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# CHARACTERIZATION AND COLUMN ADSORPTIVE TREATMENT FOR COD AND COLOR REMOVAL USING ACTIVATED NEEM LEAF POWDER FROM TEXTILE WASTEWATER

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Abstract: The textile wastewater samples before treatment processes has been collected and characterized using standard methods, in which COD, color and other contaminations are high and prior to remove before discharge. Feasibility of column adsorption of components contributing COD and color onto activated Neem Leaf Powder using sulphuric acid (a-NLP) from textile wastewater has been studied in this investigation. The effect of process parameters like different flow rate, bed-height and pH for COD and color removal has been analyzed, in which adsorption reached saturation faster with increasing the flow rate and pH; while it was the advantage of column adsorption with the increase in the a-NLP bed. The data were applied to Thomas, Yoon-Nelson, Bed Depth Service Time (BDST) and Adams and Bohart Model to evaluation of efficacy of the column. The maximum adsorption capacity related to Adams and Bohart model was found to be 725.7 and 380.4 mg/g for COD and color respectively at flow rate of 5 ml/min and bed height of 15 cm when a-NLP was used.

Keywords: Textile wastewater, Column adsorption, Activated NLP, COD, Color, Column model

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# INTRODUCTION

The textile industry is confronted with serious environmental problems associated with its immense wastewater discharge, substantial pollution load, extremely high salinity, and alkaline, heavily colored effluent. Particular sources of recalcitrance and toxicity in dye-house effluent are two frequently used textile auxiliaries; i.e. dye carriers and biocidal finishing agents (Alaton et al., 2006). Disposal of dyeing industry wastewater pose one of the major problems, because such effluents contain a number of contaminants including acid or base, dissolved solids, toxic compounds, and color. Out of these, color is the first contaminant to be recognized because it is visible to the human eye. Removal of many dyes by conventional waste treatment methods is difficult since these are stable to light and oxidizing agents and are resistant to aerobic digestion (Poots et al., 1978).

Adsorption is an efficient and economically feasible process for separation and purification. It plays an important role in a number of natural and industrial systems. The performance of any adsorption-based process greatly depends on the effectiveness of its design and operating conditions (Shim et al., 2004). There are a number of configurations dedicated to undertaking adsorption separation and purification process such as batch, fixed-bed, and fluidized bed. The major difference between batch and fixed-bed operation is in equilibrium establishment. In a batch operation, the adsorbent and adsorbate are in contact for a period of time until equilibrium is reached. In a column operation, adsorbate continuously enters and leaves the column; therefore equilibrium is never achieved at any stage. As the solution flows down the column, the feed zone which is the upper part of the packed adsorbent will be saturated and the low concentration of adsorbate will encounter fresh adsorbent material at the bottom of the packing. The overall performance of the column is judged by its service time, which can be defined as the time the adsorbed adsorbate breaks through the column bed and is detected in the effluent (Hanafiah et al., 2010).

Over the years, the fixed bed adsorption filter has become the most commonly used configuration in water treatment. The advantages of fixed bed configuration in water treatment include: inherent production of high quality removals, its simplicity, ease of operation and handling as well as the possibility of in situ regeneration. Moreover, the configuration is suitable for use as a point-of-use (POU) system and ideal for an individual household, especially in developing countries. In addition, the configuration can be useful as a point-of-entry (POE) system particularly in serving a small or large community as a function of water demand profile (Onyango *et al.*, 2006). Also, in fixed bed the adsorbate is continuously in contact with a given quantity of fresh adsorbent thus providing the required concentration gradient between adsorbent and adsorbate for adsorption (Gayatri & Ahmaruzzaman, 2010). For treatment of high volume, as compared to batch treatment, continuous treatment is a lot more time efficient (Halim & Mee, 2011).

In our previous work, we have shown that a-NLP has excellent potential over normal NLP for the removal of dye from synthetic dye solution (Patel & Vashi, 2013). The batch treatment is useful in providing information about effectiveness of dye-biosorbent system and sorption capacity parameter. However, the data obtained under batch conditions are generally not applicable to most treatment system (such as column operations) where contact time is not sufficient enough for the attainment of equilibrium. Hence, packed column operation is preferred over the bench-scale operation for the removal of micro-pollutants when dealing with large volumes of wastewater (Patel & Vashi, 2012). As per author's best knowledge, there is a no column adsorption experiment conducted to remove components contributing to COD and color using naturally prepared materials. Present investigation was indented for characterization of textile wastewater and removal of COD and color using lab scale column adsorption study using naturally prepared a-NLP. The effect of fed height, flow rate and pH were exploited. The adsorption models viz. Thomas, Yoon-Nelson, Bed Depth Service Time (BDST) and The Adams and Bohart Model were studied to experimental data predict the breakthrough curves and to determine the characteristic parameters of the column useful for process design.

# **METHODS AND MATERIALS**

## Adsorbent

The Neem (scientific name: *Azadirachta indica*) belongs to the meliaceae family and is native to Indian sub-continent. Its seeds and leaves have been in use since ancient times to treat a number of human ailments and also as a household pesticide. The mature leaves of Neem used in the present investigation are collected from the available trees near Navyug Science College, Gujarat. The mature leaves of plant washed thrice with water to remove dust and water soluble impurities and were dried until the leaves become crisp. The dried leaves were crushed and powdered and further washed with distilled water till the washings were free from color and turbidity. Then this powder was stirred with excess amount of 0.1 N sulphuric acid for 30 min.

Thereafter, it washed with de-ionized water to remove untreated acid and dried in an oven at  $60 \pm 2$  °C,

thus a-NLP prepared. Previously Neem leaf powder was utilized as adsorbent for removal of various contaminations from its aqueous solution/ wastewater by investigators (Sharma & Bhattacharyya, 2004, Sharma *et al*, 2010, Sharma & Uma, 2010). Also, the structure and chemical constitution of Neem leaf powder was described by Ganguli (2002).

#### **Experimental Design**

The textile wastewater samples were withdrawn from Pandesara, GIDC, Gujarat, India. Samples were collected in sampling bottles and placed in ice box to preserve the characteristics of wastewater and were analyzed as per standard method (APHA, 1993). For removal of COD and color, continuous column experiments of textile wastewater were carried out in a glass column with internal diameter of 2 cm.

The column was provided with five sampling points at 5 cm intervals. At the bottom of the column 2 cm high layer of glass beads were used to ensure uniform inlet flow to the column. For each experiment, column was packed with a-NPL (20.1  $\pm$  0.5 gm) over this glass beads to a height of 25 cm. The wastewater was introduced into the column in bottom to top mode using a peristaltic pump at desired flow rate. Before wastewater was passed through the column, deionised water was pumped through the column in a down-flow direction to wet the adsorbate completely. The pH of system was maintained by 1.0 N HCl or 1.0 N NaOH during column experiment. Effect of various flow rate (5, 10, 15 and 20 ml/min), bed-height (5, 10, 15 and 20 cm) and pH (4, 6, 8 and 10) were studied. All other chemicals used were of analytical reagent grade. The schematic diagram of fixed bed column used in adsorption study is shown in Fig. 1.



Fig. 1 Schematic diagram of fixed bed column for COD and color removal form textile wastewater

#### **Column Adsorption Model**

To design a column adsorption process it is necessary to predict the breakthrough curve or concentration-like profile and adsorption capacity of the adsorbent for the selected adsorbate under the given set of operating conditions. It also important for determining maximum sorption column capacity, which is significant parameter for any sorption system. The Thomas, Yoon-Nelson, Bed Depth Service Time (BDST) and Adams and Bohart Model were most commonly used to analyze the behavior of adsorbent-adsorbate system.

The Thomas solution is one of the most general and widely used methods in column performance theory. The expression by Thomas for an adsorption column is given as follows.

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp[k_{\rm Th}(q_{0x} - c_0 V_{\rm eff})/v]}$$
(1)

where,  $C_t$  effluent dye concentration (mg/l),  $C_o$  initial dye concentration (mg/l), x is mass of the used adsorbent (g),  $V_{eff}$  throughput volume of the dye solution, v flow rate (ml/min).  $k_{TH}$  is Thomas rate constant and  $q_o$  maximum dye adsorption capacity of the adsorbent (mg/g), which is calculated from plot of  $\ln[(C_t/C_o) - 1]$  vs. t.

The linear form of Yoon-Nelson model is

$$\operatorname{In}\left(\frac{C_{t}}{(C_{o}-C_{t})}\right) = k_{\mathrm{YN}}t - t_{1/2}k_{\mathrm{YN}}$$
(2)

where  $k_{YN}$  is Yoon-Nelson constant,  $\tau$  ( $t_{1/2}$ ) is time required for 50 % adsorbate breakthrough and t is a sampling time. A plot of ln ( $C_t$ / ( $C_o - C_t$ )) vs. t gives straight line curve with a slope of  $k_{YN}$  and intercept of –  $t_{1/2}k_{YN}$ . Base of  $t_{1/2}$ , the adsorption capacity,  $q_{oYN}$  was find out using

$$q_{oYN} = \frac{q_{(total)}}{X} = \frac{C_o Q t_{1/2}}{1000 X}$$
(3)

so, adsorption capacity  $(q_{oYN})$  related to Yoon-Nelson varies as a inlet dye concentration (C<sub>o</sub>), flow rate (Q), 50% breakthrough time derived from Yoon-Nelson equation (t<sub>1/2</sub>) and weight of adsorbent (X) (Priya et al., 2011).

The Bed Depth Service Time model relates the service time of a fixed-bed with the height of adsorbent in the bed, hence with its quantity, because quantity is directly proportional to the bed height. The measurement of sorbent quantity is more precise than the determination of the respective volume, especially for the case of granules. Therefore, sorbent quantity is being preferably used, instead of the bed height. The linear form of BDST model (El Qada, *et al.* 2006) is

$$t = \frac{N_0}{C_0 F} Z - \frac{1}{K_a C_0} \ln\left(\frac{C_0}{C_t} - 1\right)$$
(4)

where t is the service time (min),  $N_o$  the adsorption capacity (mg/l), F is the superficial liquid velocity (cm/min), Z the height of column (cm) and K<sub>a</sub> the rate constant of adsorption (L/ mg min) at time t. A plot of t versus bed depth, Z, should yield a straight line where  $N_o$  and K<sub>a</sub>, the adsorption capacity and rate constant, respectively, can be evaluated. Application of the BDST model requires specification of the breakthrough time, which was selected arbitrarily in this work as the time corresponding to C<sub>t</sub>/C<sub>o</sub> = 0.2, 0.4 and 0.6.

Bohart and Adams established the fundamental equations that describe the relationship between  $C_t/C_o$  and time in an open system for the removal of COD and Color using a-NLP. In spite of the fact that the original studies of Adams–Bohart were performed with the gas–charcoal adsorption system, its overall approach can be applied successfully in quantitative description of other systems. The model proposed assumes that the adsorption rate is proportional to both the residual capacity of the a-NLP and the concentration of the sorbing species. Assuming certain conditions, the linear form of this model (Maiti *et al.*, 2008) is

$$\ln\left(\frac{C_{t}}{C_{o}}\right) = k_{AB} C_{o} t - k_{AB} N_{o}\left(\frac{Z}{U}\right)$$
(5)

where, U is the flow rate calculated by dividing the flow rate by the column cross-sectional area (cm/min), Z is the bed depth (cm) of the column, and  $N_o$  is the adsorption capacity coefficient saturation concentration (mg/L) and  $k_{AB}$  is the kinetic constant (L/mg min), which are calculated from plot of ln (Ct/Co) vs. time, t.

#### **RESULTS AND DISCUSSION**

## **Characterization of Textile wastewater**

The individual and average values of various physicochemical parameters of six wastewater samples from textile mill, Pandesara, GIDC, Surat before treatment processes, has been presented in **Table 1**. It can be seen that the composition of the wastewater generated in an industry varies hourly as well as daily and volume of effluent continuously increases with startup of the operation, till the shutdown.

The pH of textile mill effluent ranges from 4.5 to 7.1 having average value of 5.8, suggesting nearly acidic. The color of the wastewater is light or dark yellow having color unit 286 Hazen. Color in textile wastewater indicates the uses of various types of dyes in

textile processes. Color can be considered as the earliest pollutant to be detected in polluted water. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and affects the quality of water-bodies. Color may significantly affect photosynthetic activity in aquatic life reducing light penetration and may also be toxic to some aquatic life (Saranraj et al., 2010). The wastewater has COD and BOD values (average) of 1519 and 812 ppm respectively, indicating presence of organic/ inorganic chemicals in wastewater. Because of high BOD, the untreated textile wastewater can cause rapid depletion of dissolved oxygen if it is directly discharged into surface water sources (Palamthodi et al., 2011). The high COD concentrations in wastewater treatment systems are toxic to biological life and will affect aquatic environment such as aquatic plants and fishes (Somasiri et al., 2008).

The average value of total dissolved solids was found to be 5332 ppm. The total dissolved solids are due to the chemicals used in the processing units and other operations, as well as other soluble organic and inorganic substance present in the samples. The average value of Hardness was found to be 982 ppm, indicating presence of dissolved divalent metallic cations as  $Ca^{+2}$ ,  $Mg^{+2}$ ,  $Fe^{+2}$ ,  $Mn^{+2}$  and  $Sr^{+2}$  and anions as bicarbonates, chlorides and sulphates of which the most abundant in natural waters are Calcium and Magnesium in textile wastewater. Hard water may be increased eczema in children and affected cardiovascular health.

Oil and grease varies between 10.5 to 14.4 ppm. Presence of oil and grease in the effluent suggests the consumption of oil and grease by different units. Oil and grease content in the wastewater should be monitored carefully before discharging because it completely covers the surface of water and retard dissolved oxygen content of water. Extensive spreading of oil and grease affects the floating plantation and marine life severely and causes lethal toxicity on aquatic flora and fauna. The average value of Chloride and Sulphate were found to be 526 and 846 ppm respectively. The presence of Sulphates and Chlorides depends widely on the methods and material used in production of textile and the quality of raw water.

The combined wastewater of textile industry show considerable amount of chloride indicating presence of soluble salts containing chloride anion. Higher amount of sulphate may have cathartic effects and dehydration. High chloride may cause surface salt formation over a period of time, thereby causing increased alkalinity of the soil, thereby resulting in loss of soil fertility In plants, chlorides tend to accumulate in the tissues, especially the leaves. Chloride accumulation in plants is closely related to the chlorine concentration in the external solution and the genotype. Also, average value of Electrical Conductivity (EC) was found to be 8525  $\mu$ s/cm. Excessive EC level may be irrigate crop fields.

# **Column Adsorption Treatment**

#### **Effect of flow-rate**

COD and color removal in an upflow a-NLP bed was examined at different flow rates of 5, 10, 15 and 20 ml/min and be-height of 15 cm at neutral pH. The resultant breakthrough graph was mentioned Fig. 2 and 3 respectively, in which the column was found to perform better at a lower flow rate which resulted in a longer breakthrough and exhaustion time. At a higher flow rate, the adsorption capacity was lower due to insufficient residence time of the solute in the column and diffusion of the solute into the pores of the adsorbent, and therefore, the solute left the column before equilibrium occurred. The breakthrough and



Fig. 2 Break through curve for COD removal onto a-NLP: Effect of Flow-rate [Q = 5, 10, 15 and 20 ml/min, pH = 7 and Z = 15 cm]



Fig. 3 Break through curve for color removal onto a-NLP: Effect of Flow-rate [Q = 5, 10, 15 and 20 ml/min, pH = 7 and Z = 15 cm]

exhausting times for COD at a flow rate of 20 to 5 ml/min were increasing from 165 to 390 min and 615 to 825 min, respectively. The breakthrough and exhausting times for color for the flow rates of 20 to 5 ml/min were increasing from 240 to 435 min and 550 to 825 min, respectively using a-NLP.The flow rate is an important factor in column adsorption study, because, the flow rate of the fluid phase affects the thickness of boundary layer surrounding particles and external mass-transfer coefficient that is a function of the latter. As indicate in these figures at lowest flow rate of 5.0 ml/min, relatively higher removal of COD and color were observed. But, as the wastewater continued to flow, the concentration of contamination in the effluent rapidly increased, the bed becomes saturated and the concentration of indicator of contaminations (COD and color) in the effluents suddenly rose. The sharper breakthrough curves were obtained and breakthrough and exhausting time at higher flow rates were increased (Ahn & Lee, 2003).

## Effect of bed-height

The effect of bed height for removal of COD and color from textile wastewater using a-NLP bed at heights of 5, 10, 15 and 20 cm and flow rate of 15 ml/min were mentioned in **Fig.** 4 and 5 respectively, which both the breakthrough and exhaustion time increased with increasing the bed height. The breakthrough and exhausting times for the bed heights of 5 to 20 cm were increasing from 195 to 450 min and 505 to 850 min, respectively for COD. Also, breakthrough and exhausting times for the bed heights of 5 to 20 cm were increasing from 255 to 480 min and 540 to 735 min, respectively for color. As the bed height increases,



**Fig. 4** Break through curve for COD removal onto a-NLP: Effect of Bed height. [Q = 15 ml/min, pH = 7 and Z = 5, 10, 15 and 20 cm]

dyeing mill wastewater had more time to contact with adsorbent that resulted in higher removal efficiency of results in a decrease in the solute concentration in the effluent at the same time. The slope of breakthrough curve decreased with increasing bed height, which resulted in a broadened mass transfer zone. High uptake was observed at the highest bed height due to an increase in the surface area of biosorbent, which provided more binding sites for the sorption (Murutu *et al.*, 2012).



Figure 5: Break through curve for color removal onto a-NLP: Effect of Bed height. [Q = 15 ml/min, pH = 7 and Z = 5, 10, 15 and 20 cm]

# Effect of pH

**Figures 6–7** represents the effect of pH for COD and color removal respectively on the breakthrough curves, in which textile wastewater were inserted at flow rate 15 ml/min, through the a-NLP packing column controlling pH 4, 6, 8 and 10 and then after the sample was collected from at bed-height of 15 cm. The breakthrough time increased with increasing pH, in



Fig. 6 Break through curve for COD removal onto a-NLP: Effect of pH. [Q = 15 ml/min, pH = 4, 6, 8 and 10 and Z = 15 cm]

4. Further, column was difficult to be completely exhausted at basic pH i.e. the breakthrough and exhaust time was much higher, found to be 210 and 480 min respectively for COD and also, 45 and 735 min respectively for color at pH 10. So, higher removal of COD and color was found at acidic pH. Also, least removals were found for pH than investigated parameters, like flow-rate and bed-height. Though, the



Fig. 7 Break through curve for color removal onto a-NLP: Effect of pH. [Q = 15 ml/min, pH = 4, 6, 8 and 10 and Z = 15 cm]

which it can be clear that at acidic pH, the breakthrough and exhaust time were very low i.e. 150 and 435 min respectively for COD and 210 and 480 min respectively for color at pH factor pH is an important parameter in adsorption studies, but due to presence of various elements in textile wastewater such as starches, dextrin, gums, glucose, waxes, pectin, alcohol, fatty acids, acetic acid, soap, detergents, sodium hydroxide, carbonates, sulfides, sulfites, chlorides, dyes, pigments, carboxymethyl cellulose, gelatin, peroxides, silicones, flourcarbons, resins; the moderate removal of COD and color was found with change of factor, pH.

# **Column Adsorption Model**

Thomas parameters [Rate Constant,  $K_{TH}$  (ml/mg min) and Adsorption Capacity,  $q_o$  (mg/g)] from Thomas plot i.e. ln[( $C_t/C_o$ ) – 1] vs. t, Yoon Nelson parameter [Rate Constant,  $K_{YN}$  (1/min), 50% Breakthrough Time,  $t_{1/2}$ (min) and Adsorption Capacity,  $Q_{oYN}$  (mg/g)] from Yoon-Nelson plot i.e. ln[ $C_t/(C_o - C_t)$ ] vs. t and Adam Bohart parameters [Rate Constant,  $K_{AB}$  (l/mg min) and Adsorption Capacity,  $N_o$  (mg/l)] from Adam Bohart plot of ln( $C_t/C_o$ ) vs. t for COD and color removal from textile wastewater using a-NLP at different flow-rate (5, 10, 15 and 20 ml/min), bed height (5, 10, 15 and 20 cm) and pH (4, 6, 8 and 10) were depicted in **Tables 2–4**  respectively. Also, graphical curves of Thomas, Yoon-Nelson and Adam Bohart plot indicate straight line, suggesting applicability of all these investigated models.

From Table 2, it is cleared that as the flow rate increases (5 to 20 ml/min), the value of  $K_{YN}$  (0.0182 to 0.0206 1/min) and  $K_{AB}$  (21.65 X 10<sup>-4</sup> to 25.49 X 10<sup>-4</sup> 1/(mg min)) increases, but K<sub>TH</sub> (-0.0910 to -0.1080 ml/(mg min)),  $q_o$  (70.74 to 27.14 mg/g),  $t_{1/2}$  (630.9 to 415.6 min),  $Q_{oYN}$  (70.70 to 26.85 mg/g) and N<sub>o</sub> (725.69 to 87.36 mg/l) decreases for COD using a-NLP. Further, as flow rate increases (5 to 20 ml/min), the value of  $K_{VN}$ (0.0118 to 0.0268 1/min) and  $K_{AB}$  (23.81 X 10<sup>-4</sup> to  $30.04 \text{ X} 10^{-4} \text{ l/(mg min)}$  increases, but K<sub>TH</sub> (-0.0923 to -0.1339 ml/(mg min)),  $q_o$  (68.46 to 21.54 mg/g),  $t_{1/2}$ (680.4 to 402.2 min),  $Q_{oYN}$  (68.88 to 28.95 mg/g) and N<sub>o</sub> (380.41 to 80.85 mg/l) decreases for color using a-NLP. The maximum adsorption capacity related to Adams and Bohart model was found to be 725.7 and 380.4 mg/l for COD and color respectively at flow rate of 5 ml/min and bed height of 15 cm when a-NLP was used.

The results of **Table 3** suggested that as the bed height increases (5 to 20 cm), the value of  $K_{TH}$  (-0.0951 to -0.1325 ml/(mg min)),  $K_{YN}$  (0.0270 to 0.0190 1/min),  $Q_{oYN}$  (57.41 to 32.24 mg/g) and  $K_{AB}$  (34.11 X 10<sup>-4</sup> to 23.21 X 10<sup>-4</sup> l/(mg min)) decreases, but  $q_o$  (32.83 to 57.01 mg/g),  $t_{1/2}$  (378.8 to 674.6 min) and  $N_o$  (287.89 to 670.66 mg/l) increases for COD using a-NLP. Further, as the bed height increases (5 to 20 cm), the

 

 Table 2. Thomas, Yoon Nelson and Adam and Bohart parameter for COD and color removal by column adsorption onto a-NLP at different flow-rate.

Adsorbent: a-NLP; Flow-rate: 5, 10, 15 and 20 ml/min; Bed- height: 15 cm; pH: 7								
Type of Column Adsorption Model								
D	Flow	Thomas	Model Yoon Nelson			Adam and Bohart		
Para	rate						$K_{AB} \; X$	
meter	(ml/	К <sub>ТН</sub> ,	q <sub>o</sub> ,	K <sub>YN</sub> ,	t <sub>1/2</sub> ,	Q <sub>oyn</sub> ,	10 <sup>4</sup> ,	N <sub>o,</sub>
	min)	mi/(mg	mg/g	1/min	min	mg/g	l/(mg	mg/l
		11111)					min)	
COD	5	-0.0910	70.74	0.0182	630.9	70.70	21.65	725.69
	10	-0.0919	62.39	0.0184	537.1	62.00	22.33	481.88
Color	15	-0.0951	45.71	0.0190	488.7	45.81	23.20	198.74
	20	-0.1080	27.14	0.0206	415.6	26.85	25.49	87.36
	5	-0.0923	68.46	0.0118	680.4	68.88	23.81	380.41
	10	-0.0945	65.13	0.0182	609.1	65.10	24.45	300.25
	15	-0.0950	49.59	0.0185	510.2	51.84	29.40	189.54
	20	-0.1339	21.54	0.0268	402.2	28.95	30.04	80.85

 
 Table 3. Thomas, Yoon Nelson and Adam and Bohart parameter for COD and color removal by column adsorption onto a-NLP at different bed-height.

Adsorbent: a-NLP; Flow-rate: 15 ml/min; Bed-height: 5, 10,										
15 and 20 cm; pH: 7										
		Type of Column Adsorption Model								
Para meter	Bed	Thomas Model		Yoon Nelson		Adam and				
						Bohart				
	Height	V				K <sub>AB</sub> X				
	(cm)	$\kappa_{TH}$ , m1/(ma	q <sub>o</sub> ,	K <sub>YN</sub> ,	t <sub>1/2</sub> ,	$Q_{oYN}$ ,	10 <sup>4</sup> ,	N <sub>o,</sub>		
		min)	mg/g	1/min	min	mg/g	l/(mg	mg/l		
		mm)					min)			
COD	5	-0.0951	32.83	0.0270	378.8	57.41	34.11	287.89		
Color	10	-0.1004	42.59	0.0229	500.5	50.55	25.29	343.83		
	15	-0.1045	50.55	0.0201	593.9	42.51	24.56	445.84		
	20	-0.1325	57.01	0.0190	674.6	32.24	23.21	670.66		
	5	-0.1246	38.34	0.0327	450.5	53.24	38.86	78.9		
	10	-0.1358	43.50	0.0303	511.1	47.06	36.69	178.2		
	15	-0.1517	47.54	0.0272	558.6	43.54	36.57	257.3		
	20	-0.1633	53.13	0.0249	624.3	38.44	35.00	310.9		

value of  $K_{TH}$  (-0.1246 to -0.1633 ml/ (mg min)),  $K_{YN}$  (0.0327 to 0.0249 1/min),  $Q_{oYN}$  (53.24 to 38.44 mg/g) and  $K_{AB}$  (38.86 X 10<sup>-4</sup> to 35.00 X 10<sup>-4</sup> l/(mg min)) decreases, but  $q_o$  (38.34 to 53.13 mg/g),  $t_{1/2}$  (450.5 to 624.3) and  $N_o$  (78.9 to 310.9 mg/l) increases for color using a-NLP. The maximum adsorption capacity related to Adams and Bohart model was found to be 670.66 and 310.9 mg/g for COD and color respectively at flow rate of 15 ml/min and bed height of 20 cm when a-NLP was used.

Same behavior can be observed in Table 4 as per flow rate for pH, the value of  $K_{YN}$  (0.0090 to 0.0198 1/min) and  $K_{AB}$  (18.47 X 10<sup>-4</sup> to 30.21 X 10<sup>-4</sup> l/(mg min)) increases, but  $K_{\rm TH}$  (-0.1254 to -0.1847 ml/ (mg min)),  $q_0$  (50.24 to 28.45 mg/g),  $t_{1/2}$  (542.2 to 284.8 min),  $Q_{oYN}$  (40.14 to 27.51 mg/g) and  $N_o$  (545.56 to 241.14 mg/l) decreases for COD using a-NLP, when pH of system was increasing from 4 to 10. Further, as pH increases (4 to 10), the value of  $K_{\rm YN}$  (0.0147 to 0.0258 1/min) and  $K_{AB}$  (13.45 X 10<sup>-4</sup> to 28.45 X 10<sup>-4</sup> l/(mg min)) increases, but  $K_{TH}$  (-0.1685 to -0.2233 ml/ (mg min)),  $q_o$  (48.57 to 35.44 mg/g),  $t_{1/2}$  (574.8 to 352.2 min),  $Q_{o\rm YN}$  (47.47 to 34.48 mg/g) and  $N_o$  (275.48 to 65.44 mg/l) decreases for color using a-NLP. The maximum adsorption capacity related to Adams and Bohart model was found to be 545.56 and 275.48 mg/g for COD and color respectively at flow rate of 15 ml/min, pH 8 and bed height of 15 cm when a-NLP was used.

The BDST parameters [Rate Constant,  $K_a$  (ml/(mg min)) and Adsorption Capacity,  $N_o$  (mg/l)] were calculated from plot of t versus bed depth, Z and mentioned in **Table 5**, in which value of constant,  $K_a$  was decrease and No was increase with increasing ratio of  $C_t/C_o$  for COD and color. The value of  $K_a$  was found

at pii.										
Adsorbent: a-NLP; Flow-rate: 15 ml/min; Bed-height: 15 cm;										
pH: 4, 6, 8 and 10										
Para meter		Type of Column Adsorption Model								
	рН	Thomas	Model	Voon Nalson			Adam and			
		Thomas Model Foon Nelson			SOII	Bohart				
		V					K <sub>AB</sub> X			
		$K_{TH}$ , ml/(mg	q <sub>o</sub> ,	K <sub>YN</sub> ,	t <sub>1/2</sub> ,	$Q_{oYN}$ ,	10 <sup>4</sup> ,	N <sub>o,</sub>		
		min)	mg/g	1/min	min	mg/g	l/(mg	mg/l		
		mm)			-		min)			
COD	4	-0.1254	50.24	0.0090	542.2	240.14	18.47	545.56		
Color	6	-0.1327	45.14	0.0101	414.5	35.84	21.54	425.25		
	8	-0.1547	35.45	0.0147	313.2	30.25	26.25	300.83		
	10	-0.1847	28.45	0.0198	284.8	27.51	30.21	241.14		
	4	-0.1685	48.57	0.0147	574.8	47.47	13.45	275.48		
	6	-0.1987	42.57	0.0184	525.5	42.58	15.25	205.12		
	8	-0.2020	39.85	0.0202	425.8	37.48	19.69	115.22		
	10	-0.2233	35.44	0.0258	352.2	234.48	28.45	65.44		

 

 Table 4. Thomas, Yoon Nelson and Adam and Bohart parameter for COD and color removal by column adsorption onto a-NLP at pH.

 Table 5. BDST parameter for COD and color removal by column adsorption onto a-NLP.

Parameter	Constant	$C_t/C_o$			
1 draineter	Constant	0.2	0.4	0.6	
COD	N <sub>o</sub> , mg/l	5.88	6.56	7.11	
COD	$K_a X 10^3$ , ml/(mg min)	29.49	7.72	-6.84	
Color	N <sub>o</sub> , mg/l	5.13	5.88	6.05	
	$K_a \ge 10^3$ , ml/(mg min)	44.01	11.42	9.84	

to be 29.49 to -6.84 ml/(mg min) and N<sub>o</sub> was found to be 5.88 to 7.11 mg/l for COD at  $C_t/C_o$  of 0.2 to 0.6 respectively. Also, value of K<sub>a</sub> was found to be 44.01 to 9.84 ml/(mg min) and N<sub>o</sub> was found to be 5.13 to 6.05 mg/l for color at  $C_t/C_o$  of 0.2 to 0.6 respectively. The maximum adsorption capacity related to BDST was found to be 7.11 and 6.05 mg/g for COD and color respectively at  $C_t/C_o = 0.6$  using a-NLP. Further, linear graphs of BDST model were suggested applicability of this model.

### CONCLUSION

Textile industry effluents are a major source of water pollution because dyes and other contaminants present in the wastewater undergo chemical as well as biological changes, consume dissolved oxygen, destroy aquatic life and pose a threat to human health as many of these contaminants are highly toxic in nature. So, these contaminations are to be removed prior to discharge. Higher adsorption efficiencies for compound contributing to COD and color onto a-NLP are found using fixed bed column method. Breakthrough curves are plotted for COD and color removal using a-NLP at different parameters like flow-rate (5 to 20 ml/min), bed-height (5 to 20 min) and pH (4 to 10). The breakthrough and exhausting time for each parameter are mentioned, which suggested higher removals of COD and color are found using parameter, bed-height. Graphs of Thomas, Yoon Nelson, Adam Bohart and BDST model are plotted and their parameters are calculated for COD and color removal from textile wastewater using a-NLP at different parameters. Linear graphs of these models are suggested applicability of these models. As flow rate and pH increases, the value of  $K_{YN}$  and  $K_{AB}$  increases, but  $K_{TH}$ ,  $q_o$ ,  $t_{1/2}$ ,  $Q_{oYN}$  and  $N_o$ decreases for COD and color using a-NLP. The value of  $K_{TH}$ ,  $K_{YN}$ ,  $Q_{oYN}$  and  $K_{AB}$  decreases, but  $q_o$ ,  $t_{1/2}$  and  $N_o$ increases for COD using a-NLP, when bed-height is increases. Also, value of Ka is decrease and No is increases with increasing ratio of Ct/Co for COD and color. The maximum adsorption capacity related to Adams and Bohart model is found to be 725.7 and 380.4 mg/l for COD and color respectively at flow rate of 5 ml/min and bed height of 20 cm when a-NLP is used.

### REFERENCES

- Ahn, H. & Lee, C. (2003) Adsorption Dynamics of Water in Layered Bed for Air-Drying TSA Process, *AIChE Journal* 49(6), 1601-1609. doi: 10.1002/aic.690490623.
- Alaton, I.A., Insel, G., Eremektar, G., Babuna, F.G. & Orhon, D. (2006) Effect of Textile Auxiliaries on the Biodegradation of Dyehouse Effluent in Activated Sludge, *Chemosp.* 62, 1549– 1557. DOI:10.1016/j.chemosphere.2005.06.010.
- APHA (American Public Health Association), Standard Methods for the Examination of Water and Wastewater, Fed. Reg. 44: 27362-27375, Washington, DC, 18 Edn., 1992.
- El Qada, E.N., Allen, S.J. & Walker, G.M. (2006) Adsorption of Basic Dyes onto Activated Carbon Using Microcolumns, *Ind. Eng. Chem. Res.* **45**, 6044-6049. doi:10.1021/ie060289e.
- Ganguli, S. (2002) Neem: A therapeutic for all seasons, *Curr. Sci.* **82**(11), 1304.
- Gayatri, S.L. & Ahmaruzzaman Md. (2010) Adsorption technique for the removal of phenolic compounds from wastewater using low-cost natural adsorbent, *Assam Uni. J. Sci. Technol.: Phys. Sci. Technol.* 5(II), 156-166.
- Halim, H.N.A. & Mee K.L.K. (2011) Adsorption of Basic Red 46 by Granular Activated Carbon in a Fixed bed Column, In Proceeding of International Conference on Environment and Industrial Innovation (IPCBEE) Vol. 12, ACSIT Press, Singapore, 263-267.
- Hanafiah, M.A.K.M., Zakaria, H. & Ngah, W.S.W. (2010) Base Treated Cogon Grass (Imperata cylindrica) as an Adsorbent for the Removal of Ni(II): Kinetic; Isothermal and Fixed-bed Column Studies, *Clean – Soil, Air, Water* 38(3), 248 – 256.
- Maiti, A., DasGupta, S., Basu, J.K. & De, S. (2008), Batch and Column Study: Adsorption of Arsenate Using Untreated Laterite as Adsorbent, *Ind. Eng. Chem. Res.* 47, 1620-1629. doi:10.1021/ie070908z.
- Murutu, C., Onyango, M.S., Ochieng, A., Otieno, F.A.O. (2012) Fluoride removal performance of phosphoric acid treated lime: Breakthrough analysis and point-of-use system performance, *Water SA* **38**(2), 279-289.
- Onyango, M.S. & Matsuda, H. (2006) Fluoride Removal from Water Using Adsorption Technique, Chapter 1, Elsevier, UK, pp. 4.
- Palamthodi, S., Patil, D. & Patil, Y. (2011) Microbial degradation of textile industrial effluents, *Afr. J. Biotechnol.* 10(59), 12657-12661. DOI: 10.5897/AJB11.1618.

- Patel, H. & Vashi, R.T. (2013) A comparison study of removal of Methylene Blue Dye by adsorption on Neem Leaf Powder (NLP) and Activated NLP, J. Environ. Eng. Landsc., 21(1), 36-41. doi: 10.3846/16486897.2012.671772.
- Patel, H. & Vashi, R.T. (2012) Fixed bed column adsorption of Acid Yellow17 dye onto Tamarind Seed Powder, *Can. J. Chem. Eng.* 90(1), 180-185. DOI: 10.1002/cjce.20518.
- Poots, V.J.P., Mckay, G. & Healy, J.J. (1978) Removal of basic dye from effluent using wood as an adsorption, *Water Pollut. Control Fed.* 50, 926.
- Priya, P.G., Basha, C.A. & Ramamurthi, V. (2011) Removal of Ni(II) Using Cation Exchange Resins in Packed Bed Column: Prediction of Breakthrough Curves, *Clean – Soil, Air, Water* **39**(1), 88-94. DOI: 10.1002/clen.200900178.
- Saranraj, P., Sumathi, V., Reetha D. & Stella, D. (2010) Decolourization and Degradation of Dirct Azo Dyes and Biodegradation of Textile Dye Effluent by using Bacteria Isolated from Textile Dye Effluent, J. Ecobiotechnol. 2/7, 12-16.

- Sharma, A. & Bhattacharyya, K.G. (2004) Adsorption of Chromium (VI) on Azadirachta Indica (Neem) Leaf Powder, Adsorption 10, 327-338. DOI: 10.1007/s10450-005-4818-x
- Sharma, S.K. & Mudhoo, Jain, A.G. & Sharma (2010) Corrosion inhibition and adsorption properties of *Azadirachta indica* mature leaves extract as green inhibitor for mild steel in HNO3, *Green Chem. Lett. Rev.* 3(1), 7-15. DOI:10.1080/17518250903447100.
- Sharma, Y.C. & Uma (2010), Optimization of Parameters for Adsorption of Methylene Blue on a Low-Cost Activated Carbon, J. Chem. Eng. Data 55, 435-439. DOI: 10.1021/je900408s
- Shim, W.G., Lee, J.W., Rhee, H. & Moon, H. (2004) Adsorption dynamics for the capillary condensation of trichloroethylene vapor on mesoporous material, *Korean J. Chem. Eng.* 21(2), 469-476.
- Somasiri, W., Li, X., Ruan, W. & Jian, C. (2008) Evaluation of the efficacy of Upflow Anaerobic Sludge Blanket reactor in removal of colour and reduction of COD in real textile wastewater, *Biores. Teechnol.* **99**(8), 3692-3699. DOI:10.1016/j.biortech.2007.07.024.