can be obtained from the plot of $\ln\left(C_t / (C_o - C_t)\right)$ versus t (min). Adam-Bohart model [12] is expressed in a liner form and is represent with Eq.5. the assumption in this model, the rate of adsorption is based on the concentration of the adsorbing species and residual capacity of the adsorbent. The Adams–Bohart model is generally used for the description of the initial part of the breakthrough curve.

$$\ln\left[\frac{C_t}{C_o}\right] = k_{AB}C_o t - \frac{k_{AB}N_o Z}{U_o} \qquad (5)$$

Where k_{AB} is the Adam – Bohart kinetic constant $(L/mg\min)$. U_o is the linear velocity of the bed $(cm/\min)$. Z and N_o are the column depth (cm) and saturation concentration (mg/L) respectively. The value of k_{AB} and N_o can be obtained from the plot of $\ln(C_t/C_o)$ versus t.

4. Results and discussion

The performance of the fixed bed has been studied with three models proposed by Thomas, Yoon – Nelson and Adam – Bohart. The plot of the breakthrough curve, which is the ratio of effluent concentration to the inlet concentration (C_t/C_o) vs time t were analyzed with these three models. These models provide information on the influence parameters such as kinetic coefficients and saturation concentration on the solid phase. The successful design of a fixed bed requires prediction of breakthrough curve for the adsorbate-adsorbent system. The three model can be used in describing the behavior of the fixed bed and its scale up for industrial applications.

4.1 Effect of initial concentration

The increase in the inlet adsorbate concentration into the fixed bed has been studied. The inlet concentration were varied from 10 (mg/l) to 50 (mg/l). For the $10(mg/l)$ adsorbate concentration, the shape of the breakthrough curve was observed to be a gradual curve. While for the higher concentrations, the breakthrough curves were seen to increase drastically at the initial stage of operation. The effect of the inlet concentration on the shape of the breakthrough curve is shown in the Fig.5a, Fig.5b, Fig. 6a and Fig. 6b. It is clearly seen that as the inlet

adsorbate concentration increases the corresponding breakthrough curve shifts towards the left. This indicates the decrease in mass transfer zone. Further the shape of the breakthrough found to very stiffly as concentration increase from 10 ppm to 50 ppm. This effect can be readily seen in the quantification of break through characteristics times.

4.2 Adsorption modelling for breakthrough curve

The ln (C_o/C_t – 1) vs t data were fitted to determine the Thomas rate constant and maximum solid phase concentration. The square of correlation coefficient, R^2 is found to be more than 0.93. The Thomas kinetic coefficient (K_T) and maximum solid phase concentration (mg/g) obtained from Eq. 3 is shown in table 1. From table 1 it is clear that as the inlet concentration increased from 10 ppm to 50 ppm, the value of $q_{\max}$ increased but the value of K_T decreased for most of the cases in the concentration range that has been examined. This may be attributed to the drop in concentration difference (i.e., driving force). The comparison of the experimental values and the correlated values according to the Thomas model are shown in Fig. 5 a and Fig.5 b. The ln((C_t/(C_0-C_t)) vs t data were fitted to determine the Yoon – Nelson model constants, K_{YN} and τ. The correlation results are shown in table 2, it is clear that the rate constant K_{YN} increased and τ decreased with the increasing in inlet concentration of the adsorbate from 10 ppm to 50 ppm . The comparison of the experimental values and the correlated values according to the Yoon – Nelson model are shown in Fig.6 a and Fig.6 b.

The $\ln(C_t/C_o)$ vs t data were fitted to determine the Adam-Bohart model constants. The correlation values of N_o and k_{AB} are presented in table 3 together with the correlation coefficients. From the table 3 it is clear that the model is poorly predicting the breakthrough curve and the N_o and k_{AB} shows mixed trend. The comparison of the experimental values and the correlated values according to the Adam-Bohart model are not shown here due to its poor correlation.

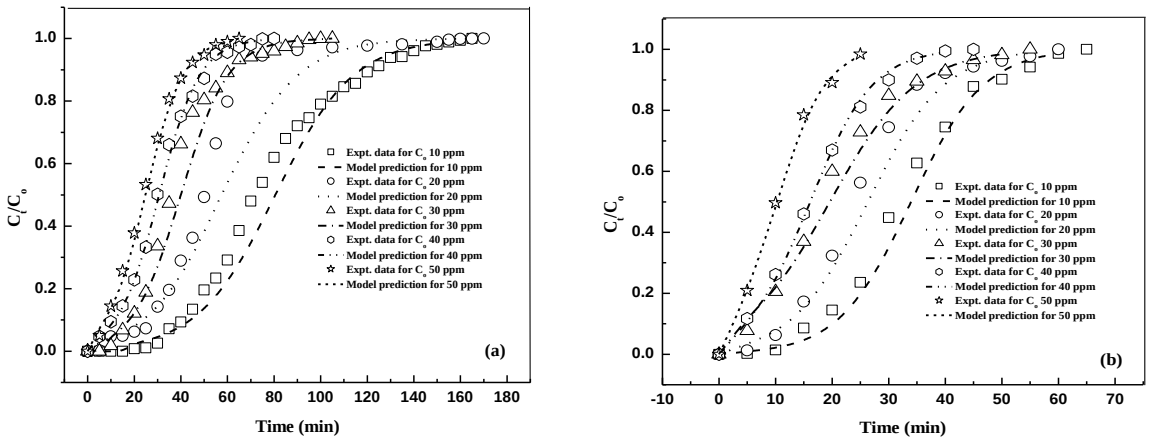

Fig.5. Breakthrough curves for adsorption of (a) Indigo carmine dye (b) Eosin Y dye onto chitosan for different initial concentration at temperature 303.15 K. The dash dotted lines indicate Thomas model predictions. (Flow rate 15 ml/min, adsorbent dose 5 gm.)

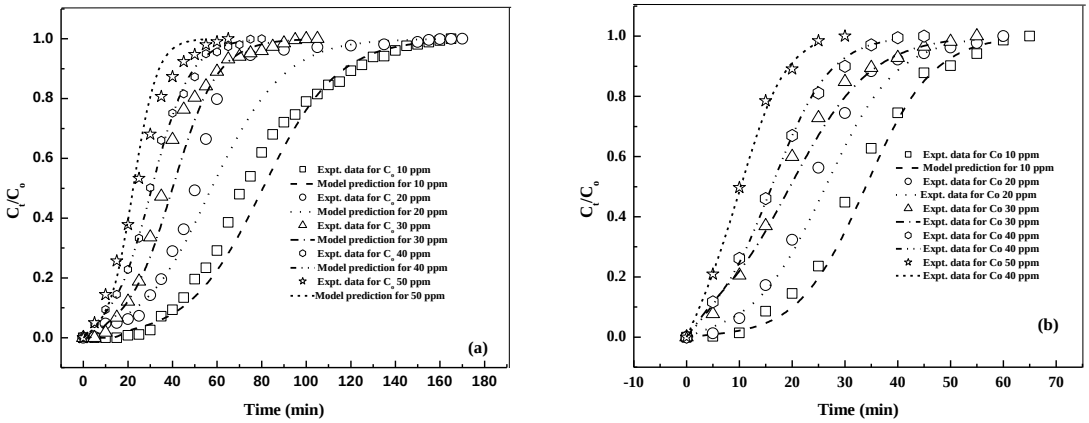

Fig.6. Breakthrough curves for adsorption of (a) Indigo carmine dye (b) Eosin Y dye onto chitosan for different initial concentration at temperature 303.15 K. The dash dotted lines indicate Yoon Nelson model predictions. (Flow rate 15 ml/min, adsorbent dose 5 gm.)

Table 1. Parameters predicted by the Thomas model

Compound name	$C_o\,(mg/l)$	$Q(ml/\min)$	$k_T\,(ml/\min\,mg)$	$q_{\max}\,(mg/g)$	R^2
Indigo Carmine	10	15	0.487	0.372	0.969
	20	15	0.374	0.522	0.930
	30	15	0.402	0.751	0.950
	40	15	0.360	0.979	0.968
	50	15	0.317	1.210	0.993
Eosin Y	10	15	0.558	0.884	0.965
	20	15	0.411	1.138	0.957
	30	15	0.268	1.530	0.984
	40	15	0.313	1.860	0.980
	50	15	0.270	2.930	0.982

Table 2. Parameters predicted by the Yoon – Nelson model

Compound name	$C_o\,(mg/l)$	$Q(ml/\min)$	$k_{YN}(\min^{-1})$	$\tau(\min)$	R^2
Indigo Carmine	10	15	0.0604	80.58	0.968
	20	15	0.0652	57.44	0.930
	30	15	0.1006	39.97	0.948
	40	15	0.1176	30.65	0.968
	50	15	0.1277	24.79	0.993
Eosin Y	10	15	0.1645	33.95	0.965
	20	15	0.1599	26.35	0.957
	30	15	0.1365	19.60	0.984
	40	15	0.1939	16.12	0.980
	50	15	0.2629	10.25	0.980

Table 3. Parameters predicted by the Adam – Bohart model

Compound name	$C_o\,(mg/l)$	$Q(ml/\min)$	$k_{AB}(L/mg\min)$	$N_o\,(mg/L)$	R^2
Indigo Carmine	10	15	0.00272	934.56	0.709
	20	15	0.001095	1871.69	0.576
	30	15	0.00108	1707.31	0.647
	40	15	0.00098	1762.14	0.802
	50	15	0.00091	1782.28	0.769
Eosin Y	10	15	0.00929	357.05	0.770
	20	15	0.00733	322.78	0.730
	30	15	0.00481	299.38	0.744
	40	15	0.00564	247.27	0.822
	50	15	0.007368	162.73	0.837

4.3 Freundlich and Langmuir model

The q_e and Ce data obtained from the breakthrough curves were used to fit the Freundlich [13] and Langmuir models [14]. Both the models were found to correlate q_e vs C_e data. The square of correlation coefficients is observed to be more than 0.98. The model constants were reported in table 4. The experimental and the model predictions curves were shown in Fig.7 a and Fig. 7 b.

Table 4. Isotherm parameters for adsorption of dye on to chitosan at T= 303.15 K

Compound name	Freundlich constants		R^2	Langmuir constants		R^2
	$K_F\left((mg/g)/(mg/l)^{1/n}\right)$	$1/n$		$q_m(mg/g)$	$K_L(l/mg)$	
Indigo Carmine	1.4035	0.2612	0.98	4.407	0.1823	0.994
Eosin Y	0.544	0.2612	0.998	2.679	0.1126	0.990

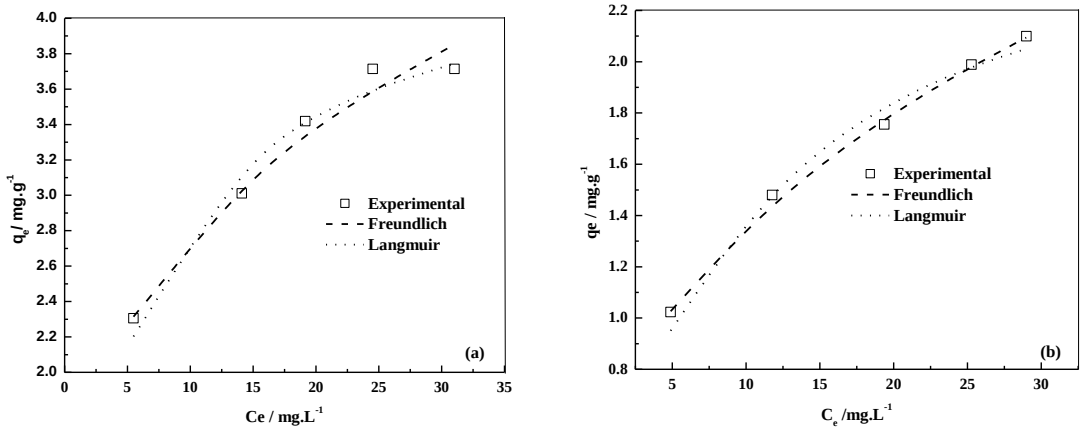

Fig.7 Comparison of experimental values with Freundlich and Langmuir isotherm models for adsorption of (a) Indigo carmine dye and (b) Eosin Y dye onto chitosan.

4.4 Characteristics of break through curve

Important characteristics of fixed bed such as break through time(t_b),stoichiometric wave front time(t_s) and exhaust time(t_u) are estimated using stranded procedure described in the literature [15,16]. In this work, a new integration approach was applied for calculating the stoichiometric wave front time. In the proposed new approach, the breakthrough curve is fitted with higher order polynomial and the same is evaluated for obtaining stoichiometric wave front time with the usual equal area criterion (i.e., area below the break through curve between t_b and t_s is equal to the area above the curve between t_s and t_u) [16]. The expression used in the calculation of stoichiometric wave front time is

$$t_s = t_u - \int_{t_b}^{t_u} f(t)\,dt \qquad (5)$$

where $f(t)$is higher order polynomial. 8th order polynomial is found to be suitable for all the systems consider in this work. The evaluated characteristics parameters are reported in table 5. The results show that there is drop in all characteristic time quantities when the concentration increased from 10 ppm to 50 ppm. This may be attributed to sharp increase in the break through curve stiffness when adsorbate concentration increased from 10 ppm to 50 ppm.

Table 5 Characteristic parameters of fixed bed at fixed flow rate, $Q = 15\ \mathrm{ml/min}$

Compound name	$C_o\,(mg/l)$	Break through time, t_b (min)	Stoichiometric wave front time, t_s (min)	Exhaust time, t_u (min)
Indigo Carmine	10	31.92	71.83	165
	20	10.67	50.17	160
	30	13.19	37.98	105
	40	5.34	30.95	75
	50	4.00	24.68	65
Eosin Y	10	12.5	32.44	65
	20	8.50	24.67	60
	30	3.30	19.50	55
	40	2.45	16.57	40
	50	1.19	10.66	30

5. Conclusions

On the basis of the experimental results of this investigation, the chitosan can be used as an adsorbent for the treatment of dye effluent containing anionic dyes. The adsorption isotherm of Indigo carmine and Eosin Y from aqueous solution on chitosan in a fixed bed at 303.15 K was determined. The Thomas model and Yoon-nelson model adequately described the adsorption of Indigo carmine and Eosin Y onto chitosan in column mode. The estimated characteristic parameters of fixed bed such as break through time, stoichiometric wave front time and exhaust time may be used in scale up.

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