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Packed bed column studies for the removal of Acid blue 92 and Basic red 29 using non-conventional adsorbent

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The adsorptive removal of Acid blue 92 and Basic red 29 dyes was achieved using a packed column prepared by *Euphorbia antiquorum L* activated carbon. The effects of various factors like influent concentration, flow rate and bed height were analysed. The column experiments using *Euphorbia antiquorum L* activated carbon showed that adsorption efficiency increases with increase in the influent concentration and bed depth and decreases with increasing flow rate. Column adsorption performance was evaluated using Thomas and Yoon-Nelson kinetic models. The adsorption capacity calculated by Thomas and Yoon-Nelson models were compared with the experimental adsorption capacity. The Yoon-Nelson model describes the adsorption behaviour of the selected adsorbent-adsorbate system more reasonably than Thomas model and Basic red 29 adsorption behaviour fits exceptionally well with the Yoon-Nelson model.

Keywords: Fixed bed column, Activated carbon, Adsorption, *Euphorbia antiquorum L*, Acid blue 92, Basic red 29

Dye bearing wastewater poses a serious threat to the aquatic environment due to its appearance and toxicity. The removal of colour from wastewater is a major problem for developing countries due to lack of efficiency of the conventional methods and high cost involved for the treatment process. Many techniques like electrochemical coagulation, reverse osmosis, nano filtration, adsorption using activated materials etc., are used for the removal of solute from wastewater. Adsorption has been found to be an efficient and economical process to treat dyeing industry effluent.

Low-cost adsorbents prepared from agro wastes find an extensive application for the wastewater treatment. Exploration of good low cost adsorbent may contribute to the sustainability of the environment and also offer promising benefits for the commercial purpose in future. The cost of activated carbon prepared from the biomaterials are negligible when compared to the cost of commercial activated carbon and also they are renewable sources of raw materials for the production of activated carbon. Activated carbon has been prepared from different materials like agricultural wastes[1,2], oil palm waste[3], babool seed[4], Tamarind kernel powder[5], orange waste[6], palm shell[7], rice husk[8], saw dust[9], corncob[10], eucalyptus bark[11], pine saw dust[12], pistachio shells[13], etc.

The information obtained from adsorption kinetics and isotherm studies in a batch mode is useful for the determination of the effectiveness of the adsorbent for the selected adsorbate from its aqueous solution. The batch mode analysis is not sufficient while designing a treatment system for continuous operation. For example, packed bed columns do not necessarily operate under equilibrium conditions because of the short contact time. The other operational problems such as uneven flow pattern in the column, recycling and regeneration cannot be effectively studied in batch experiments. The above said factors makes it necessary to analyse the adsorbate-adsorbent system by column mode.

The objective of the present work is to analyse the effects of initial dye concentration, flow rate and bed height for the adsorption of Acid blue 92 and Basic red 29 onto an activated carbon prepared from *Euphorbia antiquorum L* (EAAC) wood in column mode. The plant is wide spread throughout peninsular India up to an altitude of 800 m. It can easily be propagated from seed or vegetatively and most importantly has no known use.

Modeling of column adsorption

Full-scale column operation can be designed on the basis of data collected at laboratory level. Many mathematical models have been proposed in the past for the evaluation of efficiency and applicability of the column models for large-scale operations. To design a column adsorption process it is necessary to predict the breakthrough curve or concentration-time profile and adsorption capacity of the adsorbent for the selected adsorbate under the given set of operating conditions. Many models have been developed to predict the adsorption breakthrough behaviour with high degree of accuracy. The Thomas model and Yoon-Nelson model were used in this study to analyse the behaviour of the selected adsorbent-adsorbate system.

Thomas model[14]

Successful design of a column adsorption process requires prediction of the concentration-time profile or breakthrough curve for the effluent. The Thomas model is used to calculate the adsorption rate constant and the solid phase concentration of the dye on the adsorbent from the continuous mode studies. The kinetic model suggested by Thomas is one of the widely used kinetic models for the evaluation of column performance. The Thomas model has the following form

$$\frac{C_t}{C_0} = \frac{1}{1+\exp\left[k_T\left(q_{0(T)}.m - C_0.v\right)\right]/r} \quad \ldots(1)$$

where, C_t is effluent dye concentration (mg/L) at time t, C_0 is initial dye concentration (mg/L), k_T is Thomas rate constant, (L/min.mg), $q_{0(T)}$ is maximum dye adsorption capacity (mg/g), m is mass of the adsorbent (g), v is effluent volume (mL) and r is flow rate (mL/min). The value of time, t = v/r.

The constants k_T and q_0 are determined from a plot of C_t/C_0 against t for a given set of conditions using non-linear regression analysis.

Yoon-Nelson model[15]

Yoon and Nelson have proposed a less complicated model to represent the breakthrough of gases onto activated charcoal. The model was proposed 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 and the probability of adsorbate breakthrough on the adsorbent. The linear form of Yoon-Nelson model is represented as

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = k_{YN}.t - \tau.k_{YN} \quad \ldots(2)$$

where, k_{YN} is Yoon-Nelson rate constant, τ is the time required for 50% of adsorbate breakthrough and t is the sampling time. A plot of $1n(\frac{C_t}{C_0 - C_t})$ versus t gives a straight line with a slope of k_{YN} and intercept of $-\tau.k_{YN}$.

Based on Yoon-Nelson model, the amount of dye being adsorbed in a fixed bed is half of the total dye entering the adsorption bed within 2τ period[16]. For a given bed

$$q_{0YN} = \frac{q_{(total)}}{m} = \frac{\frac{1}{2}C_0[(r/1000)\times 2\tau]}{m} = \frac{C_0.r.\tau}{1000m} \quad \ldots(3)$$

From this equation, the adsorption capacity, $q_{0(YN)}$ varies as a function of inlet dye concentration (C_0), flow rate (r), weight of adsorbent (m) and 50% breakthrough time.

Error analysis[17]

The adsorption capacity obtained by the Thomas Model and Yoon-Nelson Model was compared with the experimental adsorption capacity using the following error analysis method.

$$Sd = \sqrt{\sum\frac{(q_{0(\exp)} - q_{0(cal)})^2}{N}} \quad \ldots(4)$$

where, $q_{0(\exp)}$ is experimental adsorption capacity, $q_{0(cal)}$ is the adsorption capacity calculated using Thomas and Yoon-Nelson kinetic models and N is the number of experimental points run.

Experimental Procedure

Preparation of adsorbent (EAAC)

Euphorbia antiquorum L wood was cut into pieces of 2 to 3 cm size, dried in sunlight for 10 days. The dried material soaked in a boiling solution of 10% H_3PO_4 for one hour and kept at room temperature for 24 h. After 24 h the wood material separated, air dried and carbonized in muffle furnace at 400°C. The carbonized material was powdered and activated in a muffle furnace at 800°C for a period of 10 min. Then the carbon was washed with plenty of water to remove residual acid, dried, sieved to a particle size of 300 to 850 µm and stored in a tight lid container for further adsorption studies.

Table 1 — Some of selected physico-chemical properties of EAAC.

Sl. No.	Properties	Values
1	*p*H	6.90
2	Bulk density, g/mL	0.48
3	Specific gravity	0.94
4	Porosity, %	55.32
5	Surface area (BET), m^2/g	918
6	Methylene blue value, mg/g	375

The characteristics of the activated carbon (EAAC) were studied as per the standard procedures[18,19] and few important parameters are given in Table 1. Surface area of the activated carbon samples were measured at 77K using N_2 gas sorption analyzer (Nova 1000, Quanta Chrome Corporation, USA). A detailed study on the characteristics of various types of EAAC has already been reported elsewhwere[20].

Preparation of dye solutions

The dyes Acid blue 92 (Molecular Formula $C_{26}H_{16}N_3Na_3O_{10}S_3$, C.I No. 13390, F.W 695.59, λmax 571 nm) and Basic red 29 (Molecular Formula $C_{19}H_{17}ClN_4S$, C.I No. 11460, F.W 368.89, λmax 511 nm) (analytical grade) were procured from a local chemical company. A stock solution 1000 mg/L was prepared by dissolving appropriate quantity of the dye in measured quantity of double distilled water, and used after dilution as required. The structures of selected dyes are given in Fig. 1a and 1b.

Column studies

Fixed bed column studies were carried out using a glass column of 1.2 cm inner diameter and 40 cm length. The activated carbon was packed in the column with two layers of glass wool at the top and bottom as shown in Fig. 2. The dye solution of specified concentration was charged from the bottom of the column in up flow method at fixed inflow rate using peristaltic pump. The effluent samples were collected at specified intervals and analysed for the residual dye concentration using (Elico Make) Bio UV-Vis spectrometer at 571 nm for Acid blue 92 and at 511 nm for Basic red 29.

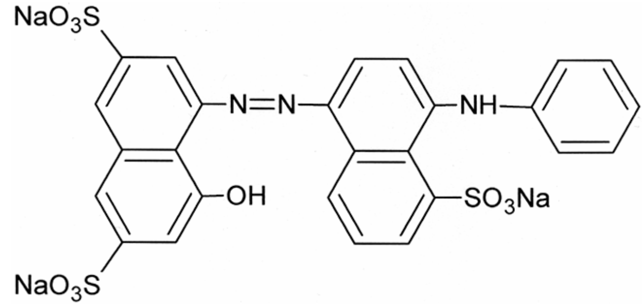

Fig. 1a — Structure of Acid blue 92.

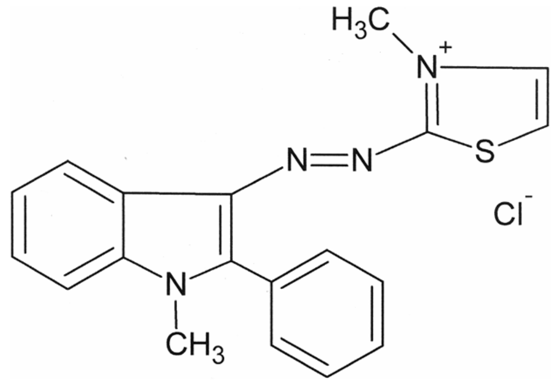

Fig.1b — Structure of Basic red 29.

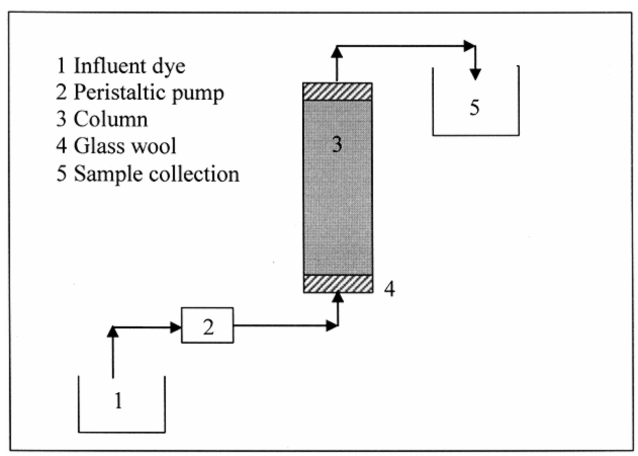

Fig. 2 — Flow chart of up flow packed bed column.

Results and Discussion

Effect of initial dye concentration

The adsorption of Acid blue 92 and Basic red 29 was analyzed using fixed bed column as a function of influent dye concentration, bed height and flow rate. The adsorption breakthrough curves were obtained for the selected dyes at 25, 50 and 75 mg/L at a flow rate of 10 mL/min and bed height of 5.0 cm (Figs 3 and 4). On increasing the initial dye concentration, the breakthrough curves becomes steeper and the breakthrough volume decreases. The equilibrium sorption capacity at

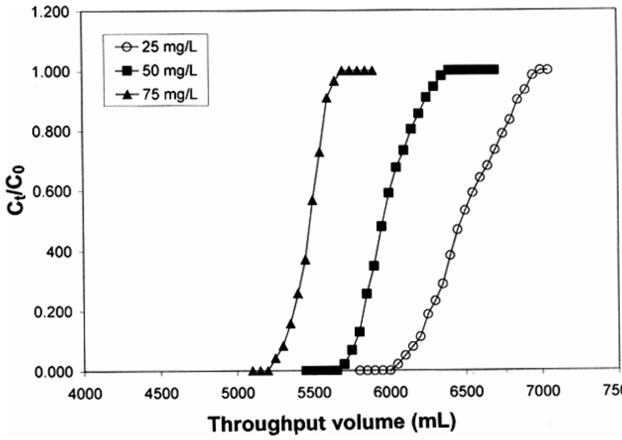

Fig. 3 — Effect of influent concentration for the removal of Acid blue 92 on EAAC column.

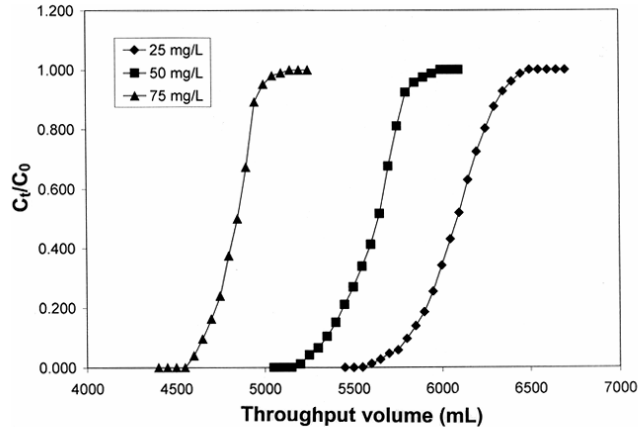

Fig. 4 — Effect of influent concentration for the removal of Basic red 29 on EAAC column.

Table 2 — Results of Thomas and Yoon-Nelson kinetic model for the adsorption of Acid blue 92 and Basic red 29 onto EAAC column.

	Acid blue 92							Basic red 29						
Concentration, mg/L	25	50	75	50	50	50	50	25	50	75	50	50	50	50
Flow rate, mL/min	10	10	10	5	15	10	10	10	10	10	5	15	10	10
Bed height, cm	5.0	5.0	5.0	5.0	5.0	7.5	10.0	5.0	5.0	5.0	5.0	5.0	7.5	10.0
$q_{0(exp)}$, mg/g	58.2	157.1	275.5	128.6	102.0	104.6	91.8	56.6	106.1	140.8	118.4	99.0	98.5	86.2
Thomas model														
k_T, mL/min/mg	1.64	0.66	0.45	0.31	1.44	0.60	0.46	0.88	0.58	0.60	0.21	1.17	0.54	0.42
$q_{0(T)}$, mg/g	66.6	124.3	164.0	141.7	113.5	119.2	99.5	74.7	133.6	178.5	157.2	145.0	118.8	108.2
r^2	0.836	0.875	0.879	0.903	0.887	0.901	0.888	0.859	0.801	0.918	0.821	0.792	0.901	0.875
Sd	0.33	1.26	4.29	0.50	0.44	0.36	0.29	0.70	1.06	1.45	1.49	0.62	0.78	0.85
Yoon-Nelson model														
$q_{0(YN)}$, mg/g	66.4	122.4	167.3	137.3	106.0	110.4	97.4	61.9	113.9	147.5	128.4	105.0	104.3	92.2
$k_{(YN)}$, L/min	0.070	0.103	0.156	0.038	0.238	0.084	0.066	0.097	0.106	0.155	0.044	0.214	0.093	0.069
τ, min	650	599	546	1345	846	816	954	606	558	482	1259	343	772	904
r^2	0.968	0.973	0.983	0.982	0.960	0.993	0.989	0.966	0.978	0.984	0.996	0.998	0.992	0.996
Sd	0.32	1.34	4.16	0.34	0.15	0.22	0.22	0.20	0.30	0.26	0.38	0.23	0.22	0.23

various initial dye concentrations are given in Table 2. At higher concentration the availability of the dye molecules for the adsorption sites is more, which leads to higher uptake of dye at higher concentration even though thebreakthrough time is shorter than the breakthrough time of lower concentrations[21].

The results indicate that the adsorbent is capable of holding a maximum of 275.5 mg/g of Acid blue 92 and 140.8 mg/g of Basic red 29 at 75 mg/L of influent concentration.

Influence of bed height

The breakthrough curves for the adsorption of Acid blue 92 and Basic red 29 on to EAAC at various bed height by fixing the influent concentration at 50 mg/L and flow rate at 10 mL/min are given in the Figs 5 and 6. The results indicate that the throughput volume of dye solution increases with increase in bed height, due to the availability of more number of sorption sites (i.e the total surface area increases)[22,23]. The equilibrium sorption capacity decreases with increase in bed height. In the continuous flow method the probability of contact between the adsorbate and the adsorbent is less when compared to batch mode, which ultimately results in lesser equilibrium sorption capacity in column mode.

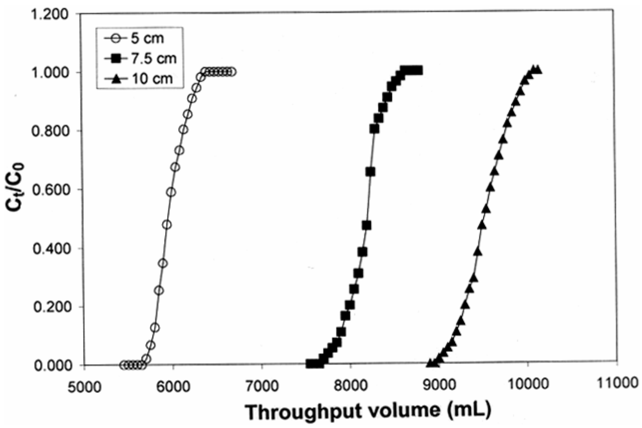

Fig. 5 — Effect of bed height for the removal of Acid blue 92 on EAAC column.

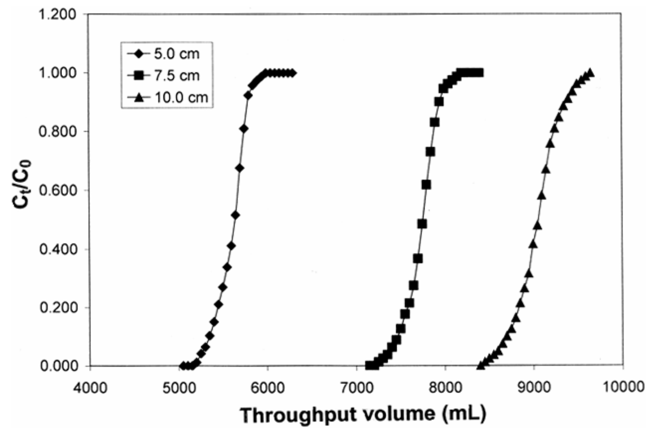

Fig. 6 — Effect of bed height for the removal of Basic red 29 on EAAC column.

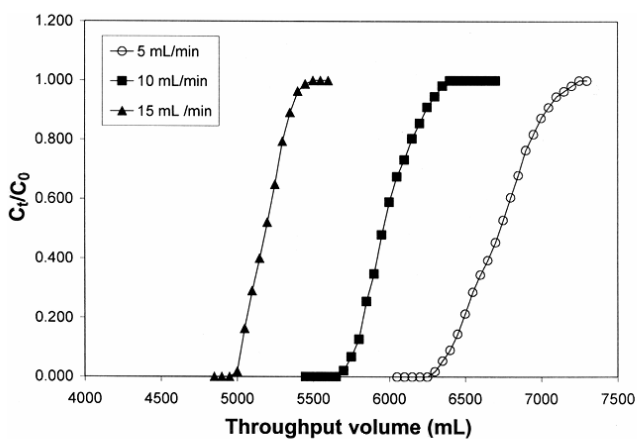

Fig. 7 — Effect of flow rate for the removal of Acid blue 92 on EAAC column.

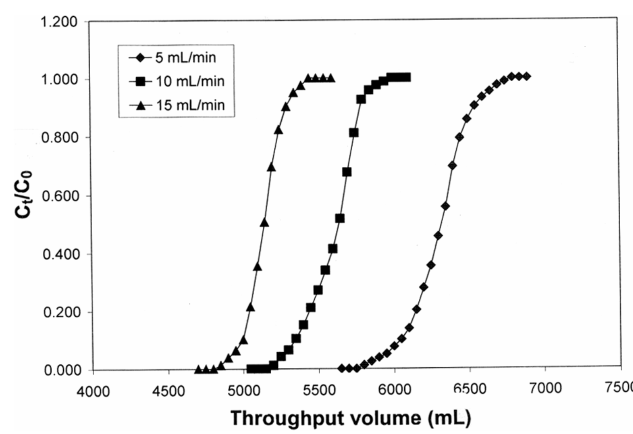

Fig. 8 — Effect of flow rate for the removal of Basic red 29 on EAAC column.

Influence of flow rate

The effect of flow rate for the adsorption of Acid blue 92 and Basic red 29 on to EAAC at flow rates of 5.0, 10.0 and 15.0 mL/min at an influent concentration of 50 mg/L and bed height of 5.0 cm is shown in the Figs 7 and 8. From the figures it is clear that rapid uptake is noticed in the initial stages and rate decreases thereafter and finally reaches a saturation. On increase in flow rate, the breakthrough curves becomes steeper and reaches the breakthrough quickly. At higher flow rate, the contact time between the adsorbate and adsorbent is minimized, leading to an early breakthrough[24].

The breakthrough volume of Basic red 29 dye is lower than Acid blue 92. This can be attributed to the size of dye molecule, since Basic red 29 is bulkier than Acid blue 92. In the case of Basic red 29 the rate of adsorption is lower than Acid blue 92 leading to a lower break though volume for a given flow rate. The extent of adsorption depends on the size of adsorbate and other factors like surface functional groups, type of pores present on the carbon, intra particle mass transfer etc.[25,26]. The effect of flow rate is helpful for the large-scale treatment systems in order to utilize the bed for its maximum capacity with minimal flow rate[27].

Thomas model

The adsorption data were applied to Thomas model and the results are presented in Table 2. In general, the Thomas rate constant decreases with increase in influent dye concentration, decreases with increase in bed height and increases with increase in flow rate. The equilibrium sorption capacity $q_{0(T)}$ decreases while increasing the flow rate from 5.0 to 15 mL/min and increases while increasing the influent concentration for both the dyes.

Yoon-Nelson model

The Yoon-Nelson rate constant k_{YN} increases with respect to concentration for both the selected dyes. This is due to the fact that increase in initial dye concentration increases the competition between adsorbate molecules for the adsorption sites, which ultimately results in increased uptake rate. The rate constant increases with increase in flow rate and decreases with increase in bed height. At high flow rate the number of dye molecules passing through a particular adsorbent is more, which increases the rate. At higher bed height the adsorbate molecules has more time to travel through the column which results in the reduced adsorption rate. It is known that k_{YN} and τ are inversely related, as expected the time required for 50% breakthrough τ decreases with increasing the influent concentration and increasing the flow rate and increases with increasing the bed height.

The column adsorption capacity calculated based on the results of Yoon-Nelson model, $q_{0(YN)}$ increases with increasing the initial concentration and decreases with increasing the flow rate and bed height for both the dyes investigated.

The similar variation of column adsorption capacity was observed for Thomas and Yoon-Nelson model under given set of operating conditions. The adsorption capacity calculated based on Yoon-Nelson model has good agreement with the observed value with high r^2 value and very low Sd, whereas the q_0 calculated by Thomas model shows large deviation from the observed q_0 with poor correlation coefficient and high Sd. In general, the Yoon-Nelson model describes the adsorption behaviour of Acid blue 92 and Basic red 29 onto EAAC column more reasonably than Thomas model. Out of the two dyes tested, the Basic red 29 adsorption behaviour fits exceptionally well with the Yoon-Nelson model with good correlation coefficient and very low Sd.

Conclusion

The adsorbent prepared from *Euphorbia antiquorum L* is an effective adsorbent for the removal of dyes from wastewater. The removal efficiency of dye from wastewater strongly depends on influent concentration, flow rate and bed height. The prepared adsorbent is capable of holding a maximum of 275.5 mg/g of Acid blue 92 and 140.8 mg/g of Basic red 29 at 75 mg/L of influent concentration. The adsorption capacity increases with increase in influent concentration, decreases with increase in flow rate and bed height. The column performance was analysed using Thomas model and Yoon-Nelson model. Yoon-Nelson model describes the adsorption behaviour of Acid blue 92 and Basic red 29 onto EAAC column more reasonably than Thomas model with high correlation coefficient and low Sd.

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