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Dynamic Sorption of Methylene Blue (MB) Dye in Continuous Column Using Bio-Sorbent (*Ailanthus excelsa* Roxb)

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Abstract: Industrial waste containing dye poses a threat to the ecosystem and human as well as aquatic life. Methylene blue (MB, a cationic dye) has been used in excess amounts in textile, pulp and paper, rubber, plastics, cosmetics, pharmaceutical, and food industries. MB dye released in water sources makes the water toxic in nature. So, to remove the dye from wastewater various methods (physical, chemical and biological) are adopted for treatment purposes. Among them, adsorption is found to be more economical and eco-friendlier in comparison to others. Various adsorbents reported have been the literature for the removal of MB dye such as wheat straw, rice husk, cashew nut shell, sawdust, wood, pine needles, green grass, eucalyptus bark, peanut shell, coconut shell, coir dust, etc.

In this experimental study, *Ailanthus excelsa* Roxb. (AER) is utilised for the treatment of MB dye from the wastewater in continuous mode by varying the different parameters viz., bed height, flow rate, and the initial concentration of MB dye. Yoon-Nelson and Clark's models have been applied to predict the break through curve and to find out the characteristic parameters of column suitable for process design. The study reported that Clark's model was found to be fit for the breakthrough curve. The findings revealed that *Ailanthus excelsa* Roxb. has a high adsorption potential, and it could be used to treat dye-containing effluents.

Key words: Methylene blue, dynamic sorption, continuous column, modelling.

Introduction

With the advent of the 21st century, humanity is facing a lot of problems related to water quality and quantity. The rigorous progress in the areas of industrialisation and urbanisation has accompanied with it a diminution of environmental quality (Adegoke and Bello, 2015). Albeit this advancement includes the execution of ecologically acknowledged cycles, huge amounts of industrial wastes are released into natural recipients. Industrial wastewater contains different heavy metals that are not biodegradable and accumulate readily in aquatic organisms. To diminish the heavy metals, dye and other impurities in the environment, it is important to treat wastewater before its release (Biswas and Mishra, 2015). In industries, the most common method used for wastewater treatment are primary and secondary treatments. These treatment methods do not normally guarantee expulsion up to permitted focusses (Biswas et al., 2020). For the complete expulsion, the suitable process is those of tertiary treatment, like adsorption, ion exchange, advanced oxidation process,

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Nomenclature

Ci- Initial Concentration of dye (ppm)
Ct- Dye concentration at time t (ppm)
τ - time required for 50% adsorbate break through. (minute)
BTC- Breakthrough curve
AER- Ailanthus Excelsa Roxb
MB- Methylene Blue
K_{YN} -Yoon Nelson rate constant (min^{-1})
t- time (minute)
t_e- Exhaustion Time (minute)
ppm- parts per million.
H- Height of the Bed (cm)
Q- Flowrate in column (mL/min)
M- Mass of the adsorbate (gm)
A-Constant in Clark's model
r- Constant in Clark's model ($minute^{-1}$)
W_{total}- Total quantity of dye molecules into the column (g)
Q_{total}- Total column capacity (mg)
$Q_{e\ exp}$- Experimental biosorption capacity (mg/g)-
V_{eff}- Total volume treated (mL)

membrane separation, electrocoagulation, etc. Each process has its own merits and demerits (Patel, 2019). The adsorption procedure is very widely used due to its effortlessness just as the accessibility of a wide scope of adsorbents and it ends up being a successful and alluring cycle for evacuation of non-biodegradable contaminants (also, dyes and colours) from wastewater (Alardhi et al., 2020). Activated carbon is the most successful and broadly utilised as an adsorbent since it has amazing adsorption capacity (Al-Husseiny, 2014). In any case, especially in agricultural nations, the application of activated carbon is found to be significant. So, it is desirable to use low-cost adsorbents like mechanical waste, normal material, domestic waste, agricultural waste or rural waste (Altufaily et al., 2019). These materials do not need any costly or extra pretreatment steps and could be utilised as adsorbents for the expulsion of colours or dye from water effluent. Such low-cost adsorbents have acceptable performance at the lab scale for the treatment of coloured wastewater effluents (Kumari et al., 2020).

In the present examination, methylene blue was chosen for assessing the capability of AER leaves to eliminate colour from water effluent. Already, a few analysts had demonstrated that few easily available materials, for example, wheat straw, rice husk, banana peel, cashew nut shell, cereal chaff, sawdust, monster duckweed, wood, pine needles, green grass, eucalyptus bark, peanut shell, coconut shell, coir dust, sewage waste, fire clay, fly ash and zeolite (Akbar et al., 2020; Hussain et al., 2020; Jain et al., 2020; Song et al., 2011; Tomar et al., 2020; Zhang et al., 2011) help in the expulsion of MB from its watery arrangements. In contrast with different adsorbents, the limit of MB adsorption onto AER leaves is observed to be good. As a waste, it is likewise modest, so the leaf waste can be used to eliminate MB from the arrangement (Charola et al., 2018; Markovska et al., 2001). The current work aims to investigate the plausibility of using AER leaf powder for the adsorptive expulsion of MB from wastewater. The impact of flowrate, dye concentration and bed height on MB adsorption using AER was examined. The Yoon–Nelson model and Clark model were used to anticipate the presentation.

Mathematical Model

Dynamic Modelling Description

A breakthrough curve is a plot of Ct/Ci vs. time. Breakthrough time and shape of the curve are very important characteristics to determine the response of the adsorption curve. The performance of a continuous column is described through the concept of the breakthrough curve. The main purpose of conducting the lab tests is to get a concentration-time profile or a breakthrough curve so that the performance of the column in continuous mode can be described or calculated. Various mathematical models were studied for understanding BTC. Among them, the unsteady model viz. the Yoon-Nelson model and Clark's model were studied to analyse the experimental data.

Yoon Nelson Model

It is a simple model to analyse the breakthrough performance of the column. The Yoon Nelson model requires no detailed data concerning the physical properties of the column, the type of the adsorbent and characteristics of the adsorbate. This model assumes that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate breakthrough on the adsorbate (Chen et al., 2016). Yoon-Nelson equation is expressed as:

$$\frac{C_t}{C_i} = \frac{1}{1+\exp[K_{YN}(\tau - t)]} \quad (1)$$

From a plot of ln $[C_t/(C_i-C_t)]$ vs time, the value of K_{YN} and τ can be determined.

Clark's Model

Clark's proposed a new simulation of the breakthrough curve in 1987. This model is based on the concept of mass transfer along with the Freundlich isotherm (Ostaszewski et al., 2021). The formula applied by the authors used the value of *n,* which was obtained from the Freundlich isotherm during the batch study. Clark's equation is expressed as:

$$\frac{C_t}{C_i} = \left(\frac{1}{1+Ae^{-rt}}\right)^{1/(n-1)} \quad (2)$$

The parameters *A* and *r* may be determined from the slope and intercept for the plot of $\ln[(C_i/C_t)^{(n-1)} - 1]$ vs. time.

Material and Method

Methylene Blue Solution

Methylene blue dye is cationic dye and basic in nature with a molecular formula of $C_6H_{18}ClN_3S$. The dye was purchased from Central Drug House Pvt Limited, India. The chemical structure (Rastogi et al., 2008) of MB is shown in Figure 1. In this study, a stock solution of MB dye (100 ppm) was prepared by dissolving MB dye in distilled water; thereafter, various concentration ranges of MB were prepared by its dilution as per requirement (Goswami et al., 2020).

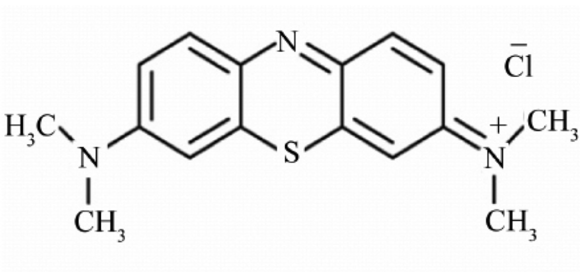

Figure 1: Structure of MB dye.

Preparation of Adsorbent

AER trees are located at Institute Campus in abundance. Initially, the dust and other impurities were removed from the leaves with distilled water, thereafter, the leaves were dried for 90-120 minutes in an oven at 105ºC till they turn pale yellow and crushed in crusher. The crushed leaves were again rewashed with double distilled water, strained and dried in an oven at 150 °C for 24 hrs. until completely dry. The obtained powder sample was allowed to cool, followed by screening. The fine powder was then passed through the sieves of various sizes (75-600 µm). The prepared adsorbent of desired size (300-600 µm) was put away in an airtight container for future use.

Experimental Procedure

All the experiments for adsorption column studies were performed in a Pyrex glass tube with an inner diameter of 2.54 cm and a height of 60 cm as shown in Figure 2. AER adsorbent was packed in the column at different bed stature in the range from 5 to 7 cm. MB dye concentration ranging from 25 to 100 ppm was pumped through a glass column using a peristaltic pump with different flow rates going from 3 to 7 mL/min. After a fixed time, the effluent MB solution concentration was measured using a double beam UV- spectrophotometer at 665 nm.

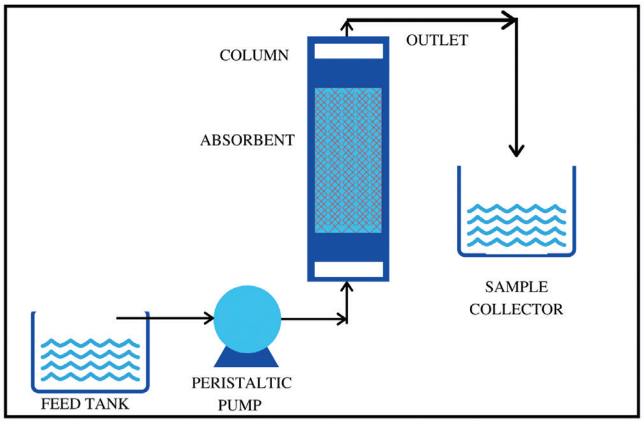

Figure 2: Experimental setup for continuous adsorption of MB dye.

Result and Discussion

Continuous column study has been performed by varying the following parameters: flowrate (3-7 mL/min), bed height (5-7 cm), initial concentration of MB dye (25-100 ppm).

Effect of Bed Height

The effect of column bed height on the removal of MB using prepared AER adsorbent is shown by the breakthrough curve (BTC) given in Figure 3. It is observed that with increasing the bed height from 5 to 7 cm, exhaustion time and breakthrough time increase at a constant flowrate of 6 mL/min and 100 ppm initial dye concentration. This enhancement is due to increase in the surface area of adsorbent, which makes more locations for the adsorption of MB dye because an emanating grouping of MB colour diminishes at higher bed stature under a similar contact time. It is likewise ascribed from Figure 3 that the slope of BTC diminishes on expanding the mass of the adsorbent which is demonstrated by the augmenting of the solute move (MB dye) range and subsequently the rate expulsion gets expanded under higher bed height. Similar results towards BTC have been observed by different authors (Goswami et al., 2020; Hannachi and Hafidh, 2020; Hayati et al., 2018; Nakkeeran et al., 2020).

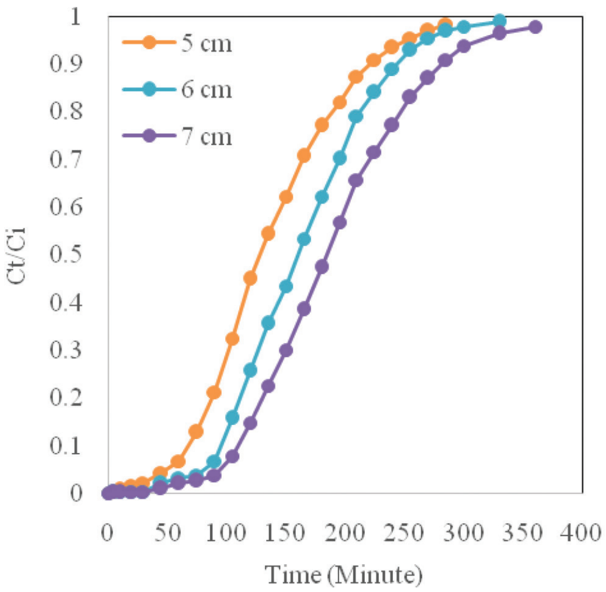

Figure 3: Effect of bed height on break through curve.

Effect of Flow Rate

The effect of MB dye flow rate on BTC is represented in Figure 4 by varying the MB flowrate from 3 to 7 mL/min under a constant bed height of 6 cm and a constant MB dye concentration of 100 ppm. It is seen that the breakthrough happened quickly with a higher stream flow rate because adsorption capacity diminished due to deficient contact time for adsorption of MB on adsorbent accordingly dissemination of MB dye molecules into the pores of adsorbent decreased and consequently solute exit from the continuous column without adequate adsorption before achieving equilibrium. Furthermore, it tends to be credited that the presentation of the continuous column was discovered to be more viable at a low flowrate of 3 mL/min at fixed bed height (6 cm) and dye concentration of 100 ppm. This might be because of the explanation that MB had more contact time with the adsorbent at a low flowrate of MB dye. The most extreme rate expulsion of MB dye was discovered to be 98% at a feed flow rate of 3 mL/min. The same pattern of BTC is discovered and reported by many researchers (Cundari et al., 2020; Dawood et al., 2018; Han et al., 2009; Tan et al., 2008).

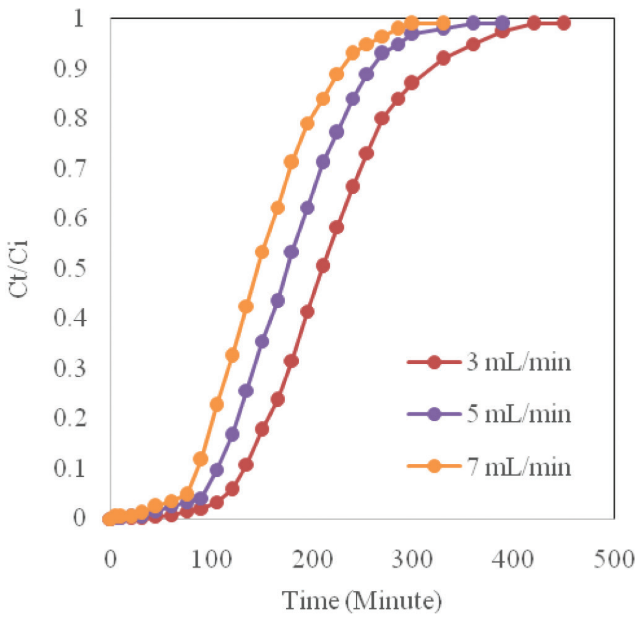

Figure 4: Effect of flowrate on break through curve.

Effect of Initial Dye Concentration

Different initial concentrations of MB viz., 25, 50 and 100 ppm were measured to estimate the adsorbent performance at the constant bed height i.e., 6 cm and constant flow rate of 6 mL/min. Figure 5 reveals that the breakthrough time decreases as the initial concentration of MB increases and it is also seen that BTC scattered more at lower MB concentration (25 ppm) as the breakthrough time gets expanded. With the rise in initial concentration of MB, total time, as well as adsorption capacity, increased as shown in Table 1 along with BTC seems to be sharper. The breakthrough time marginally expanded with diminishing initial concentrations and better column execution was accomplished since there was a lower rivalry between the molecules of MB dye under diminished dissemination or then again mass transfer at lower concentration (Şentürk and Alzein, 2020). In addition, the adsorbent gets bushed more readily because the active sites of the adsorbent become saturated by the dye molecules in the column. Hence, the percentage of removal decreases with increasing the initial dye concentration. The same pattern of BTC is discovered and reported previously (Djelloul and Hamdaoui, 2015; López-Cervantes et al., 2018; Stavrinou et al., 2020; Zhou et al., 2011).

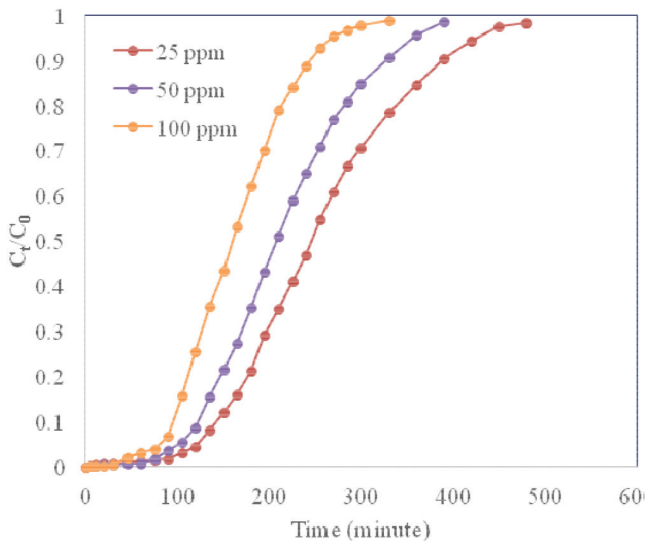

Figure 5: Effect of initial dye concentration on break through curve.

Column Data Modelling

Yoon−Nelson model and Clark's model were studied to determine the adsorption capacity, kinetic parameters and breakthrough performance. Detailed information about the equations (1 and 2) used to calculate the parameter of the selected models is also given. The parameters estimated by using models in addition to R^2 values for every fitting are provided in Table 1.

Yoon−Nelson Model

A plot of $\ln(C_t/[C_i\text{-}C_t])$ vs. time was used to evaluate the Yoon−Nelson model constants shown in Table 2. It is exhibited from Table 2 that τ decreases with increasing the flowrate and initial dye concentration, while it is increases with increasing the bed height where the amount of adsorbent is more. It also observed that K_{YN} increases on increasing the flowrate and dye concentration and decreases with increasing the bed height of the column. Value of correlation coefficient (R^2) for the Yoon−Nelson model ensures favourable MB adsorption process.

Clark's Model

A plot of $\ln[(Ci/Ct)^{\wedge(n-1)}]$ vs. time was used to evaluate Clark's model constants shown in Table 2. From the batch study, it was found that the Freundlich isotherm

Table 1: Study on MB Adsorption using AER with different operating conditions in column

H	*Q*	C_i	t_e	W_{total}	Q_{total}	$Q_{e\ exp}$	V_{eff}	*% Removal*
5	5	100	285	142.5	68.475	32.817	1425	48.0526
6	5	100	330	165	81.735	26.1143	1650	49.5364
7	5	100	360	180	95.18	26.0659	1800	52.8778
6	3	100	420	126	64.782	20.6978	1260	51.4143
6	7	100	300	210	101.115	32.3061	2100	48.15
6	5	50	390	97.5	53.285	17.0245	1950	54.6513
6	5	25	450	56.25	31.41	10.0355	2250	55.84

Table 2: Breakthrough model parameters for dye adsorption

Column Parameter	H	5	6	7	6	6	6	6
	Q	5	5	5	3	7	5	5
	Ci	100	100	100	100	100	50	25
Yoon -Nelson Model	K_{YN}	0.0319	0.0303	0.0291	0.0274	0.0337	0.0259	0.0222
	T	147.26	173.54	201.25	230.143	160.46	220.92	262.63
	R^2	0.972	0.9808	0.98	0.9754	0.9824	0.9848	0.9873
Clark's model	r (min^{-1})	0.0241	0.0242	0.0212	0.0195	0.0252	0.0184	0.0149
	A	5.658	7.241	7.426	8.101	6.878	7.184	6.73
	R^2	0.9969	0.997	0.9971	0.9988	0.9972	0.9907	0.9926

was the best fit for the adsorption of dye on AER. Freundlich constant (1/n) was found to be 0.7133. As seen from Table 2, the value of *r* increases on increasing the flowrate and dye concentration. With the experimental result and data regression, it can be observed that Clark's model has a good correlation with the effect of initial MB dye concentration, bed height and flow rate.

Conclusion

This examination was directed to explore the likely utilisation of AER as a novel adsorbent to eliminate MB dye from wastewater effluents with continuous adsorption. Column study revealed that MB dye concentration, flow rate and bed height altogether affected the breakthrough curve. Optimal conditions like lower flow rate, higher bed stature and low dye concentration caused the higher evacuation of MB. In the column study, the highest adsorption capacity was determined as 32.8 mg/g. Yoon-Nelson and Clark's models very much portrayed the column information. Clark's model was discovered to be appropriate for the adsorption of MB dye based on the R^2 value. Most importantly, it appears to be appropriate to take note of the outcomes featured that AER could be utilised as a promising adsorbent for the expulsion of MB colour from fluid arrangements since the AER leaves were effectively and financially accessible in enormous quantities. Designing of adsorption section with AER proposes that AER can be utilised as an easy adsorbent in an eco-accommodating way. Further examination is required towards utilising other kinetics models, for example, the pore dispersion model, Adam Bohrat, and many more for studying a more effective approach towards this aspect.

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References

Adegoke, K.A. and O.S. Bello (2015). Dye sequestration using agricultural wastes as adsorbents. *Water Resources and Industry*, **12:** 8-24.

Akbar, N.A., Rosman, N.D., Hambali, S. and A.A. Bakar (2020, December). Adsorption of methylene blue by banana stem adsorbent in a continuous fixed bed column study. *In: IOP Conference Series: Earth and Environmental Science,* **616(1)**: 012058. IOP Publishing.

Alardhi, S.M., Albayati, T.M. and J.M. Alrubaye (2020). Adsorption of the methyl green dye pollutant from aqueous solution using mesoporous materials MCM-41 in a fixed-bed column. *Heliyon*, **6(1)**: e03253.

Al-Husseiny, H.A. (2014). Adsorption of methylene blue dye using low-cost adsorbent of sawdust: batch and continues studies. *Journal of Babylon University/Engineering Sciences,* **22(2):** 296-310.

Altufaily, M.A.M., AL-Mansori, N.J. and A.F.M. AL-Qaraghulee (2019). Mathematical modelling of fixed-bed columns for the adsorption of methylene blue on to fired clay pot. *International Journal of ChemTech Research,* **12 (02)**: 70-80.

Biswas, S. and U. Mishra (2015). Continuous fixed-bed column study and adsorption modelling: Removal of lead ion from aqueous solution by charcoal originated from chemical carbonization of rubber wood sawdust. *Journal of Chemistry*, **2015**: 1-9.

Biswas, S., Mohapatra, S.S., Kumari, U., Meikap, B.C. and T.K. Sen (2020). Batch and continuous closed circuit semi-fluidized bed operation: Removal of MB dye using sugarcane bagasse biochar and alginate composite adsorbents. *Journal of Environmental Chemical Engineering,* **8(1)**: 103637.

Charola, S., Yadav, R., Das, P. and S. Maiti (2018). Fixed-bed adsorption of reactive orange 84 dye onto activated carbon prepared from empty cotton flower agro-waste. *Sustainable Environment Research*, **28(6)**: 298-308.

Chen, J.P., Wang, L.K., Wang, M.H.S., Hung, Y.T. and N.K. Shammas (Eds.). (2016). *Remediation of Heavy Metals in the Environment.* CRC Press.

Cundari, L., Fakhri, M.N. and M.Z. Rizki (2020). Adsorption of synthetic dye by betel nuts activated carbon in a fixed-bed column, experiments and prediction of breakthrough curves. *In Journal of Physics: Conference Series*, **1500**: 012051.

Dawood, S., Sen, T.K. and C. Phan (2018). Performance and dynamic modelling of biochar and kaolin packed bed adsorption column for aqueous phase methylene blue (MB) dye removal. *Environmental Technology*, **40(28):** 3762-3772.

Djelloul, C. and O. Hamdaoui (2015). Dynamic adsorption of methylene blue by melon peel in fixed-bed columns. *Desalination and Water Treatment,* **56(11):** 2966-2975.

Goswami, V., Upadhyaya, R. and S.K. Meher (2020). Column study for adsorption of methylene blue dye using *Azadirachta indica* adsorbent. *Asian Journal of Water, Environment and Pollution,* **17(4):** 47-52.

Han, R., Wang, Y., Zhao, X., Wang, Y., Xie, F., Cheng, J. and M. Tang (2009). Adsorption of methylene blue by phoenix tree leaf powder in a fixed-bed column: Experiments and prediction of breakthrough curves. *Desalination*, **245(1-3)**: 284-297.

Hannachi, Y. and A. Hafidh (2020). Biosorption potential of Sargassum muticum algal biomass for methylene blue and lead removal from aqueous medium. *International Journal of Environmental Science and Technology*, **17(9)**: 3875-3890.

Hayati, B., Maleki, A., Najafi, F., Gharibi, F., McKay, G., Gupta, V.K. and N. Marzban (2018). Heavy metal adsorption using PAMAM/CNT nanocomposite from aqueous solution in batch and continuous fixed bed systems. *Chemical Engineering Journal*, **346**: 258-270.

Hussain, N.A.H.M., Jaafar, J., Ibrahim, S.C., Baki, A., Othman, Z., Ramli, S. and W. Tahir (2020). Sorption of methylene blue onto sugarcane bagasse: A column study. *International Journal of Emerging Trends in Engineering Research*, **8(1 Spec)**: 90-96.

Jain, S.N., Tamboli, S.R., Sutar, D.S., Jadhav, S.R., Marathe, J.V., Shaikh, A.A. and A.A. Prajapati (2020). Batch and continuous studies for adsorption of anionic dye onto waste tea residue: kinetic, equilibrium, breakthrough and reusability studies. *Journal of Cleaner Production*, **252**: 119778.

Kumari, R., Mohanta, J., Dey, B. and S. Dey (2020). Eucalyptus leaf powder as an efficient scavenger for congo red from water: Comprehensive batch and column investigation. *Separation Science and Technology*, **55(17)**: 3047-3059.

López-Cervantes, J., Sánchez-Machado, D.I., Sánchez-Duarte, R.G. and M.A. Correa-Murrieta (2018). Study of a fixed-bed column in the adsorption of an azo dye from an aqueous medium using a chitosan–glutaraldehyde biosorbent. *Adsorption Science & Technology*, **36(1-2)**: 215-232.

Markovska, L., Meshko, V. and V. Noveski (2001). Adsorption of basic dyes in a fixed bed column. *Korean Journal of Chemical Engineering*, **18(2)**: 190-195.

Nakkeeran, E., Patra, C., Shahnaz, T., Rangabhashiyam, S. and N.J.B.T.R. Selvaraju (2018). Continuous biosorption assessment for the removal of hexavalent chromium from aqueous solutions using *Strychnos nux vomica* fruit shell. *Bioresource Technology Reports*, **3**: 256-260.

Ostaszewski, P., Długosz, O. and M. Banach (2021). Analysis of measuring methods of the concentration of methylene blue in the sorption process in fixed-bed column. *International Journal of Environmental Science and Technology*, 1-8.

Patel, H. (2019). Fixed-bed column adsorption study: A comprehensive review. *Applied Water Science*, **9(3)**: 1-17.

Rastogi, K., Sahu, J.N., Meikap, B.C. and M.N. Biswas (2008). Removal of methylene blue from wastewater using fly ash as an adsorbent by hydro cyclone. *Journal of Hazardous Materials*, **158(2-3)**: 531-540.

Şentürk, İ. and M. Alzein (2020). Adsorptive removal of basic blue 41 using pistachio shell adsorbent-performance in batch and column system. *Sustainable Chemistry and Pharmacy*, **16**: 100254.

Song, J., Zou, W., Bian, Y., Su, F. and R. Han (2011). Adsorption characteristics of methylene blue by peanut husk in batch and column modes. *Desalination*, **265(1-3):** 119-125.

Stavrinou, A., Aggelopoulos, C.A. and C.D. Tsakiroglou (2020). A methodology to estimate the sorption parameters from batch and column tests: The case study of methylene blue sorption onto banana peels. *Processes*, **8(11)**: 1467.

Tan, I.A.W., Ahmad, A.L. and B.H. Hameed (2008). Adsorption of basic dye using activated carbon prepared from oil palm shell: Batch and fixed bed studies. *Desalination*, **225(1-3)**: 13-28.

Tomar, S., Soni, A.B. and R. Manivannan (2020). Batch and continuous adsorption of crystal violet and congo red by raw coconut fiber. *Journal of the Indian Chemical Society*, **97(7)**: 1055-1060.

Zhang, W., Dong, L., Yan, H., Li, H., Jiang, Z., Kan, X. and R. Cheng (2011). Removal of methylene blue from aqueous solutions by straw-based adsorbent in a fixed-bed column. *Chemical Engineering Journal*, **173(2)**: 429-436.

Zhou, C., Feng, S., Zhou, G., Jin, Y., Liang, J. and J. Xu (2011). A simple method for calculating the overall adsorption rate constant in the Wheeler–Jonas equation. *Adsorption Science & Technology*, **29(1):** 71-82.