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Adsorption Characteristics of Selected Dyes Using Activated Carbon Derived from *Piliostigma thonningii* (Fabaceae: Cercidoideae) Stem

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Abstract
Adsorption characteristics include the initial dye concentration effect, flow rate and adsorbent dose of dyes using activated Piliostigma thonningii Charcoal (PTC) were studied. The adsorption process of the dyes was done using column chromatographic technique at constant temperature and fixed pH of the dye's concentration. Optimization of the column adsorption parameters was conducted, and the maximum percentage removal was attained through setting the level of variables of the adsorption process to initial 100mg/L MB and BM dye concentrations, 30ppm MD dyes and a flow rate of 3mL/min. With lower initial concentration, higher bed height of the adsorbent and lower feed flow rate, the performance of the fixed-bed adsorption system was found to be better. With the highest bed height of 28cm (10g adsorbent dose), maximum adsorption capacity was achieved. The research can help in recycling the wastewater discharged by the textile industries, which will help in reducing the level of water scarcity for industrial use.

Keywords: Adsorbent, Adsorption, Column Chromatography, Dye, Flow Rate

Introduction

Increase in industrial activities alongside population expansion have no doubt shows a positive impact on humanity and indeed contributed its quota in polluting our environment (Alharthi et al., 2022). A reasonable amount of pollutants that various industries discharge poses a serious threat to the biodiversity of the Earth. Among the different kinds of environmental pollution, water pollution is one of the most dangerous. Industries that use dye are among the major contributors of water pollution, as most of those industries discharge the waste dyes and other chemicals used, directly or indirectly to the water bodies. (Maheshwari et al., 2021). Dyes present in textile effluents affects among other things the aesthetics, transparency of the water and the solubility of gases in the receiving bodies; reduces the regeneration capacity of water resources due to the reduction in sunlight penetration and the consequent altering of the photosynthetic processes (Moorthy et al., 2022); raises the level of Chemical Oxygen Demand (COD), as well as the Total Organic Carbon (TOC) (Wei et al., 2019).

Dye-containing effluents in addition, deteriorate the aquatic ecosystem which in turn affects aquatic flora and fauna (Nachiyar et al., 2023). It was estimated that 700,000 t of dyes and pigments are produced globally every year (Pinheiro et al., 2022). Industrial wastewaters carry approximately 20% of these discharged dyes (Varjani et al., 2021). These dyestuffs and solid waste result in different types of hazards which may be toxic, carcinogenic, mutagenic or even explosive (Garg & Chopra, 2022), which have a direct effect on aquatic biota and humans. In this research, continuous adsorption in a fixed-bed column using activated carbon derived from Piliostigma thonningii stem *Fabaceae cercidoideae,* called "Kalgo" in Hausa was used to measure the adsorption capacity of the said adsorbent and to optimize system variables. Adsorption in fixed bed columns using activated carbon has been widely used in industrial processes for the removal of contaminants from industrial effluents, due to the fact that it does not require the addition of chemical compounds in the separation process and that the adsorption capacity was found to be very low for the raw biomass when compared to the activated carbon derived from the biomass (Gupta & Rastogi, 2010; Jain & Suhas, 2002).

Materials and Methods

All reagents used in this work are of analytical grade and were graciously donated by the department of Chemistry, FCE, Zaria, and were used without further purification. All data presented are average of triplicate readings.

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Adsorbent Collection and Preparation

Piliostigma thonningii stem was collected locally from Shinkafi under Katsina Local Government of Katsina State, Nigeria. Distilled water was used to wash it in order to remove dust and then carbonized at 673K in a furnace. The charcoal was then ground using motor and pestle. The resultant powder was passed through standard sieves to obtain particles size of 1mm and below, and then stored in a plastic container prior to use. Some portion of the Piliostigma thonningii charcoal (PTC) was activated by soaking in 2M HCl for three hours as reported by Ahmad and Hameed, (2010). Scanning electron microscope (SEM) at 10KV and resolution range of 500 – 520 was used to analyze the morphological structure of the surface of the adsorbent before and after activation, and before and after the adsorption. An Agilent Technologies FTIR spectrometer with range of 4,000 – 650 cm^{-1} and resolution of 4cm^{-1} was used to determine the functional groups present on the surface of the adsorbent.

pH at a Point of Zero Charge (pH_{PZC})

The pH_{PZC} for the adsorbent was determined by solid addition method as reported by Ibrahim and Mohammed, (2017), with little modification. It involved measuring 40ml of 0.1M NaCl solution into a series of ten stoppered conical flasks of 250ml capacity each, the initial pH (pHi) of the solutions were adjusted between 2 and 11 by adding 0.1M HCl, and each flask was adjusted to 50ml using equal strength of NaCl, and the solutions pHi were correctly noted. 2g of the adsorbent was accurately measured and transferred to each flask and covered immediately. The suspensions were allowed to equilibrate for an hour after been kept on intermittent shaking for a period of twenty-four hours. The pH values final (pH_f) for the supernatant liquids were recorded. The change in pH (ΔpH), that is the difference between the initial and the final pH (pH_i and pH_f) values was ploted against pH_i, the point at which the resultant curve meets abscissa at which pH=0 provided the pH of zero charge. The pH for this research was measured with pH meter (Genway 5301).

Preparation of Adsorbate

The dyes used in this work, Methyl Blue (MB, $C_{37}H_{27}N_3Na_2O_9S_3$; 799.814 g/mol), Basic Magenta (BM, $C_{20}H_{19}N_3$.HCl; 337.85g/mol) and the Mixture of the two Dyes (MD) with maximum wavelength (λmax) of 610, 520 and 514nm respectively were supplied by Ceman Scientific Ltd., Kano state, Nigeria. The stock solutions (1000mg/L) of the dyes (MB, BM and MD) were prepared with deionized water. All working solutions were prepared by serial dilution of the stock solution with deionized water to the desired concentrations. A calibration curve was obtained for each dye and the dyes mixture, and the slope was used to convert the effluent absorbencies into residual concentration.

Adsorption Process

Packing of the slurry adsorbent was done using a sintered column (1cm x 50cm x 0.1cm). In order to prevent the spillage of the adsorbent during elution, cotton wool was placed on top of the it (Ibrahim & Mohammed, 2017). Beaker was used to mix the adsorbent with enough quantity of deionized water and cautiously transferred into the column. The stopcock was left uncovered to make the adsorbent settle on gravity. To avoid allowing the column to run out of liquid adsorbate, the lower meniscus of the water was established above the cotton wool (Carlotti, 2021; Ibrahim & Mohammed, 2017). 250mL volume of the dye solution was run in to the column each time through mode of down flow at an optimum flow rate of 3mL per minute. After every 4 minutes, a fraction of the eluate is collected and promptly analyzed for the remaining dye concentration using UV-spectrophotometer. Column operation for the experiment was done at room temperature.

Results

Scanning Electron Microscopy (SEM)

Results from the scanning electron micrographs (SEM) of the adsorbent before adsorption, after adsorption of MB, BM and MD are displayed in Figure 1, 2, 3 and 4 respectively.

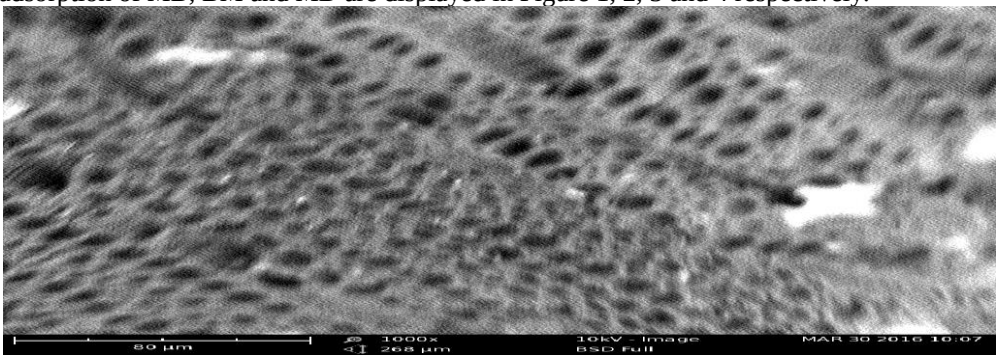

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Fig. 1: SEM picture for adsorbent before the adsorption process

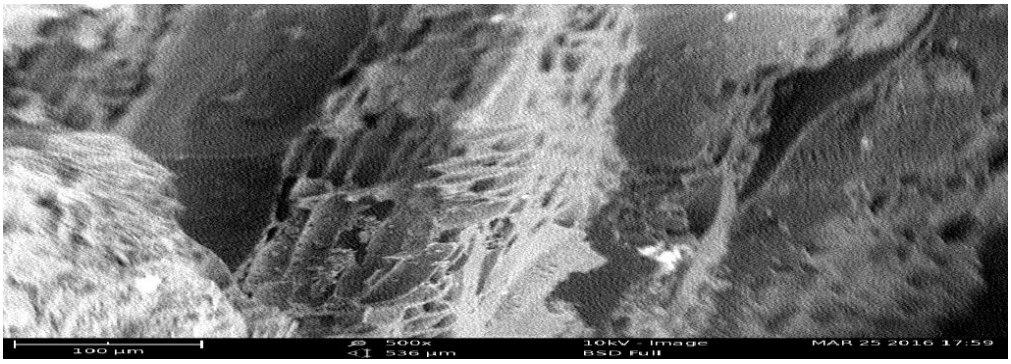

Fig. 2: Scanning Electron Microscope of MB Dye adsorbed adsorbent.

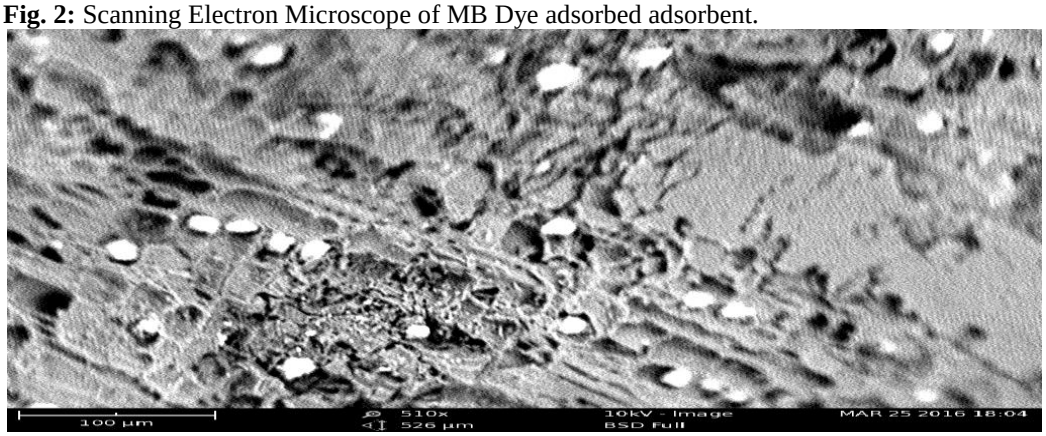

Fig. 3: SEM Picture of the adsorbent after adsorption of BM Dye

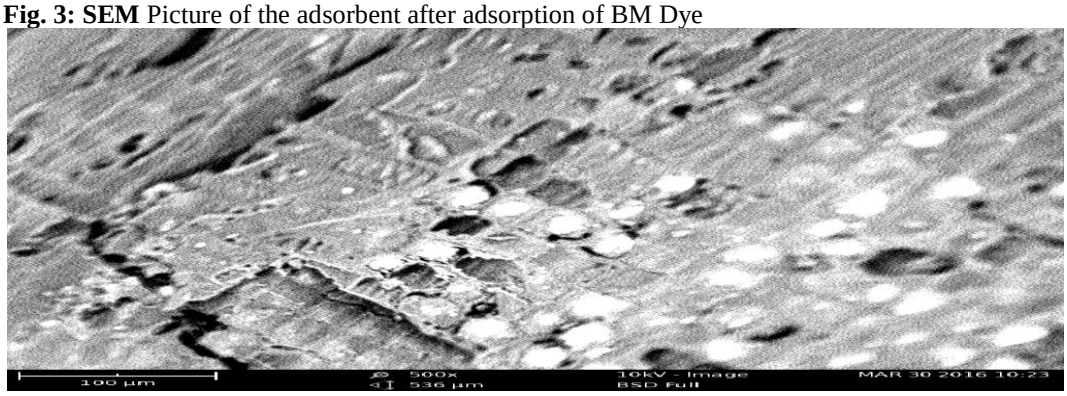

Fig. 4: Scanning Electron Microscope of MD adsorbed adsorbent.

Fourier Transform Infrared Spectroscopy (FT-IR)

Results from Fourier transform infrared spectroscopy (FT-IR) of the adsorbent before adsorption, after adsorption of MB, BM and MD are displayed in Figure 5, 6, 7 and 8 respectively.

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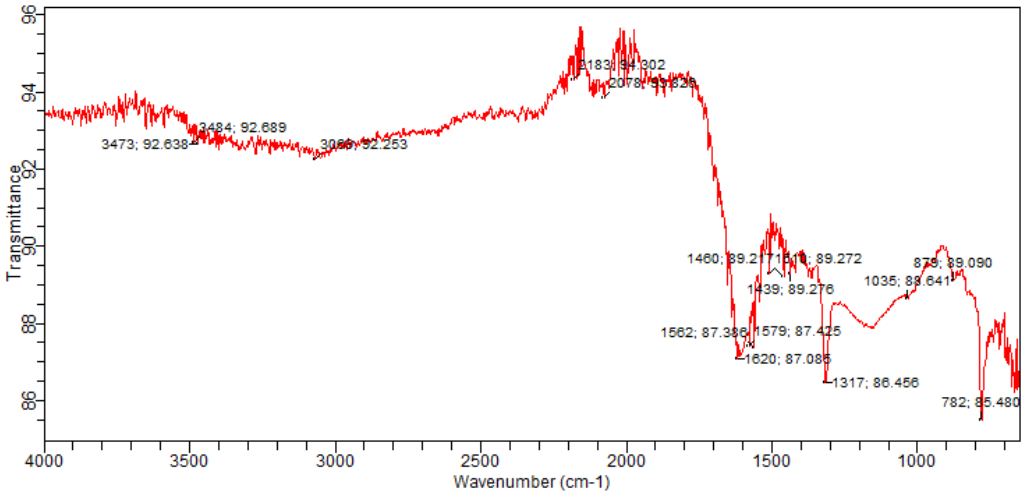

Fig. 5: FT-IR peaks for the fresh adsorbent

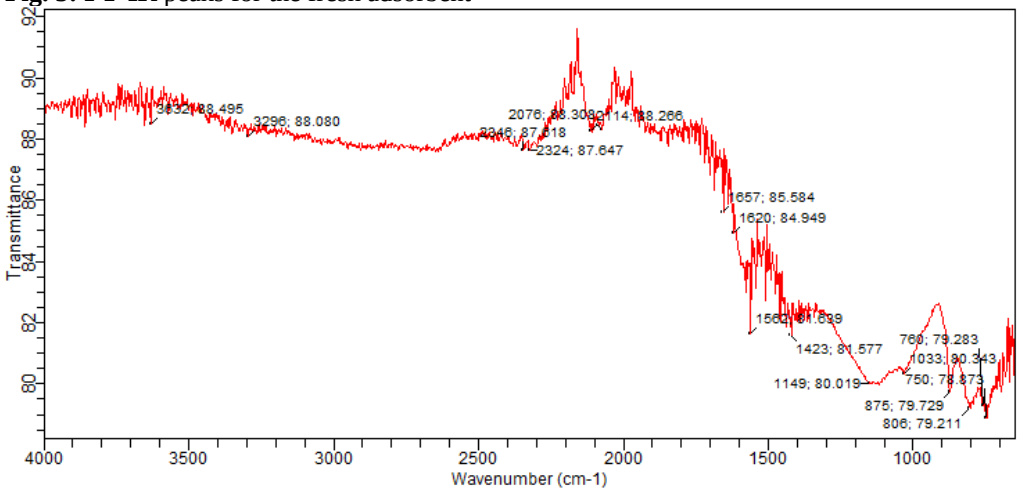

Fig. 6: FT-IR peaks for adsorbent after Methyl Blue (MB) Removal

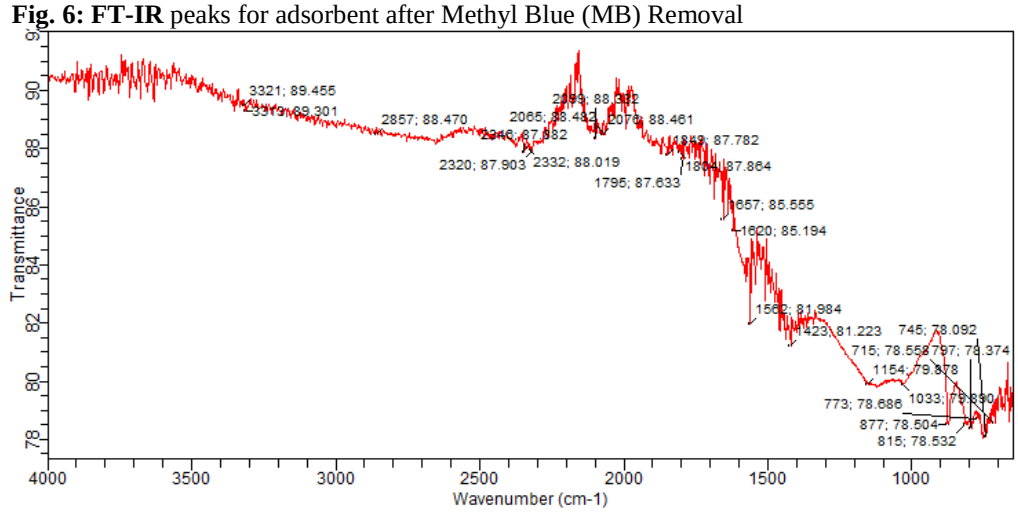

Fig. 7: FT-IR peaks for adsorbent after Magenta (BM) Removal

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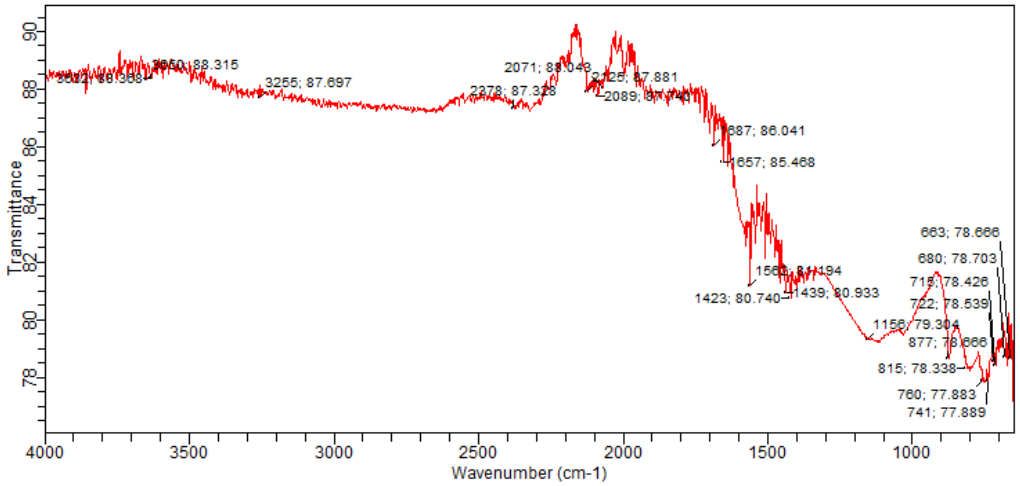

Fig. 8: FT-IR peaks for adsorbent after Mixture of Dyes (MD) Removal

Point of zero charge pH (pH_{PZC})

pH_{PZC} value of 8.22 of the adsorbent was found to be in the region of base, as shown in figure 9.

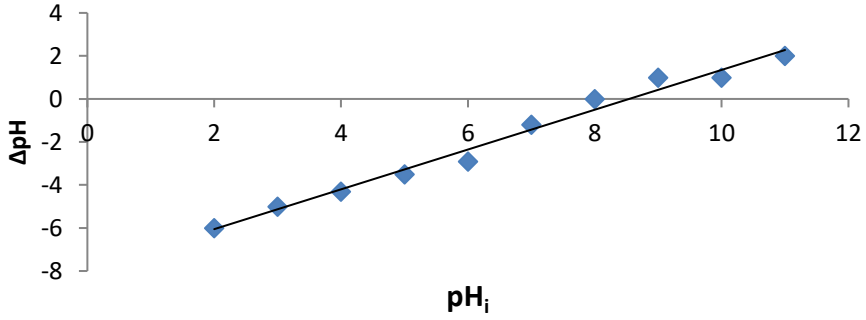

Fig. 9: Plot of pH_{PZC} for the adsorbent

Optimization of Column Parameters

Results from optimization of column parameters are shown in the following figures.

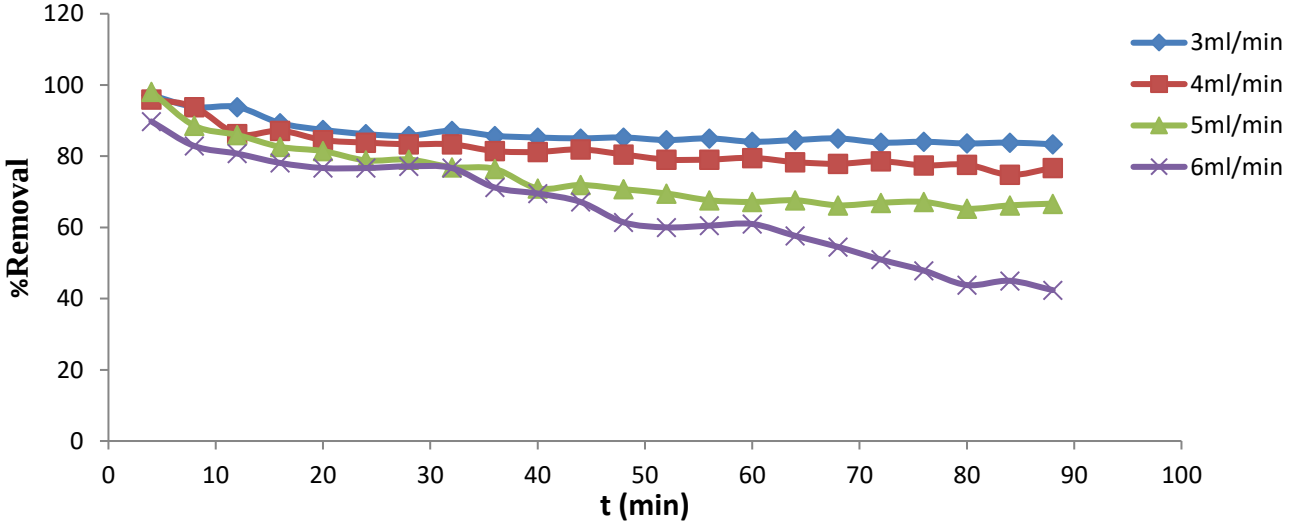

Fig. 10: Optimization of flow rate

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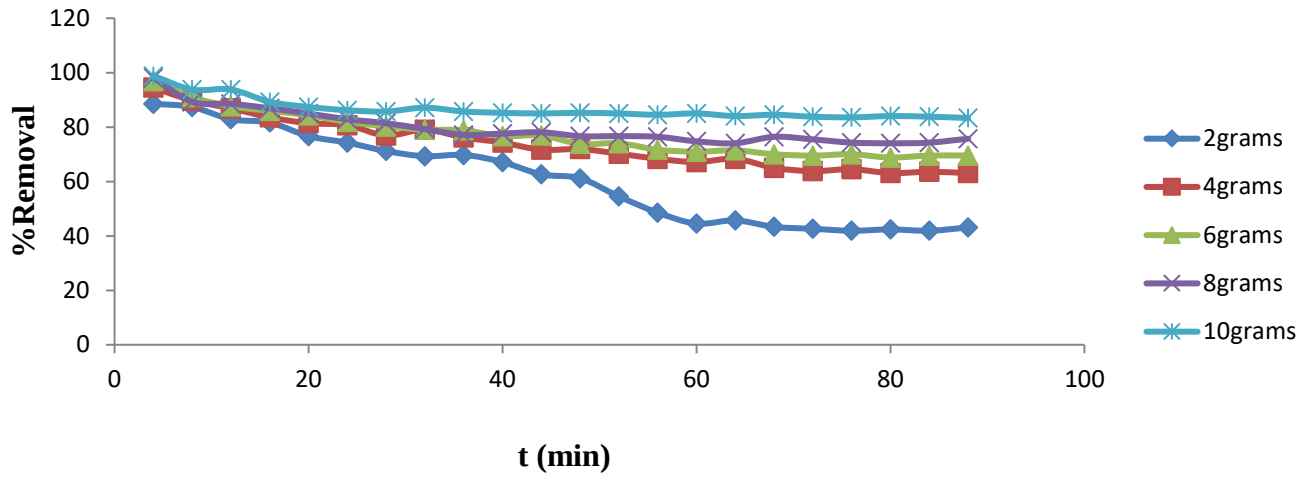

Fig. 11: Optimization of bed height for MB

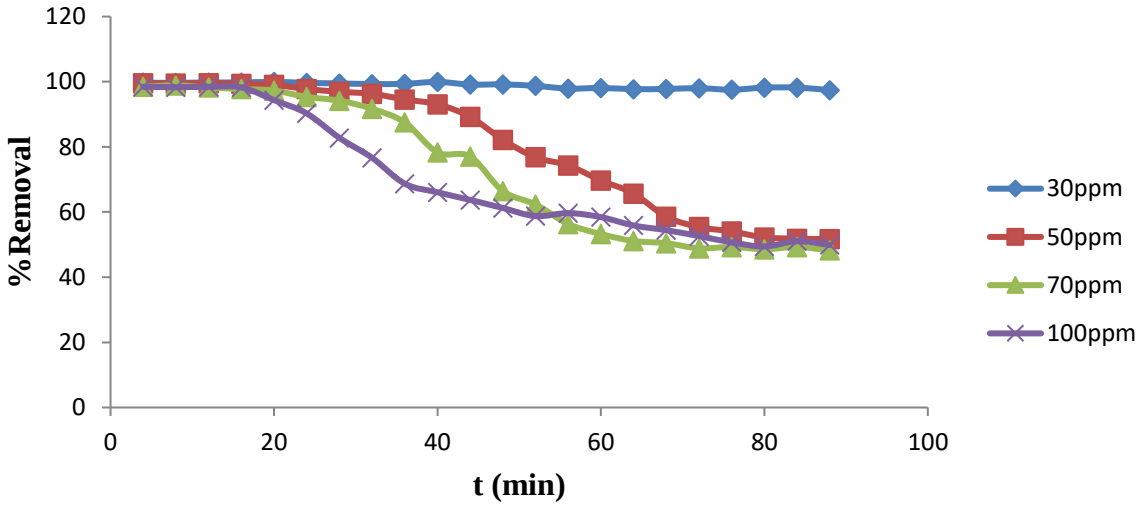

Fig. 12: Optimization of initial concentration for BM

Table 1: Yoon-Nelson Model Parameters

Yoon-Nelson Parameters	MB	BM	MD
K_{YN} (min^{-1})	0.011	0.012	0.019
τ (min)	298	380.9	217
R^2	0.759	0.755	0.921

Table 2: Adams-Bohart Model Parameters

Adams-Bohart Parameters	MB	BM	MD
K_{AB} (mg L/min)	0.5×10^{-4}	0.6×10^{-4}	3.67×10^{-4}
N_o (mgL^{-1})	36.0012	43.7520	6.7462
R^2	0.842	0.644	0.784

Modelling of Breakthrough Curves (BTCs)

Some kinetic and mass transfer models were developed to predict the dynamic behavior of the column. These models are employed to determine breakthrough performance and also to calculate the column kinetic parameters and adsorption capacity of the fixed-bed column. These models are as follows with their linearized form of equations (Mustafa et al., 2014).

Yoon–Nelson Model.

The assumption of this model is based on the rate of decrease in the adsorption probability for each adsorbate, which is proportional to the adsorbate adsorption probability and the adsorbate breakthrough

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probability on the adsorbent. For a single component system, the Yoon and Nelson equation is expressed in its linear form (Ahmad & Hameed, 2010).

$$\ln\left(\frac{C_t}{C_o - C_t}\right) = K_{YN}t - K_{YN\tau} \quad - \quad - \quad - \quad (1)$$

Plot of $\ln[C_t/(C_o - C_t)]$ against sampling time (t) gives a straight line with slope of K_{YN} and intercept $K_{YN}\tau$.

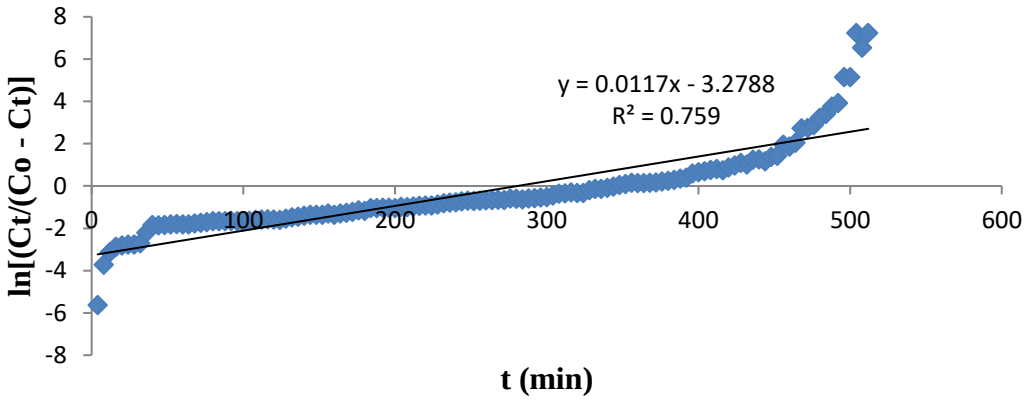

Fig. 13: Yoon-Nelson Model plot for MB

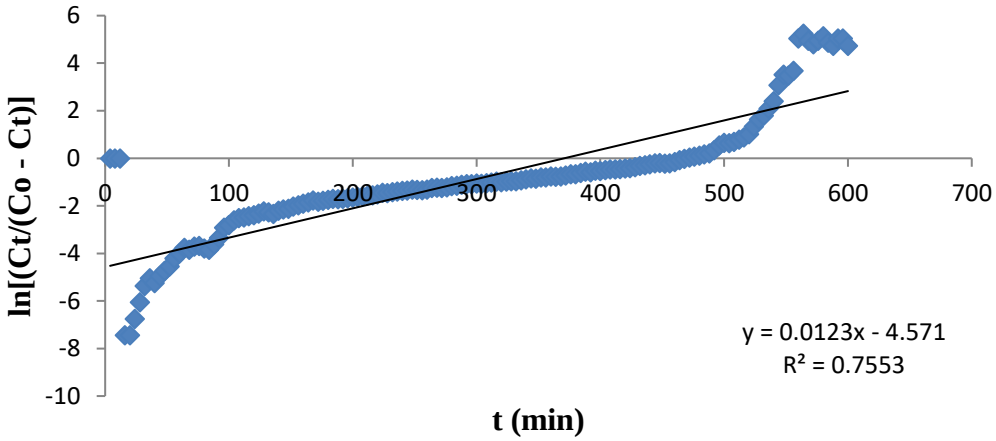

Fig. 14: Plot of Yoon-Nelson Model for BM

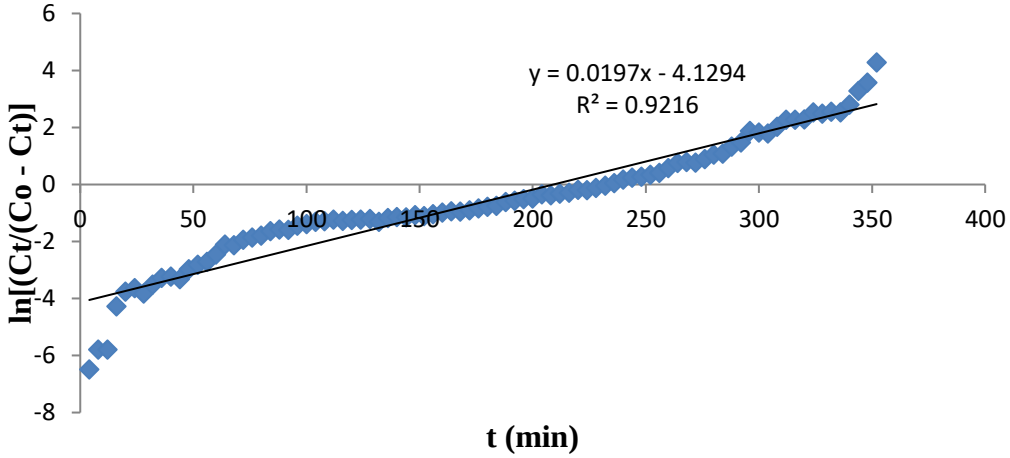

Fig. 15: Yoon-Nelson Model plot for MD

Model of Adams-Bohart

The description of the breakthrough curve initial part is done by the application of Adams-Bohart model (Ahmad and Hameed, 2010; Han et al., 2009).

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$$\ln\left(\frac{C_t}{C_o}\right) = K_{AB}t - K_{AB}N_o\frac{Z}{F} \quad - \quad - \quad - \quad (2)$$

From the plot of $\ln(C_o/C_t)$ against t, the values of N_o and k_{AB} can be obtained from the intercept and the slope respectively.

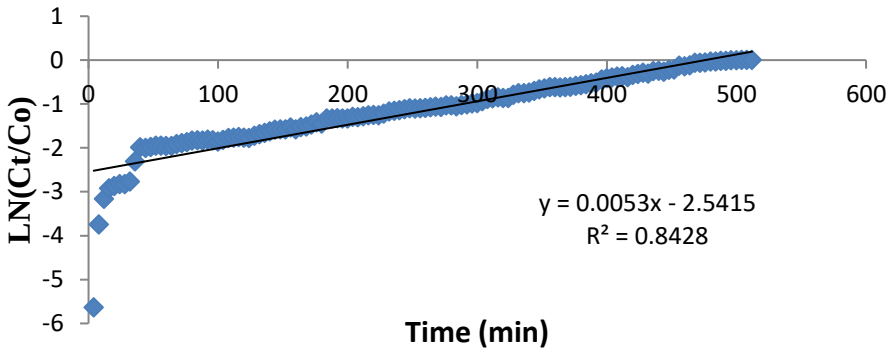

Fig. 16: Adams-Bohart Model Plot for MB

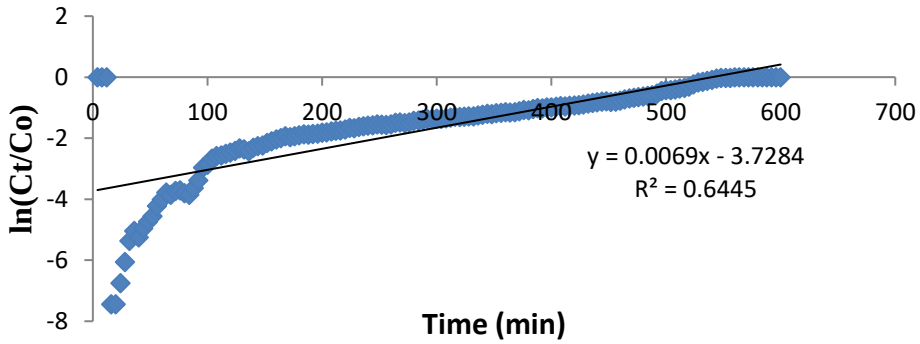

Fig. 17: Adams-Bohart Model Plot for BM

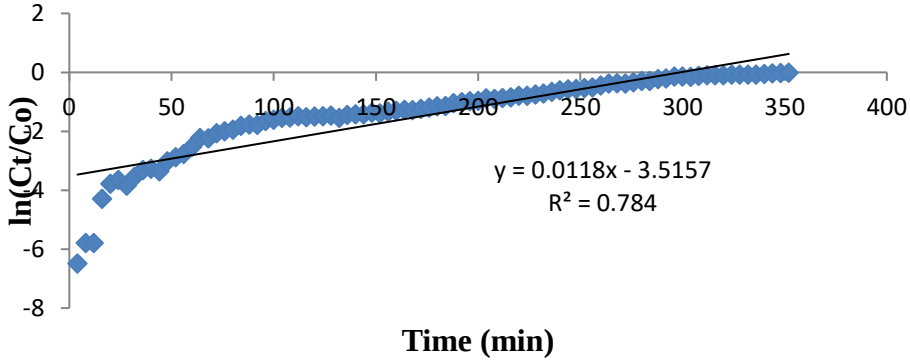

Fig. 18: Adams-Bohart Model Plot for MD

Discussion

Scanning Electron Microscopy (SEM): Presence of numerous pores in Figures 1, 2, 3 and 4 is obviously observable in the SEM result of the adsorbent prior to the adsorption, which seemed to have been filled up by the particles after the dyes adsorption. This suggests that the mass transfer zone owing to the layers of removed molecules of dyes has occupied the pores, the majority of the adsorbent material as well as the substrate surfaces. Carlotti, (2021) reported a similar result.

Fourier Transform Infrared (FT-IR) spectroscopy: The reactivity of functional groups is a very important driving force for adsorption processes that are mostly regarded as chemisorptions (Nachiyar et al., 2023). This can be understood by observing any variation in the FT-IR peaks or shift in their positions on the spectra, or the presence of new peaks or vanishing of some peaks and so on. In this research, the surface chemistry of PTC before adsorption, after adsorption of MB, BM and MD was studied using FT-IR spectroscopy, as shown in figure 5, 6,

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7 and 8 respectively. Several peaks were observed in the spectra which fall within the functional group areas of the spectra. Consequently, represents the functional groups accountable for molecules that bind the dye to the exterior of the adsorbent and its bulk.

The peaks at the finger print region vary from one set of spectra to another due to structural difference and position of the functional groups on the individual dyes as well as their active sites through which they participate in the interaction with the substrate. While in the functional group range, the spectra look very similar, with little variation. The peak at 1620cm^{-1} in figure 6 which is for the raw adsorbent is the major peak that has shifted in all the spectra after adsorption of the dyes is credited to the N-H elongating vibrations. The spectral bands observed at 2340-1680 cm^{-1} range show the occurrence of carbon-carbon double bond (C=C), whereas the peaks at1657-1423 cm^{-1} range show the occurrence of carbon-nitrogen bond (C-N). This as well guarantees the occurrence of unsaturation ultimately in the spectrum that involve either the fresh dyes or the dyes after adsorption process. Peak at 1263.48 cm^{-1} matches to the C–N elongating with the C–O vibration or amine. Peaks at 1027.32 cm^{-1} are perhaps allocated to the carbon-carbon (C–C) stretching.

Effect of Initial Flow Rate (Contact Time): Flow rate is one of the major parameters used for monitoring the efficiency of adsorbents in a dynamic adsorption operation. The flow rate effects on the dyes (MB, BM and MD) adsorption by Piliostigma thonningii charcoal was investigated by changing the rate of flow as 3, 4, 5 and 6 ml/min, whereas other parameters are kept constant. When higher flow rate was used, the velocity of adsorption zone through the column becomes high, and the contact time between the adsorbent becomes less. The makes the substrate to be hard for the dye molecules to infiltrate and diffuse intensely in to the pores of the adsorbents, which eventually leads to decrease in the capacity of the dye adsorption and the dye removal percentage. When this is reversed, the flow rate will actually go low. Furthermore, this will also affect the shape of the break through-curve (Mustafa et al., 2014; Sadaf & Bhatti, 2014; Ofamaja et al., 2009). 3ml per minute flow was adopted as the best flow rate for the whole the adsorption process because it gave the peak of the percentage removal at lengthiest time of flow (Fig. 10).

Effect of Column Bed Height (Adsorbent Dose): The curve obtained Figure 11 for MB adsorption by the adsorbent material through packing the column with various bed heights of 6cm, 9.5cm, 15cm, 22cm and 28cm corresponding to 2g, 4g, 6g, 8g and 10g of the adsorbent dose respectively, at constant flow rate of 3mL per minute, and dye concentration of 30 mgL^{-1}. The treated volume and the percentage removal per unit time increased with height of the bed. When increasing the bed height from 2g-10g, the number of active sites available for the adsorption process and the time of contact between the dye solution and the adsorbent material also increased, which lead to higher removal competency of the column. Consequently, better performance was found with higher bed columns (Ahmad & Hameed, 2010; Han et al., 2009). The bed height of 28cm (10g) showed the highest percentage removal per unit time, which was considered as the optimum bed height for the whole adsorption process.

Original Dye Concentration Effect: The effect of initial concentration of the dye solution was optimized and studied through changing the initial concentration of the dye solution, as 30ppm, 50ppm, 70ppm and 100 ppm, at maintaining the flow rate of 3mL per minute and a bed-height 28cm (10g), with usual pH of the dye solution. This was stated by the plot of percentage removal versus the time of flow (t) for every concentration of the dye solution as (Figure 12). As seen in the figure, the efficiency of the column in terms of percentage removal decrease with increasing initial concentration, because, for 30mg/L BM even at 88 min of elution, the value of %Removal was more than 90%. But for 100mg/L BM at shorter time (45 min of elution), the %Removal was less than 60%. This indicates that higher initial dye concentrations lead to higher driving force for mass transfer; hence, the adsorbent achieved saturation faster which also resulted in a decrease in exhaustion time, as reported among several others by Varjani et al. (2021). 30ppm was found to be the best concentration of the dye because it showed highest percentage removal at longer contact time of elution with extra treated volume. Similar trend will also apply to the breakthrough curve as breakthrough will occur faster at higher influent concentration than at relatively lower concentration. This was also reported by among numerous research groups (Han et al., 2009; Ahmad & Hameed, 2010).

Application of Column Kinetic Models: The BTCs for the column experimental data for MB, BM and MD were found to be fit to Adams-Bohart and Yoon-Nelson models linear forms. The individual parameters of the models. Value of R^2 gotten from 10g of the adsorbent material and the flow rate of 3mL min^{-1} for Yoon-Nelson and Adams Bohart models were tabulated in Tables 1 and 2 respectively. From Table 1, the values of τ (min) for the dyes are given representing time by which 50 percent of the adsorbent material in the column would reach the point of breakthrough. The variation in values τ (min) from one dye to another is due to the difference in their chemical

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structure as well as their nature of interaction with the substrate. The higher the value of the kinetic rate constant K_{YN} (min^{-1}), the higher is the column performance (Ahmad & Hameed, 2010). Likewise, the values of the bed volumetric sorption capacity (N_0) presented implied that when dye solution concentration reaches the values for the respective dyes at the reaction state, the first saturation level of the column was reached and it is not the same from the level of exhaustion achieved when the standardized concentration of the solution reaches 0.9 (Table 2).

Conclusion

This research showed the capacity of PTC as a suitable adsorbent for the removal of MB, BM and MD from their aqueous solutions. Optimization of column adsorption parameters was properly done, and it was found that the maximum percentage removal was attained when the process level of variables was set at 100ppm ($100mgL^{-1}$) starting MB and BM concentrations of the dyes and 30ppm MD, and 28cm height of the bed at 3mL min^{-1} of flow rate feed. With lower initial dye concentrations, lower flow rate and higher adsorbent dose, better performance of the constant bed adsorption was observed. As initial concentration of the dye increases, also the relative amount of dye solution adsorbed per unit mass of adsorbent increases, which then increases the driving force for the mass transfer which decreases the zone length adsorption. Highest bed height was found to give better adsorption capacity because increase in surface area provides more binding sites for the adsorption. Higher flow rate lead to lower adsorption capacity due to insufficient contact time of the dye in the column and diffusion of the solute left the column before equilibrium occurred. The adsorption can be clarified by using Yoon–Nelson and Adams Bohart models, despite the fact that the R^2 values were not significant suggesting poor linearity between the data (Tables 1 and 2).

Recommendations

Based om the outcome of this research, the following recommendations were made.

1. Methods used in this research if can help in recycling the waste water discharged by the textile industries which will help in reducing the level of water scarcity for industrial use.
2. Other agro-based waste materials should be tested to see their adsorptive potency.
3. The adsorbent used in this research should be employed for the removal of heavy metals present waste waters discharged by the industries.

References

Ahmad, A.A., & Hameed, B.H. (2010). Fixed-bed adsorption of reactive azo dye onto granular activated carbon prepared from waste, *J. Hazard. Mater.* 175: 298–303.

Alharthi, M., Hanif, I., & Alamoudi, H. (2022). Impact of environmental pollution on human health and financial status of households in MENA countries: Future of using renewable energy to eliminate the environmental pollution. *Renewable Energy*, *190*, 338-346.

Carlotti, J.N. (2021). *Absorbent Household Materials for the Collection of Ignitable Liquid Residues from Surfaces of Varying Porosity*. Eastern Kentucky University,

Garg, A., & Chopra, L. (2022). Dye Waste: A significant environmental hazard. *Materials Today: Proceedings*, *48*, 1310-1315.

Gupta, V.K., & Rastogi A. (2009). Biosorption of hexavalent chromium by raw and acid-treated green alga Oedogonium hatei from aqueous solutions. *J Hazard Mater* 163:396–402

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

Ibrahim, M.B., & Mohammed, M.B. (2017). Dynamic adsorption studies for the removal of Cd (II) and Ni (II) from aqueous solutions using mahogany leaves. *ChemSearch Journal*, *8*(1), 1-12.

Jain, A.K., & Suhas, B.A. (2002). Methylphenols removal from water by low-cost adsorbents, *Journal of Colloid and Interface Science*, 251, 39–45.

Maheshwari, K., Agrawal, M., & Gupta, A. (2021). Dye pollution in water and wastewater. *Novel materials for dye-containing wastewater treatment*, 1-25.

Moorthy, A.K., Shukla, S.P., Govindarajan, R.B., Kumar, K., & Bharti, V.S. (2022). Application of microalgal physiological response as biomarker for evaluating the toxicity of the textile dye alizarin red S. *Bulletin of Environmental Contamination and Toxicology*, *109*(2), 401-408.

Mustafa, T.Y., Tushar, K.S., Sharmeen A., & Ang, H.M. (2014). Fixed-bed dynamiccolumn adsorption study of methylene blue (MB) onto pine cone, *Desalination and Water Treatment*,: 1- 14 DOI:10.1080/19443994.2014.924034

Nachiyar, C.V., Rakshi, A., Sandhya, S., Jebasta, N.B.D., & Nellore, J. (2023). Developments in treatment technologies of dye-containing effluent: A review. *Case Studies in Chemical and Environmental Engineering*, 100339.

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Ofomaja, A., Naidoo, E.B., & Modise, S.J. (2009). Removal of copper (II) from aqueous solution by pine and base modified pine cone powder as biosorbent, *J. Hazard. Mater*. 168: 909–917

Pinheiro, L.R.S., Gradíssimo, D.G., Xavier, L. P., & Santos, A.V. (2022). Degradation of azo dyes: bacterial potential for bioremediation. *Sustainability, 14*(3), 1510.

Sadaf, S., & Bhatti, H.N. (2014). Evaluation of peanut husk as a novel, low cost biosorbent for the removal of indosol orange RSN dye from aqueous solutions: Batch and fixed bed studies, *Clean Technol. Environ. Policy* 16: 527–544.

Varjani, S., Rakholiya, P., Shindhal, T., Shah, A.V., & Ngo, H.H. (2021). Trends in dye industry effluent treatment and recovery of value added products. *Journal of Water Process Engineering, 39*, 101734.

Wei, C., Wu, H., Kong, Q., Wei, J., Feng, C., Qiu, G., . . . Li, F. (2019). Residual chemical oxygen demand (COD) fractionation in bio-treated coking wastewater integrating solution property characterization. *Journal of environmental management, 246*, 324-333.