Eco. Env. & Cons. 27 (August Suppl. Issue) : 2021; pp. (S275-S280)

ISSN 0971–765X

Modelling of removal of Direct blue 71 and Brilliant green dye in fixed bed column by adsorption

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(Received 27 March, 2021; Accepted 4 May, 2021)

ABSTRACT

This paper deals with the study of fixed bed column performance for the removal of Direct Blue 71 and Brilliant green dye by using lignite loaded with *Azospirillum bacteria*. Sterilized lignite was mixed with *Azospirillum* bacterial culture. Flow rate and bed height was varied to check the adsorption performance. Effect of two parameters was checked. Adsorption efficiency was increased as bed height was increased. But when flow rate was increased, somewhat adsorption was found to be decreased. The optimized condition was investigated at which the bed capacity was maximum. The maximum adsorption capacity was 0.4722 mg/g for 11 ml/min flow rate and 80 cm bed height. Adsorbent capacity at a breakthrough was 87.699 kg/m^3. The adsorbent capacity at equilibrium was 92.5715 kg/m^3. Unused bed length of column at breakthrough was 0.0421 m. Various models were studied to check the agreement of the experimental data to the predicted models. Predicted and experimental results were found to be in good agreement. Mecklenburg, Wheeler and Yoon models was suitable for the experimental data. The experimental values suggested that the column adsorption system by using lignite loaded with *Azospirillum* bacteria is effective

Key words: *Adsorption, Dye removal, Model, Biosorbent*

Introduction

In various industries, dye is used, but textile industry uses it in large scale. Presence of dye is found in wastewater of various industries. Release of dye in industrial wastewater is one of the major causes of water pollution (Najafpour *et al.,* 2006). Dyes are harmful to living being (Ai *et al.,* 2011). If dyes are not treated properly, can cause health problems in living being and the cause environmental hazards (Gul and Ozcan, 2009). In azo dyes, one or more than one azo bonds (-N=N-) are found (Sahel *et al.,* 2007). Azo dyes have carcinogenetic, lethal, and poisonous to human being. Some dyes are extremely stable and cannot be degraded by any processes (Bazrafshan *et al.,* 2012). If azo dyes containing wastewater released in the environment, it can cause environmental pollution and health problems (Luo *et al.,* 2011). Hence wastewater containing dyes should be treated properly to avoid problems. For the treatment of azo dyes containing wastewater, various methods are used. Some of the important methods are biological treatment, coagulation, electrochemical treatment and flocculation. Advantages of these methods are high removal efficiency in required time whereas the important disadvantages are high cost, need of additional steps and generation of hazardous side materials (Moghaddam *et al.,* 2010; Li *et al.,* 2011; Crini and Badot, 2008). In physical or chemical methods, adsorption process is the popular method because of low cost, simple design and can treat high concentration of dyes (Dias *et al.,* 2007). For rapid removal of dissolved dyes from effluent, physical adsorption is proven as the best method (Mishra *et al.,* 2010). As an adsorbent in adsorption process, activated carbon was mostly preferred for the removal of traces of the dye (Foletto *et al.,* 2012), but the cost of operation was very high (Gupta and Suhas, 2009). Use of biosorbents emanated from agricultural waste, industrial waste, and microbial biomasses. Fungi, bacteria, and algae was also used as bio sorbents (Crini, 2006). Preference was given to the dead and dry biosorbents as these adsorbents gave good performance. With the use of these biosorbents, environmental pollution was not observed by release of toxic side products and adsorbent recovery was very simple (Tigini *et al.,* 2011). By using agricultural by-product experiment was carried out. Breakthrough curves were studied by Thomas and Yan Model by using nonlinear regression analysis. The Outcome from that Yan model was satisfactory for the breakthrough curves (Tong Zhou *et al.,* 2015). By using sugarcane ash, experiment was performed and bed depth effect, flow rate effects on breakthrough curve was studied. The result obtained from that the percent removal of dye inversely proportional to flow rate, directly proportional to bed height, inversely proportional to initial concentration (Sachin *et al.,* 2011). Parthenium hysterophorus adsorbent was used for the removal of dyes (Robinson *et al.,* 2002). Coir pith adsorbent was used for the removal of Acid violet, acid brilliant blue, methylene blue, Rhodamine-B dyes (Banerjee *et al.,* 2006; Chiou and Li, 003). Biogas residual slurry was used as a bio adsorbent for the removal of Congo Red dye (Namasivayam and Yamuna, 1992). Removal of dye from Chitosan hydrogel beads was carried out and was found J-shaped breakthrough curve, which is given by Jonas-Wheeler model equation (Dan Xu *et al.,* 2008). By using bone char, decolourization of dye was studied, and it was observed that adsorption parameters were dependent on properties of dye molecules during kinetics and also on breakthrough curves (Reynel- Avila *et al.,* 2016). By using cross-linked fibre as adsorbent for removal of dye, experiment was performed. Adsorption of removal of dye was measured at different bed heights and dye influent concentration. From breakthrough curve experiment, it was obtained that, dye was efficiently recovered by ChF-B (Hiroyuki Yoshida and Takeshi Takemori, 1997). Column study on fixed bed was carried out by using SMA as adsorbent. From theoretically calculated values breakthrough curve was drawn, and differentiated with experimentally calculated values of breakthrough curve (Asok Adak *et al.,* 2006). Activated carbon used for the removal of the reactive yellow dye during continuous and batch experiments. Different isotherm models and column study was conducted at distinct initial concentration, bed height, and flow rate to evaluate EBCT at breakthrough point (Abbas H. Sulaymon and Waleed M. Abood, 2014). Activate carbon can be prepared from converting empty fruit cluster of palm oil for dye removal. In this fixed-bed column study was carried out at different influent concentration, flow rate and bed depth. Thomas model was used to speculate the performance of column, breakthrough curves (Manase Auta , 2012). Eucalyptus bark biomass as adsorbent was used for the removal of MB dye. Fixed bed adsorption column experiments were performed to evaluate breakthrough curve, with varying flow rate, initial concentration, and bed heights. Thomas, Yoon-Nelson model were suitable for the process. Using Eucalyptus bark biomass as adsorbent, high adsorption of MB dye removal was observed (Sharmeen Afroze *et al.,* 2016). Coal fly ash used as adsorbent for the removal of dye. Column experiments were performed, and best fit model was Yoon-Nelson. High yield of dye removal at low concentration was seen (Franco Ferrero, 2015). Alkali treated orange tree sawdust used as adsorbent for the removal of methylene blue dye. Column experiments showed that removal efficiency of dye was directly proportional to initial concentration of dye, and bed heights. And various models were applied to speculate breakthrough curves (Ahmed *et al.,* 2017).

Various methods have been attempted for the development of bio sorbent which should be effective, eco friendly and easy for regeneration. The main objective of this work was to remove azo dyes (Direct Blue 71 and Brilliant Green) by use of lignite loaded with bacteria as adsorbent.

Materials and Methods

Direct Blue 71 dye is from the tri-azo group, and its chemical formula is ($C_{40}H_{23}N_7Na_4O_{13}S_4$). Direct Blue 71 (50% purity) and Brilliant Green (90% purity) was purchased from Sigma Aldrich. Adsorbent used in the experimentation was lignite loaded with *azospirillum* bacteria. Dye was precisely weighed and dissolved in tap water to prepare a stock solution of 100 ppm. Experimental solution of required concentration was obtained by dilution of stock solution. Residual dye concentration was measured by Spectrophotometer (Shimadzu UV 1800, 240V), as per the standard methods of APHA scanning of dilute solution was performed. The maximum wavelength for Direct Blue 71 was measured as 573 nm and for Brilliant Green as 621 nm. Calibration curves of Direct Blue 71 and Brilliant Green was linear from 2 to 50 ppm.

Experimental

Continuous flow experiments were carried out in acrylic column (internal diameter - 7 cm and length - 80 cm). The acrylic column was packed by using bio adsorbent, between two layers of cotton. Before loading the solution of dye, column was cleaned with tap water at constant flow rate for 20 minutes. A column study was carried out to estimate the outcome of initial concentration of dye, Adsorbent- Bed depth, and flow rate. Using a peristaltic pump, Solution of dye was pumped into column. The initial concentration of dye was 25 ppm. The mass of bio-adsorbent in the column was 30, 40 and 50 g at depths of 5, 10 and 15 cm, respectively. And sample was collected at regular intervals. Using wavelength (570 nm and 621 nm), the calibration was done for absorbance and concentration. Batch Experiment was performed and adsorption capacity of 0.4722 mg/g was calculated for Langmuir isotherm.

Results

The outcome of this experiment showed that study of breakthrough curve varied with initial concentration of dyes, bed depth and flow rate of solution. In ideal adsorption system, breakthrough curve stick to the S-shaped outline.

Effect of adsorbent bed height

Figure 1 and 2 predicted the breakthrough curve for three different bed heights of 5, 10 and 15 cm at constant influent flow rate of 11 ml/ min and initial influent concentration of 25 ppm. Graphs showed that bed height was directly proportional to mass transfer zone. Adsorption efficiency was increased as bed height was increased. For increased flow rate adsorption was found to be decreased. Various models were studied to check the agreement of the experimental data to the predicted models.

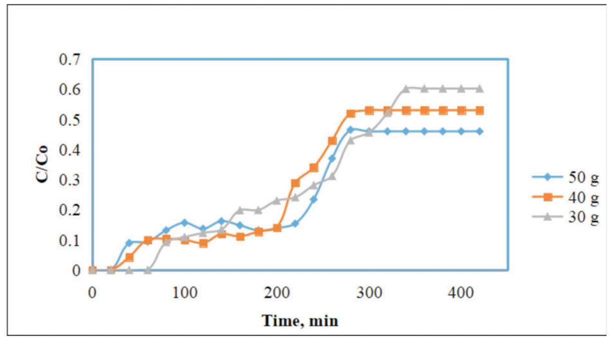

Fig. 1. Breakthrough Curve for removal of Direct Blue 71

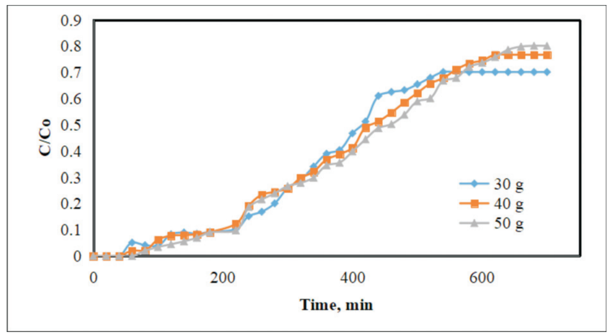

Fig. 2. Breakthrough Curve for Brilliant Green dye

Estimation of breakthrough time by calculation with the Mecklenburg equation

The Mecklenburg equation is given by,

$$T_b = \frac{W_g A n p_c}{Q C_0}\left[z + \frac{1}{a_c p_c}\left(\frac{d_G}{\eta}\right)^{0.41} \left(\frac{\eta}{p_a D_{20}}\right)^{0.67} \ln\left(\frac{C_b}{C_1}\right)\right] \text{ .. Eq (1)}$$

Where,

We = Adsorption capacity.

Q = Flow rate in l/min.

C_b = Breakthrough concentration.

C_1 = Inlet Concentration.

n = Number of Filters.

By using equation (1), breakthrough time in hours and minutes for the given breakthrough con-

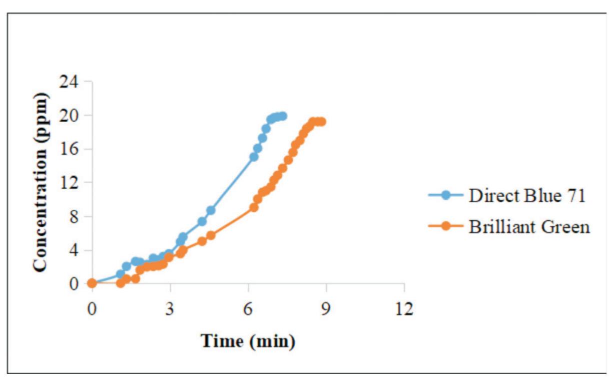

Fig. 3. Breakthrough Curve for Mecklenburg equation

centration was calculated.

Estimation of breakthrough time by calculation with the Wheeler equation

The Wheeler equation is given by,

$$T_b = \frac{W_s}{C_0\ Q\ 1000}\left[W + \frac{p_c Q\ 1000}{K_v}\ln\left(\frac{C_0}{C}\right)\right] \quad \text{.. Eq (2)}$$

Where,

$$k_v = adsorption\ rate\ constant = 14.4\frac{1000*Q}{(n*A)^{\frac{1}{2}}\ d^{-3/2}}$$

W = Total weight of adsorbent.

A = Cross sectional area of bed.

By using equation (2), breakthrough time in hours and minutes for the given breakthrough concentration was predicted. The aim in applying Wheeler model to the adsorption process was to evaluate Kv (overall adsorption rate constant) and the amount absorbed, with intention that breakthrough action of a fixed bed adsorbate could be speculate.

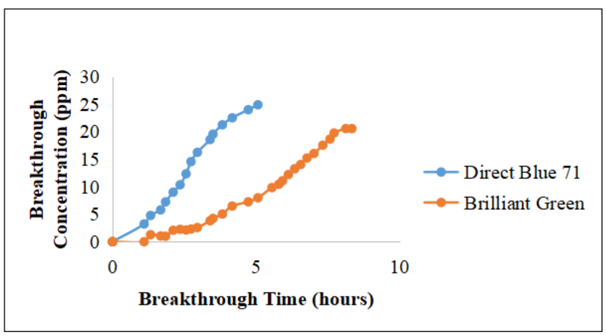

Fig. 4. Breakthrough Curve for Wheeler equation

Estimation of breakthrough time by calculation with the Yoon equation

The Yoon equation is given by equation 3

$$T_b = \frac{W_s}{C_0*Q*1000}\left[W + \frac{p_c*Q*1000}{K_v}\ln\left(\frac{C_1-C}{C}\right)\right] \quad \text{.. (3)}$$

Model developed by Yoon was applied to experimental data of removal of Direct Blue 71 and Brilliant Green dye on adsorbent. With increased bed volume, Tb was increased and rate constant was decreased. This showed that values of T_b were close to the experimental outcome. Results of this equation were similar to Wheeler Equation. At higher breakthrough concentration, breakthrough curve was present in somewhat dissimilar way giving different shape.

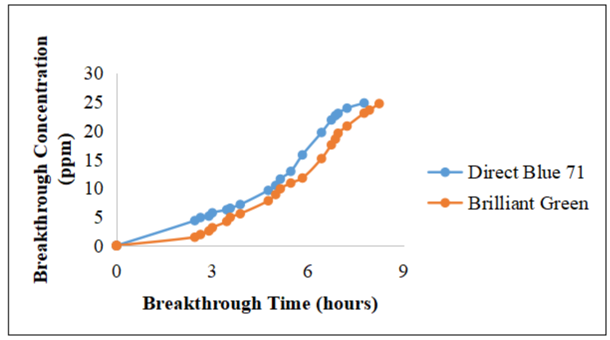

Fig. 5. Breakthrough Curve for Yoon Equation

Comparison of breakthrough curves from the different equations

Comparison of breakthrough curves by Mecklenburg, Wheeler and Yoon equations are represented by Figure 6 and 7.

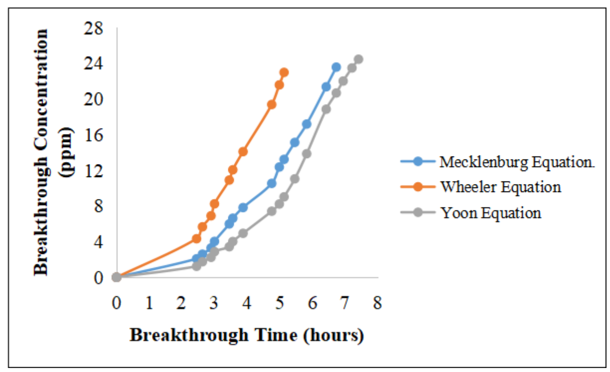

Fig. 6. Breakthrough Curve (Direct Blue 71)

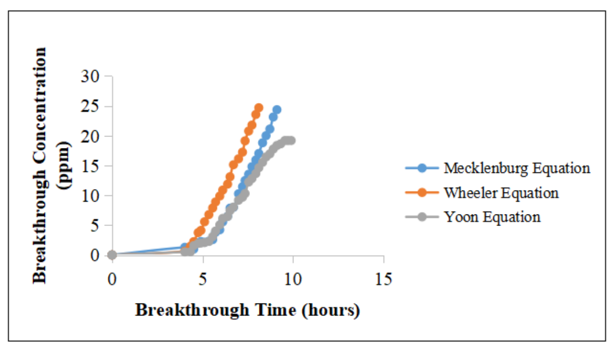

Fig. 7. Breakthrough Curve (Brilliant Green)

For the ideal process, breakthrough time exist at the middle pointed of S-shaped curve is called stoichiometric time (t*). A part of fixed bed column that was equilibrated, was real breakthrough time divided by stoichiometric time. It was given by the equation,

$$\frac{LUB}{Lt} = \frac{T_b}{1-t^*} \quad \text{.. Eq (4)}$$

Where, Lt = Total bed length.

LUB = Unused bed length at breakthrough.

If mass transfer zone shifted across bed unchanged, subsequently for the adsorption operation, LUB doesn't interchange with bed length. Therefore bed utilization efficiency enhances with length, since unused parts changed into smaller portions of the overall bed. The bed volume was 3.0787 $*10^{-3}$ m^3. Flow rate was 11 ml/min. Adsorbent capacity at a breakthrough was 87.699 kg/m^3. The adsorbent capacity at full equilibrium was calculated by using stoichiometric time, the middle point of breakthrough curve was 92.5715 kg/m^3. Unused bed length of column at breakthrough (LUB) was 0.0421 m.

Breakthrough curves were measured from the different feed composition and the flow rate. From the breakthrough data for all the runs, breakthrough capacity, MTZ length, Length of unused bed (LUB) and degree of saturation was estimated. Mass transfer zone (MTZ) and LUB was the typical adsorption design issue could be decoded using idea of equilibrium zone, co-adsorption zone and mass transfer zone. Equilibrium and co-adsorption divisions were the part of the column bed in which adsorbent was loaded to its effective equilibrium capacity. MTZ shifted to the fixed bed column at a constant velocity during loading. The length of the unused bed was just about one half of the length of the mass transfer zone. Breakthrough capacity was the function of the flow rate and the composition of the feed. It was noticed that breakthrough curves at smaller flow rate was more scattered than at higher flow rate. The shape of the breakthrough was depressed as mass transfer resistance decreased. Adsorption on lignite loaded with *azospirillum* bacteria was a productive method for the removal of Direct Blue 71 and Brilliant Green dye from the solution.

Discussion

Lignite loaded with *azospirillum* bacteria was used as adsorbent for the removal of two azo dyes, Direct Blue 71 and Brilliant Green dye in fixed-bed adsorption column. Three models, Mecklenburg, Wheeler and Yoon models were used to speculate the breakthrough curves. All the three models, (Mecklenburg, Wheeler and Yoon) contributed better interconnection toward breakthrough curves. The following interpretation may be appealed from the current investigations:

(1) Adsorption mechanism implicated an initial fast rate for the removal of the dyes because of surface adsorption observed by intraparticle diffusion.
(2) Length of MTZ, breakthrough capacity, and degree of saturation was based on the function of composition and flow rate of the feed.

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