PERFORMANCE EVALUATION OF A TRICKLING FILTER SYSTEM USING MODIFIED PALM FRUIT FIBER FOR THE REMOVAL OF CIPROFLOXACIN

ABSTRACT

The persistence of pharmaceutical pollutants particularly ciprofloxacin (CIP) in wastewater poses severe environmental and health challenges. The study explores the performance of a trickling filter (TF) system utilizing modified palm fruit fiber (MPFF) as a low-cost and biodegradation packing material for the removal of ciprofloxacin.). The modified palm fruit fiber was prepared through alkaline to enhance adsorption properties and microbial colonization. Characterization techniques, such as Fourier Transform Infrared (FTIR) was employed to determine the prevalent functional groups present in simulated ciprofloxacin pharmaceutical wastewater and on modified palm fruit fiber. Scanning electron microscopy (SEM) was employed to determine the surface morphology, microstructure and the size and shape of modified palm fruit fiber. X-ray fluorescence (XRF) was employed to determine the elemental composition of modified palm fruit fiber before and after experiment. Thermo gravimetric Analysis (TGA) was employed to determine the thermal stability of modified palm fruit fiber before and after experiment.. . Batch biodegradation was done to determine the effects of process parameters of contact time, concentration and flow rate. The optimum percentage removal of 97% was obtained at 9.3hrs, 2.6m3/hr and 131.8mg/l. The equilibrium data were analyzed using Langmuir and freundlich isotherm. The Langmuir isotherm model was the best fit because the highest coefficient determination (R^2) of value 0.9999. The obtained experimental kinetics data were fitted into

Keywords: Trickling filter, ciprofloxacin, simulated pharmaceutical wastewater, biofilter medium, removal efficiency.

1. INTRODUCTION

There were different classes of antibiotics based on their mechanism of action, chemical structure, action spectrum, and route of administration (1). The most common classification of that was based on their mode of action. They include fluoroquinolones, quinolones, β-lactams, sulfonamides, monobactams, carbapenems, and aminoglycosides. Quinolones (ciprofloxacin, levofloxacin, norfloxacin, and ofloxacin) were broad-spectrum antibiotics that were widely prescribed (1a). Ciprofloxacin (CIP) was a quinolone antibacterial agent classified as second-generation fluoroquinolone with broad-spectrum action that was commonly used to treat human and animal bacterial infections (2) was frequently detected in wastewater due to its widespread use and incomplete removal during conventional treatment processes (3). The presence of CIP or any antibacterial derivative in wastewater and surface water was considered a significant environmental hazard, even at very low concentrations. That was because these products can increase the antibiotic resistance of pathogenic bacteria and generate modifications in the biological balance of aquatic ecosystems (4). The continuous and unregulated discharge of CIP into the aquatic environment posed serious environmental and health problems to man and the aquatic lives. That has result sickness and diseases to mankind and imbalance in ecosystem and consequently the food chain was threatened. Among the various concern on humans and environment includes chronic toxicity, endocrine disruption, and direct toxicity of micro flora, even at low concentrations. The effect of CIP on the water in a low concentration affected the photosynthesis of plants, transforms the morphological structure of the algae, and then disrupts the aquatic ecosystem (5). When CIP contaminated water was consumed by humans, it might cause anger, nausea, vomiting, headache, diarrhea,

and tremor. The high concentration of CIP can cause severe kidney failure and increase liver and thrombocytopenic enzymes (6).

Several methods have been employed to remove CIP from aqueous solution. They include adsorption in activated carbon (7); zeolites (8); montmorillonites (9); microalgae intake (10); photo catalytic degradation (11) and electrocoagulation (12); coagulation, sedimentation, biodegradation, photo-transformation, electrochemical, chlorination, ozonation, and Nano filtration through membranes (13;14). There was, therefore, the need to treat the influent streams using eco-friendly and energy efficient methods, prior to discharge into the receiving waters bodies. Trickling filter techniques was simple, reliable, low-cost and effective in treating high concentrations of organic material. However, most of the treatment techniques that have been employed in time past have the issue of efficiency, generation of toxic by-products, high treatment cost, and high energy requirement, (15). Therefore, efficient and low-cost treatment options that do not introduce harmful by-products were required to eliminate antibiotics from water. Due to the inherent limitations of the existing treatment processes, trickling filter present a good alternative since it was simple, reliable, low-cost, effective in treating high concentrations of organic material, relatively low power requirement and requires moderate skill and technical expertise to operate the system (16;17). A trickling filter was an aerobic wastewater treatment process generally used for industrial effluents and domestic sewage treatment. Its operation consists of passing the effluent to be treated over a fixed bed of support medium. Natural and biodegradable materials have gained attention as alternatives for wastewater treatment. Agricultural residues like palm fruit fiber (PFF), an abundant byproduct in palm oil producing regions, have shown promise due to their porous structure and high surface. The application of palm fruit fiber (PFF) as a support medium instead of the pebbles and other biological fiber used for this purpose was the proposed innovation. The palm fruit fiber offers a great surface for biological film fixation, with very hard fibrous structure. In contact with aqueous solution, the PFF degrades very slowly and can act as stimulant for the growth of microbes. Modification processes such as alkaline treatment can further enhanced

the adsorption and microbial attachment properties of palm fruit fiber, making it a viable medium for pharmaceutical pollutant removal in biological systems (18).

2. MATERIALS AND METHODS

2.1 Materials

- ✓ **Palm fruit fiber was sourced from palm fruit bunches after separation of oil and palm kernel from palm fruit from oil processing facility in Anambra state.**
- ✓ **1000mg (1g) of ciprofloxacin tablet was dissolved in the 1000 mL standard flask with distilled water, working solutions were prepared from the stock solution and the stock solution was stored in the refrigerator to minimize degradation and prevent it from losing its integrity.**
- ✓ **Sodium hydroxide (NaOH) was used for palm fruit modification**.

2.2 Modification of Palm Fruit Fiber

500g of the PFF would be washed severally in water until there was no oil coming out of the fiber. It would then be treated with 0.5M NaOH for four days at room temperature to remove lignin and hemicellulose, improving its porosity and surface functional groups. After treatment in NaOH, the PFF would be washed in running water to remove the NaOH and sun dried to obtain fibrous PFF (19) biofilm support medium.

2.3 Experimental Setup

A bioreactor body with cylindrical shape and made of stainless steel was constructed. Its length of the reactor would be 152.4 and its diameter would be about 76.2 cm as shown below in fig 1. Modified PFF would be used as filter media in the trickling filter system for microbial growth. The PFF would be placed vertically in trickling filter system with 129.5 cm in height and diameter varies from 0.5 to 1.0 inches. A distributor would be installed at the top of reactor to spread CIP

wastewater uniformly over filter media. Flow rates would be adjusted with the help of control valves. A 6inches depth drainage layer would be constructed at the bottomof reactor for ventilation and for outflow of the wastewater from the reactor tank for final sedimentation. A settling tank would be provided for collecting and settling waste water. The system was operated at flow rate of 2.6-9.3m3/hr and contact time of 2.6-9.3hrs.

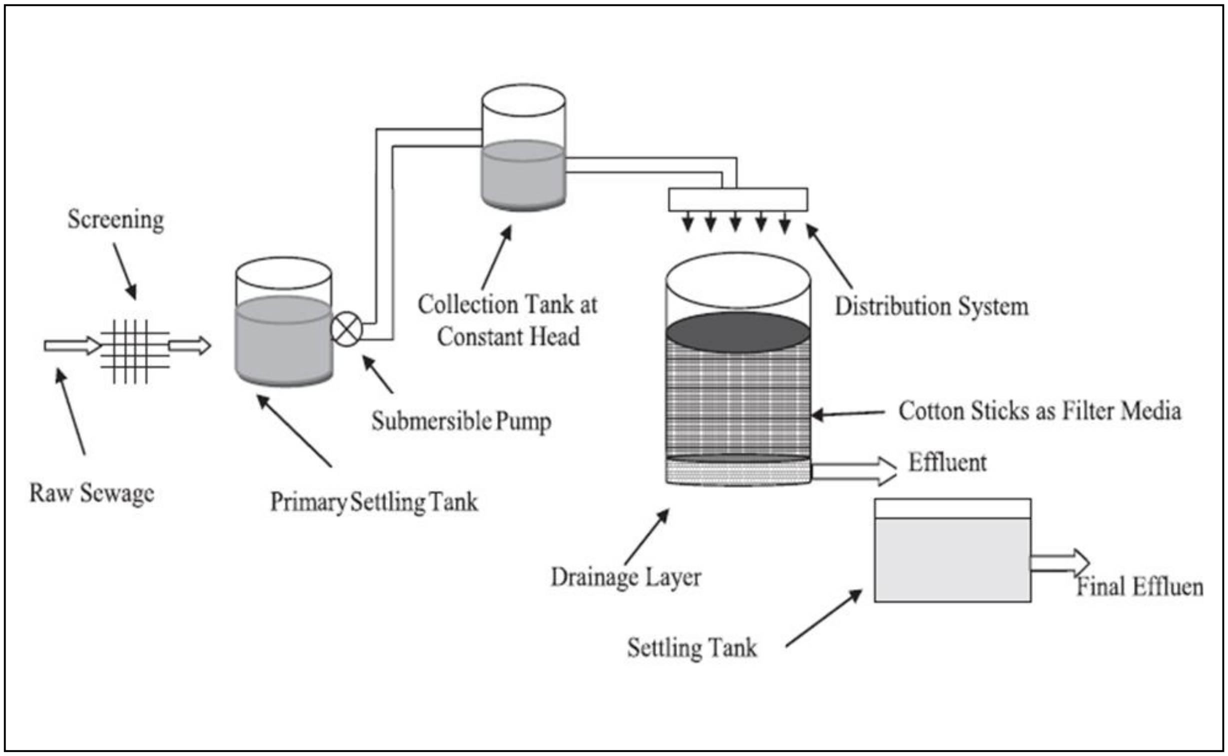


Fig 1: Schematic diagram of Trickling Filter System setup

2.4 Analytical Methods

1. **Total suspended solids were determined through gravimetric analysis**
2. **Total dissolved solid were determined through gravimetric analysis.**
3. **Biological oxygen demand were measured using standard APHA methods (APHA, 2017).**
4. **Characterization of Modified Palm Fruit Fiber: Fourier-transform infrared spectroscopy (FTIR) identified the functional groups responsible for**

adsorption. Scanning electron microscopy (SEM) was used to observe surface morphology. X-ray fluorescence (XRF) identified the elemental composition of modified palm fruit fiber while thermo gravimetric analysis (TGA) was to ascertain thermal stability of modified palm fruit fiber.

2.5 Performance Evaluation

The removal efficiency was calculated using (1)

Removal Efficiency (%) = co-ct/co × 100 (1)

2.5.1 Batch Biodegradation Studies

Biodegradation experiments were conducted to evaluate the effect of contact time (2.6hrs-9.3hrs), initial ciprofloxacin concentration (131.8-468mg/l) and flow rate (2.6-9.3m3/hr). The adsorption capacity at the time t (qt (mg/g)) and equilibrium qe (mg/g) was calculated by the following formula ( ):

$$qt = co\text{-}ct/co \times 100 \quad (2)$$

$$qe = (co\text{-}ce)/m \times v \quad (3)$$

where co, ce and ct (mg/l) are model contaminant concentrations at the intial, equilibrium stages and time t, respectively. The adsorbent mass is m (g) and v (mL) is the contaminant solution volume.

2.5.2 Biodegradation Isotherm

(20); (21) reported that biodegradation equilibrium isotherms were mathematical models used to describe the equilibrium relationship between the concentration of a pollutant or substrate and its adsorption capacity by microorganisms. That models help characterize how pollutants interact with microbial communities or surfaces at equilibrium, providing insight into the maximum sorption potential, affinity for substrates, and capacity of the system. Isotherms were widely applied in environmental engineering and microbiology to optimize conditions for bioremediation, wastewater treatment, and pollutant breakdown in soil or water. The

biodegradation isotherms of the processes were studied using model equations, such as Langmuir and Freundlich. Langmuir biodegradation isotherm model was originally developed by Irving Langmuir in 1916 to describe the dependence of the surface coverage of a degraded solute on adsorbent (22). It was reported to be the most popular model due to its good agreements with sorption experimental data (23) (24) reported that Langmuir isotherm can be mathematically represented as in equation (25):

$$Q=Q_m bc_e/1+bc_e \quad (4)$$

Linearizing equ (4) gives equ (5):

$$C_e/qe=1/KLQ_m +c_e/Q_m \quad (5)$$

Where

Qe=biodegradation capacity at equilibrium (mg/l)

C_e=equilibrium concentration of solute (mg/l)

Q_m=maximum monolayer biodegradation capacity (mg/l)

KL=Langmuir isotherm constant (dm^3/mg)

Freundlich isotherm was the earliest known relationship describing the non-ideal and reversible adsorption and also not restricted to the formation of monolayer (26). The empirical model has been reported to apply to multilayer adsorption (27) with interaction between degraded molecules (28). It was reported to be most widely used and was applicable to adsorption on heterogeneous surfaces (29) but based on the assumption that the adsorption occurs on heterogeneous sites with non-uniform distribution of energy of adsorption over surfaces (30;31).

Mathematically expressed, Freundlich isotherm was as in equation (6) (32;33):

$$Qe=K_f C_e^{1/n} \quad (6)$$

On linearization, equ (6) becomes equ (7)

$lnq_e = lnK_f + 1/n\ lnC_e$
(7)

Where

Q_e was adsorption capacity at equilibrium (mg/g)

C_e was equilibrium concentration of solute (mg/l)

K_f was Freundlich isotherm constant (mg/g)

N was biodegradation intensity

2.5.3 Biodegradation Kinetics Studies

Degradation kinetic study was the crucial because it affected the stability of pharmaceuticals throughout the stages of product development and testing (34;35). Order of degradation reactions of pharmaceuticals was generally categorized as pseudo-first-order and pseudo-second-order, intra particle diffusion and elovich kinetic model. Kinetic studies provide crucially important information on the time needed for rate of degradation. If palm fruit fiber was targeted to be used in wastewater facilities, at industrial scales, in addition to its high degrading capacity and removal efficiency, high degrading rate was also an essential required characteristic (36). In that study, four kinetic models of pseudo-first order, pseudo-second order, intra particle diffusion and elovich models were selected to evaluate the experimental data.
The pseudo-first order kinetic model indicates rate of degradation was directly correlated to the difference of uptake at concentration and time t, shown as (qe –qt) in the equation (37). The equation was expressed as follows (38; 39). A pseudo-first-order kinetic equation was given as

$Ln(qe-qt)=lnqe-k1t$ (8)

qt: The amount of solute degraded at time t (mg/g).

qe:The degradation capacity at equilibrium (mg/g).

k_1: rate constant of pseudo-first order degradation model (g/mg/hr)

t: The contact time (hr).

The pseudo-second order kinetic model was known to be successfully applied in systems where the rate controlling were degradation (40), where the removal from a solution was due to physiochemical interactions between the two phases. A pseudo-second-order model kinetic equation was given as:

$$t/qt=1/k2qe^{2} \; +1/qt \; t$$

(9)

Where:

qt = the amount of solute degraded at time t (mg/g)

qe = the degradation capacity at equilibrium (mg/g)

k2 = the rate constant of pseudo-second-order degradation model (g/mg/hr)

t = the contact time (hr).

In general, for degradation process to take place, degrading molecules need to transfer from bulk phase to the solid surface and then penetrate in the palm fruit fibers pores. Typically diffusing through pores was a slow step. Whether diffusion within the pores was the rate limiting step or not, it can be determined based on intra particular diffusion mode

$$qt = k_{diff} \, t^{1/2} + C$$

(10)

Where:

qt = the amount of solute degraded at time t (mg/g)

C = the intercept

Kdiff = the rate constant of the intra particle diffusion (g/mg/hr)

T1/2 = the half life

The elovich model was first introduced by Elovich (1956) to describe the biodegradation of solute on solid surfaces. The model was based on the premise that the rate of biodegradation decreases with increasing surface coverage. The model has been extensively adapted for liquid-phase biodegradation, particularly in environmental and industrial contexts. The mathematical expression for the model was given by:

$$dqt/dt = \beta e^{-\alpha qt} \quad (11)$$

Integrated equation (11)

$$qt = 1/\alpha \ \text{In}(\beta\alpha \times t+1) \quad (12)$$

Where

qt = the amount of solute degraded at time (t)

α represents the initial biodegradation rate

β = a constant related to the extent of surface coverage.

T = the time

That equation indicated that the adsorption rate was dependent on the amount of solute already degraded.

Rearranging equation (12)

$$B\alpha t + 1 = e^{\alpha qt} \quad (13)$$

Taking the natural logarithm, it results to:

$$\text{In}(qt) = \text{In}(\beta) + \alpha \text{In}(t) \quad (14)$$

3 RESULTS AND DISCUSSION

3.1 Characterization of Modified Palm Fruit Fiber

- **FTIR Analysis: peaks corresponding alkyene, alkene, alcohol and carboxy groups were observed confirming successful modification as showed in figure 2a-b.**

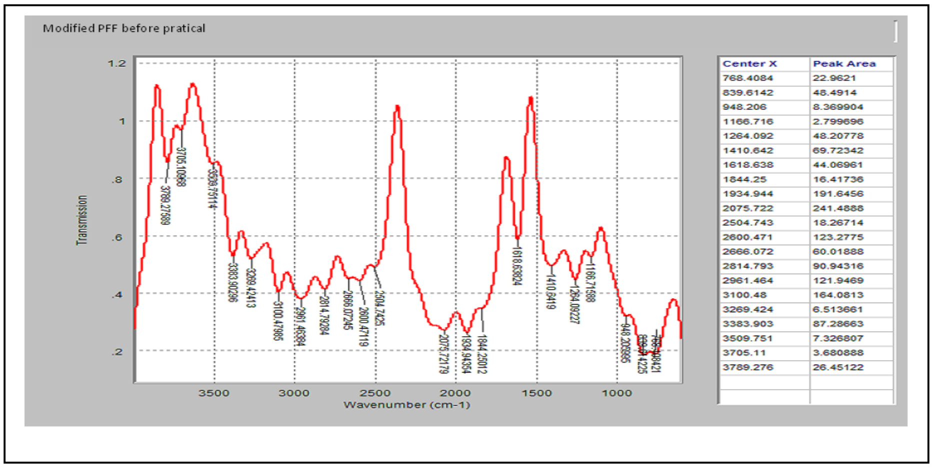


Fig 2a: FTIR Characteristics of Modified PFF before practical

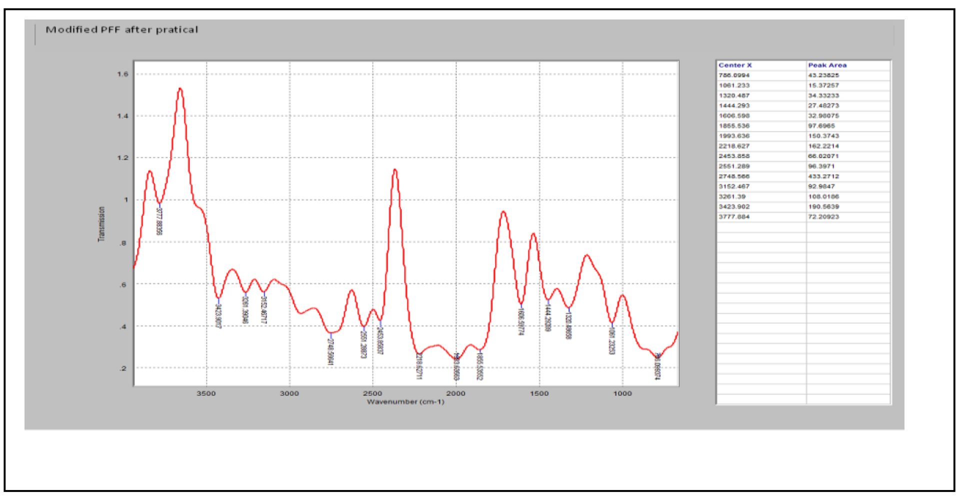


Fig 2b: FTIR Characteristic of modified palm fruit fiber after practical

- **SEM Imaging: The modified palm fruit fiber exhibited increased surface roughness and porosity which are crucial for enhanced biodegradation as showed in figure 3a-c.**

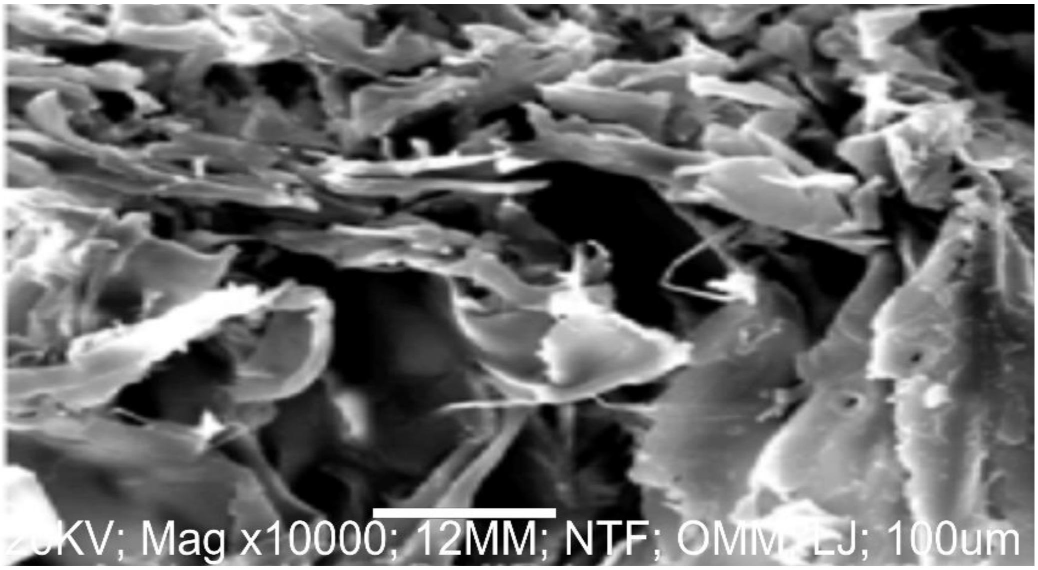


Fig 3a: Mag = X1000, W= 12mm at 100µm

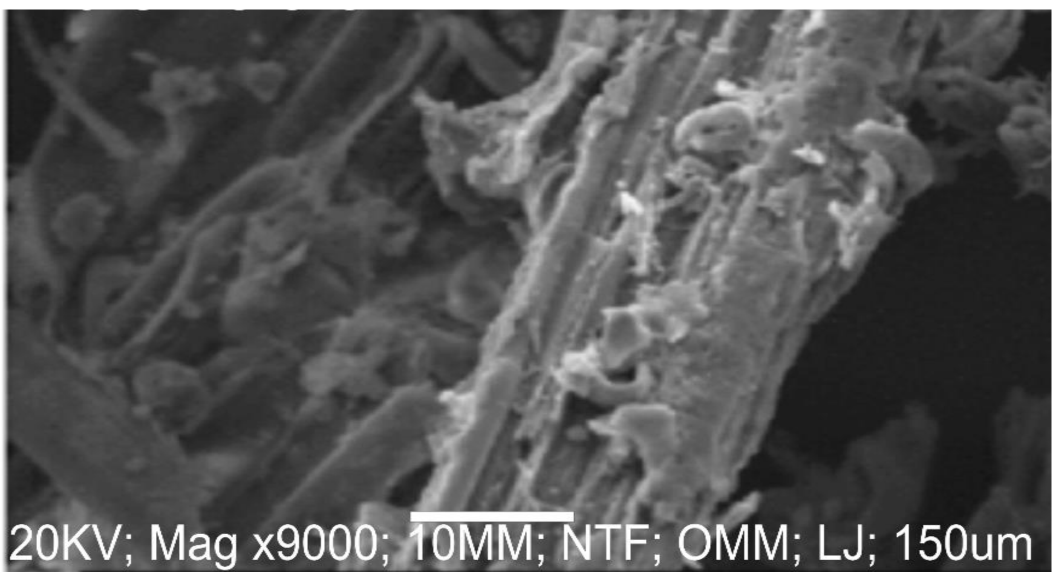


Fig 3b: Mag = X900, W =10mm at 150µm

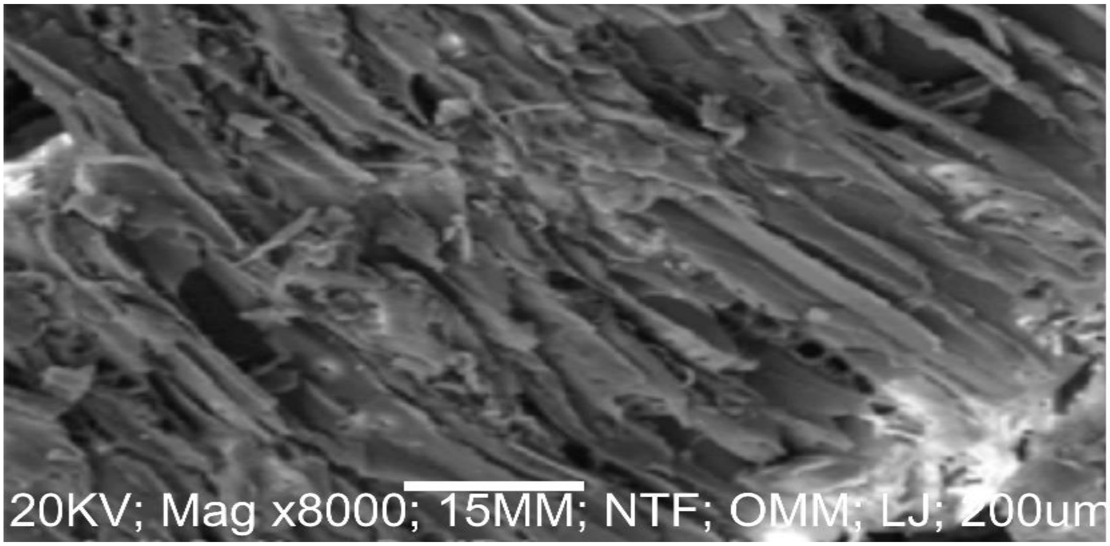


Fig 3c: Mag = X800, W = 15mm at 200µm

- **X-RF Analysis: The modified palm fruit fiber exhibited elemental composition before and after experiment as showed in table 1 below**.

Table 1: XRF Analysis of Modified Palm Fruit Fiber before and after practical

	Na_2O	MgO	AL_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Fe_2O_3	MnO
Palm before	0.17	3.24	6.50	66.95	3.70	5.40	5.50	0.50	5.50	0.02
Palm after	0.20	3.10	6.90	66.60	3.90	5.25	5.57	0.30	5.70	0.06
Average	0.09	1.2	2.2	25.5	0.5	0.5	27.0	<LD	6.0	0.2
Std. dev	0.01	0.01	0.02	0.58	0.01	0.01	0.02	<LD	0.02	0.01
Exp. Value	2-03	4.08	8.73	25.4	1.02	2.22	26.04	0.02	13.3	1.02

- **TGA Analysis: The modified palm fruit fiber exhibited decomposition or evaporation of the components within the sample after practical. Mass loss at temperatures exceeding 400^{0}C resulted in (1) charcoal from decomposition**

decomposing of residual lignin and (11) more oxidation in the air as showed in figure 4a-b below.

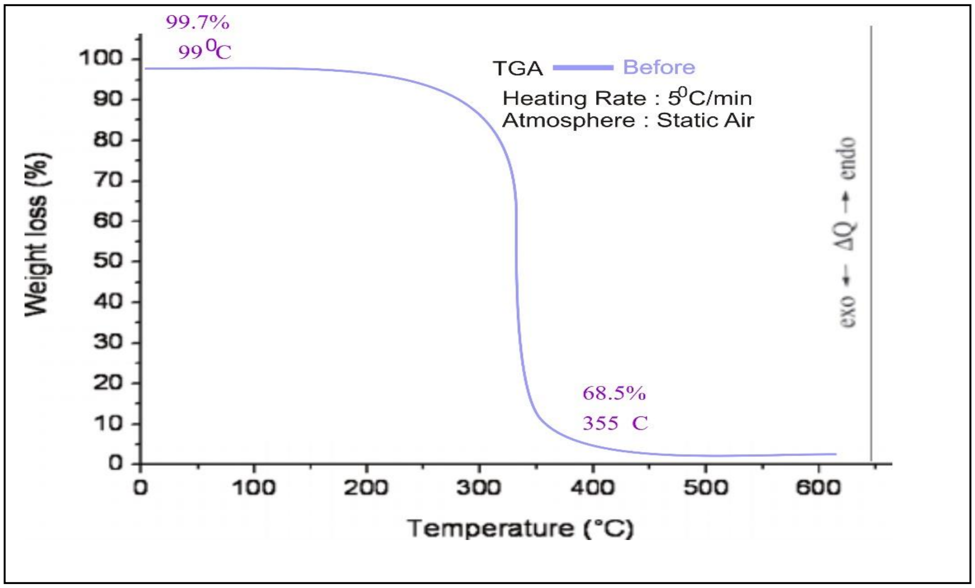


Fig 4a: TGA graph of Modified Palm Fruit Fiber before practical

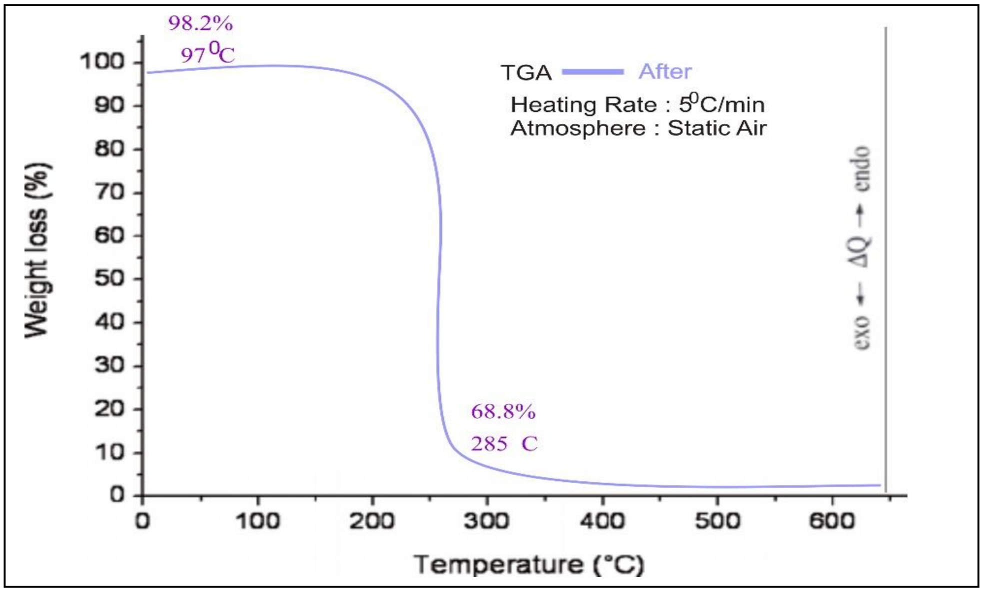


Fig 4b: TGA graph of Modified Palm Fruit Fiber after practical

3.2 Batch Biodegradation Studies of the Operating Variables on the Modified Palm Fruit Fiber

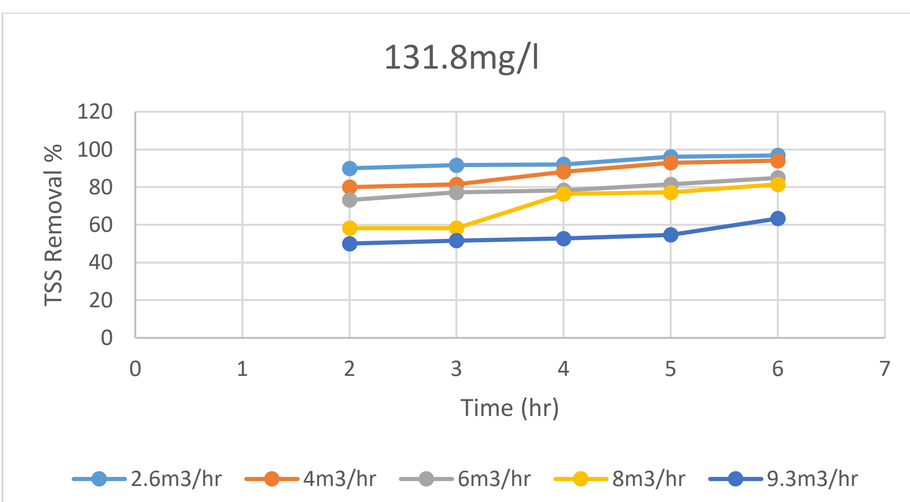
3.2.1 Effect of Combination of Flow rate and Contact time on TSS, TDS and BOD Removal Efficiency

Flow rate has significant effect on percentage removal of TSS from simulated pharmaceutical wastewater treatment. As such, the effect of combination of flow rate and contact time on performance evaluation of a trickling filter system using modified palm fruit fiber for removal ciprofloxacin from simulated pharmaceutical wastewater was evaluated using five different flow rates which are 2.6m3/hr, 4m3/hr, 6m3/hr, 8m3/hr and 9.3m3/hr, at concentration of 131.8mg/l, 200mg/l, 300mgl, 400mg/l and 468mg/l. It could be seen from fig 5a that the highest percentage removal TSS from simulated pharmaceutical wastewater was obtained at flow rate of 2.6m3/hr and concentration of 131.8mg/l. The highest percentage removal of TSS with decrease in flow rate was due to particle agglomeration and filter media performance. Decreased flow rates ensured efficient mass transfer between the liquid phase (wastewater) and solid phase (modified palm fruit fiber) and stops breakthrough occurrence (41;42;43). Therefore, the percentage removal of TSS obtained at flow rate of 2.6m3/hr at concentration of 131.8mg/l was 99.7%.

The TDS removal of ciprofloxacin from simulated pharmaceutical wastewater was obtained at five different flow rates as showed below in the figure 5b. The flow rates of 2.6m3hr, 4m3hr, 6m3/hr, 8m3/hr and 9.3m3/hr were evaluated at concentration of 131.8mg/l, 200mg/l, 300mg/l, 400mg/l and 468mg/l. There was increase in TDS percentage removal at 2.6m3/hr and concentration of 131.8mg/l. There was increase in TDS percentage removal as flow rates decreases because it allowed for longer contact times between the water and treatment media, potentially enhancing the removal efficiency of TDS from simulated pharmaceutical wastewater by

development and characterization of modified palm fruit fiber (44; 45). Increased flow rates reduced the efficiency of TDS removal due to shorter contact time between the wastewater and treatment median (modified PFF). However, excessively low flow rates might lead to issues such as increased residence time in the treatment system, which could promote bacterial growth or other undesirable reactions (46). Therefore, TDS percentage removal from simulated pharmaceutical wastewater using modified palm fruit fiber at 2.6m3/hr and concentration of 131.8mg/l was 58.7%.

Figure 5c below showed BOD percentage efficiency of ciprofloxacin by application of modified palm fruit fiber (PFF) obtained at optimum flow rates of 2.6m3/hr, 4m3/hr, 6m3/hr, and at concentrations of 131.8mg/l, From the figure, it was observed that there was increase in BOD percentage efficiency as the flow rate decreases during the biodegradation because slower flow rates can allow contact times between the water and treatment media, which enhances the biological degradation of ciprofloxacin and associated organic matter contributing to BOD. Increase flow rates could reduce the efficiency of biological processes due to shorter contact times between the wastewater and microorganisms which could result to lower BOD percentage efficiency as microorganisms have less time to metabolize organic matter, including ciprofloxacin (47; 48; 49). Therefore, the BOD percentage efficiency of ciprofloxacin is 51%.



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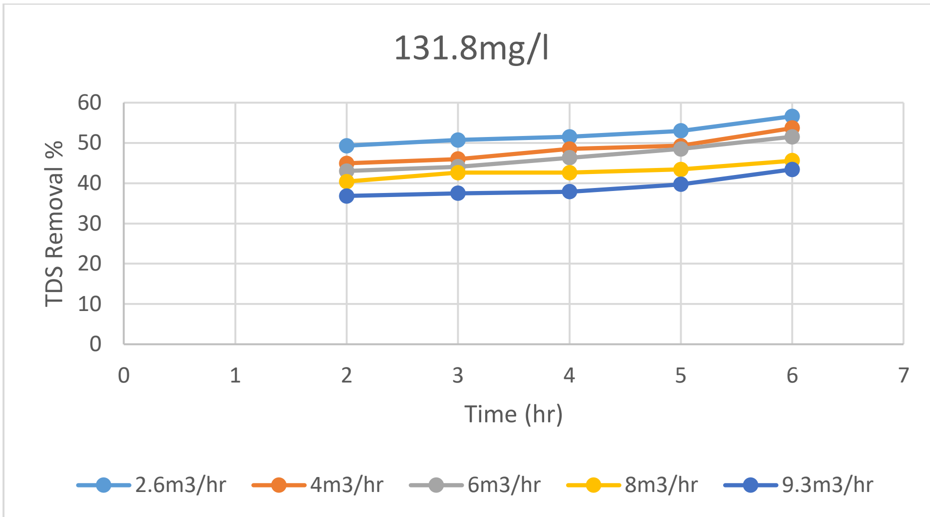

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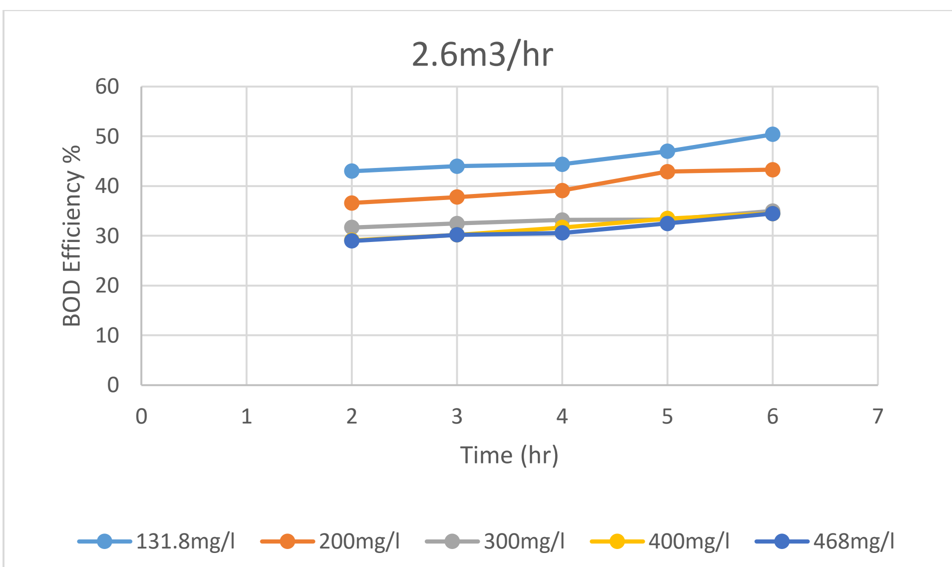

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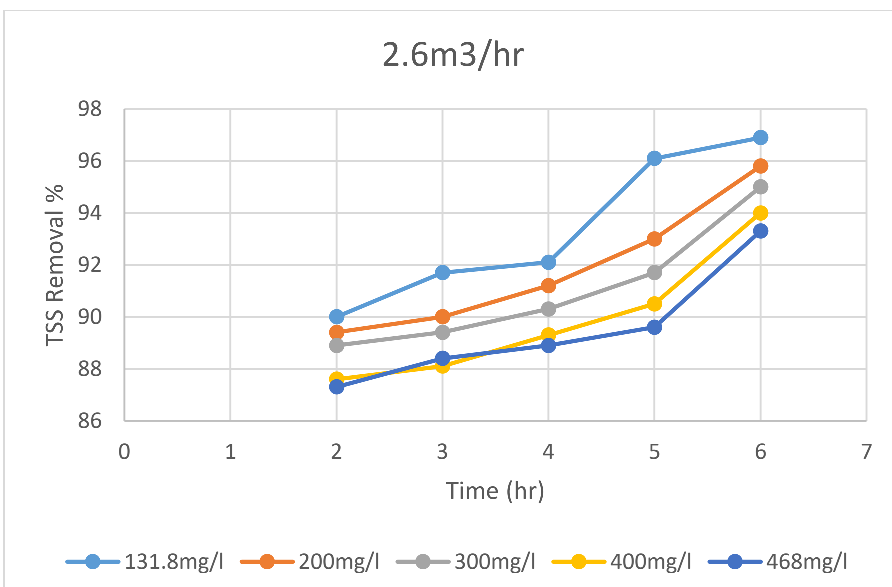
Fig 5: Effect of combination of flow rate and contact time on TSS, TDS and BOD removal efficiency from simulated ciprofloxacin pharmaceutical wastewater using modified palm fruit fiber

3.2.2 Effect of combination of concentration and contact time on TSS, TDS and BOD Removal Efficiency

Figure 6a below showed the TSS percentage removal by performance evaluation of a trickling filter system using modified palm fruit fiber for removal ciprofloxacin from simulated pharmaceutical wastewater at different concentration of 131.8mg/l, 200mg/l, 300mg/l, 400mg/l and 468mg/l and contact time of 2.6hr, 4hr, 6hr, 8hr and 9.3hr using five different flow rates of 2.6m3/hr, 4m3/hr, 6m3/hr, 8m3/hr and 9.3m3/hr. From the figure 6a below, it could be observed that TSS percentage removal increases as the concentration of simulated pharmaceutical wastewater decreases at flow rates of 2.6m3/hr and concentration of 131.8mg/l respectively because there was less quantity of ciprofloxacin to be removed. Generally, high concentrations of ciprofloxacin could lead to reduced removal efficiency due to saturation of treatment mechanisms or competition with other contaminants for biodegradation sites (50). Therefore, TSS percentage removal is higher at 131.8mg/l which was 97%.

The effect of concentration on the removal of TDS by performance evaluation of a trickling filter system using modified palm fruit fiber for removal ciprofloxacin from simulated pharmaceutical wastewater was evaluated using five different concentrations at different flow rates. The concentrations were 131.8mg/l, 200mg/l, 300mg/l, 400mg/l and 468mg/l at flow rates of 2.6m3/hr, 4m3/hr, 6m3/hr, 8m3/hr and 9.3m3/hr are presented at figure 6b below. There was increase in TDS percentage removal from simulated pharmaceutical wastewater as the concentration decreases due less competition for reactive sites or biodegradation sites on treatment media (51). Higher concentration of TDS might lead to increased competition for reactive sites or complexation with other ions in the water, which could affect the mechanisms involved in TDS removal (52; 53). Therefore, the TDS percentage removal simulated pharmaceutical wastewater was 58.7% at concentration of 131.8mg/l under flow rate of 2.6m3/hr.

The effect of concentration on BOD percentage removal of ciprofloxacin during biodegradation process were evaluated using optimum concentration of 131.8mg/l and optimum flow rate of 2.6m3/hr, 4m3/hr, 6m3/hr.. Figure 6c below showed the effect of concentration in the BOD efficiency of ciprofloxacin by application of modified palm fruit fiber using trickling filter system. It could be seen from fig 10 that the highest BOD efficiency of ciprofloxacin was obtained at concentration of 131.8mg/l in each of the three flow rate. There was increase in BOD percentage removal as the concentration of ciprofloxacin decreases due to lower concentrations of ciprofloxacin in water could lead to lower levels of organic matter, which may contribute to decreased BOD. That lower organic load can potentially overwhelm biological treatment systems, increasing the percentage of BOD efficiency (54; 55; 56).



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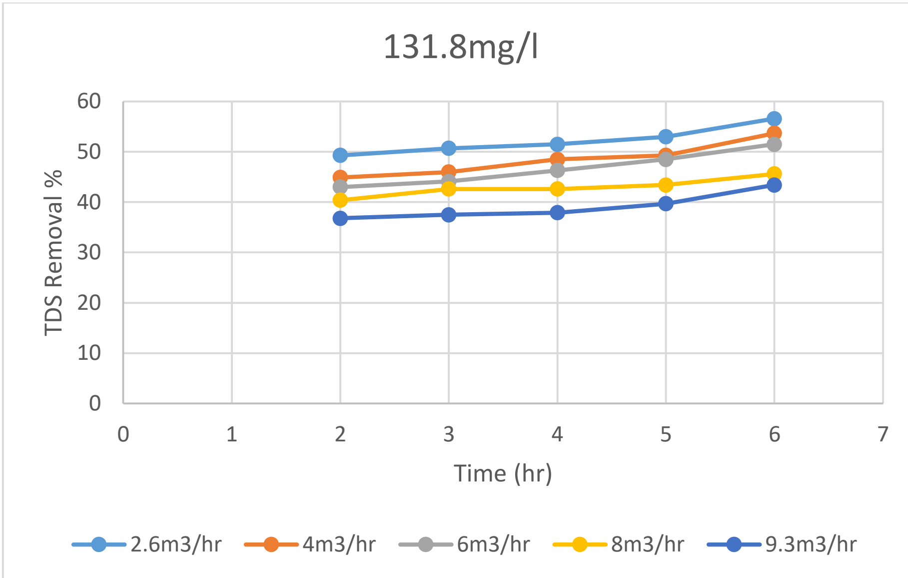

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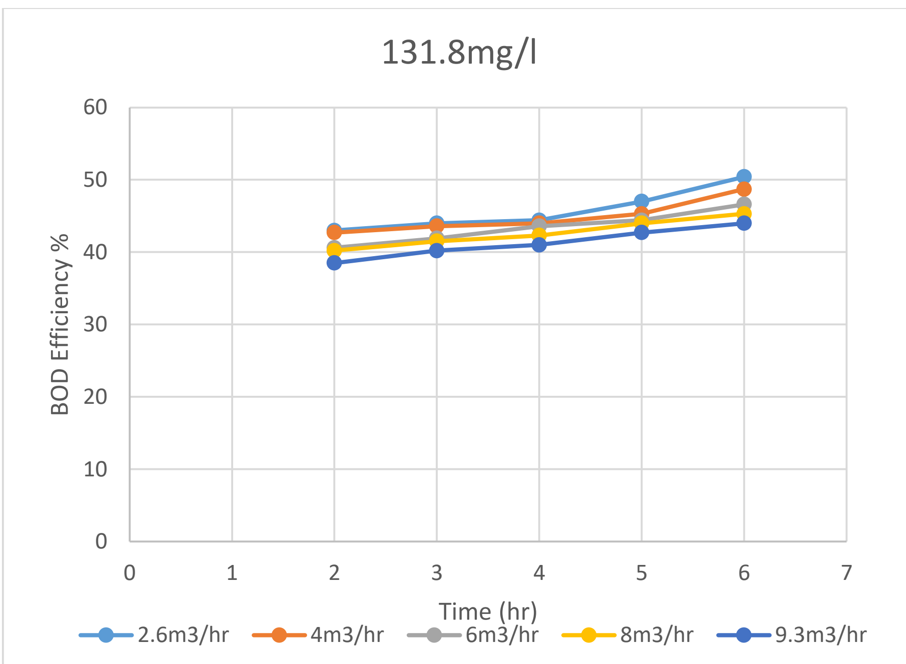

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Fig 6: Effect of combination of concentration and contact time on TSS, TDS and BOD removal efficiency from simulated ciprofloxacin pharmaceutical wastewater using modified palm fruit fiber

3.3 Ciprofloxacin Removal Efficiency

The system achieved an average ciprofloxacin removal efficiency of 97% over a 20-day operational period. The removal mechanism was attributed to a combination of adsorption onto the modified palm fruit fiber and biodegradation by attached biofilms. The results were consistent with the studies utilizing activated carbon, which reported removal efficiencies between 80% and 90% (57).

3.4 Removal of TSS, TDS and BOD

The trickling filter also demonstrated effective removal of organic and particulate matter:

- ✓ **TSS: 96%**
- ✓ **TDS:66%**
- ✓ **BOD:50.4%**

The high removal rates were attributed to the synergy between biofilm activity and the adsorption properties of modified palm fruit fiber.

3.5 Biodegradation Isotherm

Equilibrium adsorption isotherm was very useful for the analysis and design of adsorption systems. The equilibrium adsorption experiments were carried out by batch process for different simulated pharmaceutical wastewater concentrations (131.8-468mg/l) at flow rates of 2.6m3/hr, 4m3/hr and 6m3/hr. The adsorption experimental data were plotted for linear isotherm models as showed in figure 11-16 and various isotherm constants were calculated as shown in table 2a-b. The equilibrium adsorption data were analyzed by Langmuir and Freundlich isotherm models. The correlation coefficient determination (R^2) showed that the obtained equilibrium data for the optimum flow rate were better fitted to Langmuir isotherm model than the Freundlich isotherm model. The maximum adsorption values calculated from the Langmuir isotherm model were 2.693, 1.227 and 1.297mg/g at

2.6m3/hr, 4m3/hr and 6m3/hr and at concentrations of 131.8mg/l, 200mg/l and 300mg/l respectively. The essential factor (RL) values were in the range of 0.354, 0.611 and 0.367 at the flow rate of 2.6-6m3/hr and at the concentration of 131.8-300mg/l. The values of 0<RL<1 indicated that the development and characterization of modified palm fruit fiber for simulated pharmaceutical of wastewater treatment was favourable at all flow rates. Biodegradation data fit well with Langmuir isotherm, indicating monolayer adsorption with higher coefficient determination (R^2) value of 0.9998.

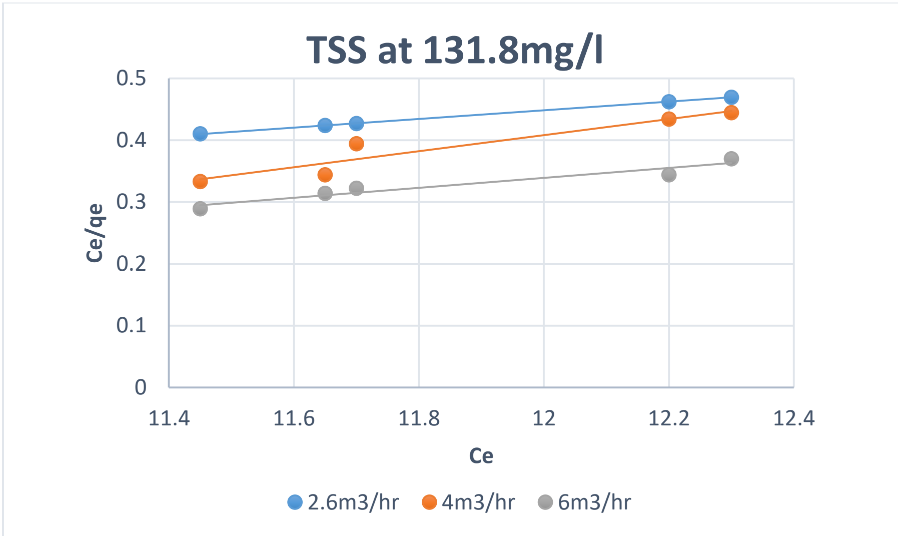
Table 2a: Langmuir isotherm parameters of TSS and TDS and BOD removal from simulated pharmaceutical wastewater at optimum flow rates

Response isotherm	Parameters	Flow rate (m3/hrs)	2.6m3/hrs	4m3/hrs	6m3/hrs
TSS Langmuir	qmax (mg/g)		2.575	0.866	1.611
	KL(l/g)		0.027	0.150	0.050
	RL		0.593	0.207	0.440
	R^2		0.9998	0.9015	0.9288
TDS Langmuir	qmax (mg/g)		9.804	10.493	7.199
	KL (l/g)		0.0009	0.0008	0.0013
	RL		0.904	0.914	0.867
	R^2		0.9998	0.9818	0.9716

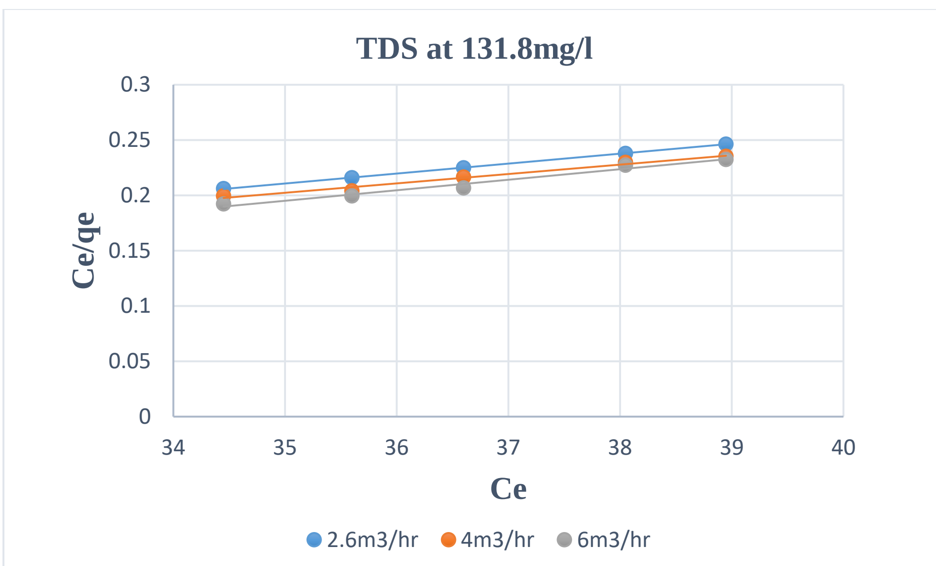
BOD Langmuir	**qmax (mg/g)**		**21.505**	**243.902**	**454.545**
	KL (l/g)		**0.0003**	**0.00002**	**0.00001**
	RL		**0.966**	**0.998**	**0.999**
	R^2		**0.9999**	**0.9798**	**0.9024**

Table 2b: Freundlich isotherm parameters of TSS, TDS and BOD removal from simulated pharmaceutical wastewater at optimum flow rates

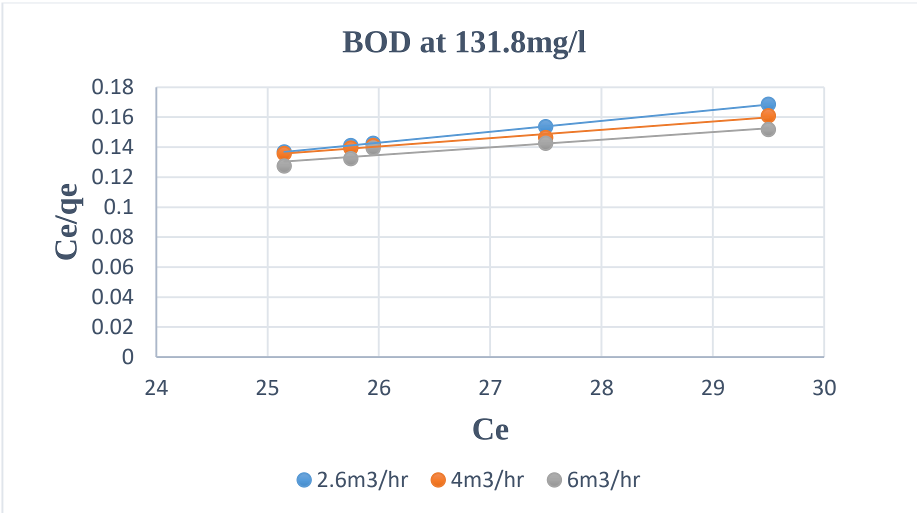
Response isotherm	**Parameters**	**Flow rates (m3/hrs)**	**2.6m3/hrs**	**4m3/hrs**	**6m3/hrs**
TSS Freundlich	**Kf (l/g)**		**239.22**	**2118.85**	**522.40**
	1/n		**-0.881**	**-1.741**	**-1.148**
	R^2		**0.9998**	**0.8969**	**0.9298**
TDS Freundlich	**Kf (l/g)**		**826.04**	**787.77**	**970.73**
	1/n		**-0.4513**	**-0.4346**	**-0.4904**
	R^2		**0.9994**	**0.9805**	**0.9742**
BOD Freundlich	**Kf (l/g)**		**491.02**	**391.02**	**375.23**
	1/n		**-0.3047**	**-0.2336**	**-0.2182**
	R^2		**0.9993**	**0.9764**	**0.9058**


TSS at 131.8mg/l
Ce/qe
0.5
0.4
0.3
0.2
0.1
0
11.4
11.6
11.8
12
12.2
12.4
Ce
2.6m3/hr
4m3/hr
6m3/hr

a

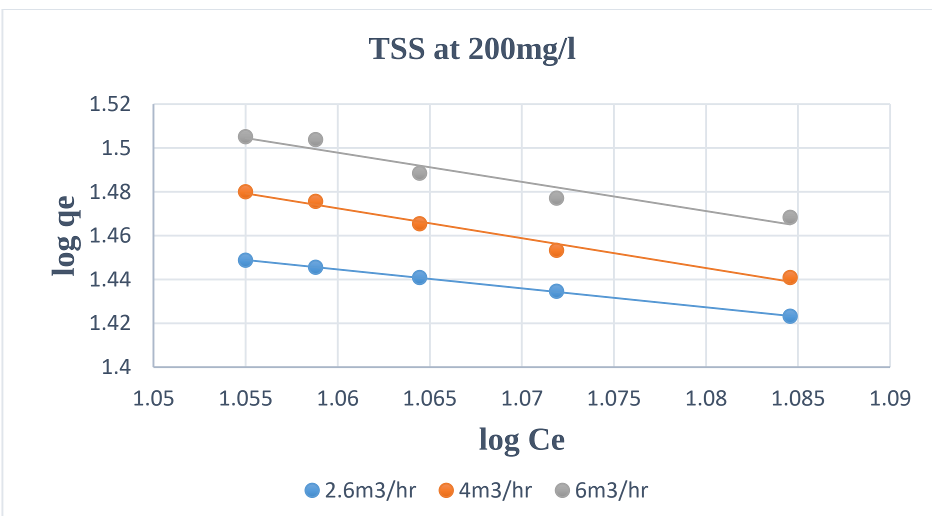

TDS at 131.8mg/l
Ce/qe
0.3
0.25
0.2
0.15
0.1
0.05
0
34
35
36
37
38
39
40
Ce
2.6m3/hr
4m3/hr
6m3/hr

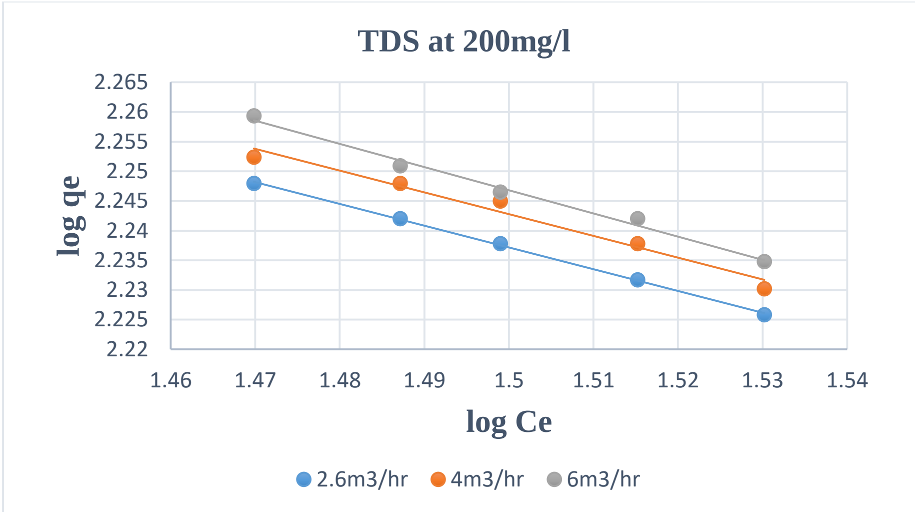
b



c

Fig 7: Langmuir biodegradation isotherm of simulated pharmaceutical wastewater for TSS, TDS and BOD percentage removal





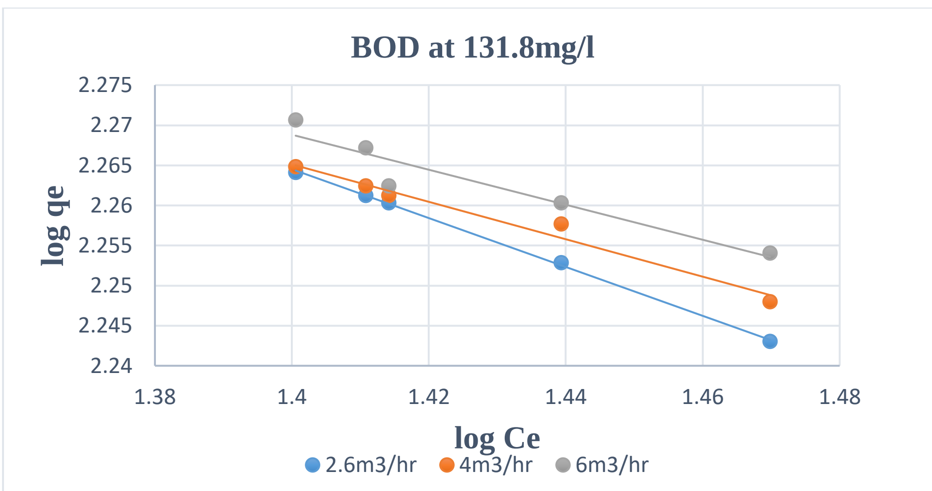


Fig 8: Freundlich biodegradation isotherm of simulated pharmaceutical wastewater for TSS, TDS and BOD percentage removal

3.6 Biodegradation kinetics Studies

The kinetic data were collected experimentally by passing different concentrations(131.8-468mg/l) of simulated pharmaceutical wastewater on modified palm fruit fiber at different contact time (2.6-9.3hr), at optimum flow rates (2.6-

6m3/hr) to evaluate the percentage removal of TSS and TDS from simulated pharmaceutical wastewater. To investigate the kinetic models, pseudo-first order, pseudo-second order, intra particle diffusion and elovich kinetic models were used. The kinetic parameters and correlation coefficient determination R^2 were listed in table 3a-3b as extracted from the kinetic plot in figure 9-12. The pseudo-second order model fitted the data with correlation coefficient (R^2) values of 0.9989, 0.9976, 0.9964 for TSS removal. 0.9988, 0.9988, 0.9972 for TDS removal and 0.8651, 0.8189, 0.9652 for BOD removal.

Table 3a: TSS Biodegradation Kinetic Parameters of Treatment of Simulated Pharmaceutical Wastewater on Modified Palm Fruit Fiber at Conc. Of 131.8mg/l and at optimum Flow rates of 2.6m3/hr, 4m3/hr and 6m3/hr

	131.8mg/l		
TSS Pseudo-first-order model	2.6m3/hr	4m3/hr	6m3/hr
Qt	3.23	8.97	1.06
K1	-0.000046	-0.00014	-0.00009
R^2	0.9349	0.9756	0.957
TSS Pseudo-second-order model			
Qt	0.0003	0.0001	0.00009
K2	0.00037	0.00011	0.000095
R^2	0.9989	0.9976	0.9964
TSS Intraparticle Diffusion model			

Qt	**0.45**	**0.42**	**1.08**
Kdiff	**0.0023**	**0.0016**	**0.0038**
R^2	**0.9756**	**0.957**	**0.8941**
Elovich kinetic model			
Qt	**0.0796**	**0.0684**	**0.0691**
A	**0.043**	**0.03**	**0.0291**
R^2	**0.8699**	**0.9532**	**0.9278**

Table 3b: TDS Biodegradation Kinetic Parameters of Treatment of Simulated Pharmaceutical Wastewater on Modified Palm Fruit Fiber at Conc. of 131.8mg/l and at optimum Flow rates of 2.6m3/hr, 4m3/hr and 6m3/hr

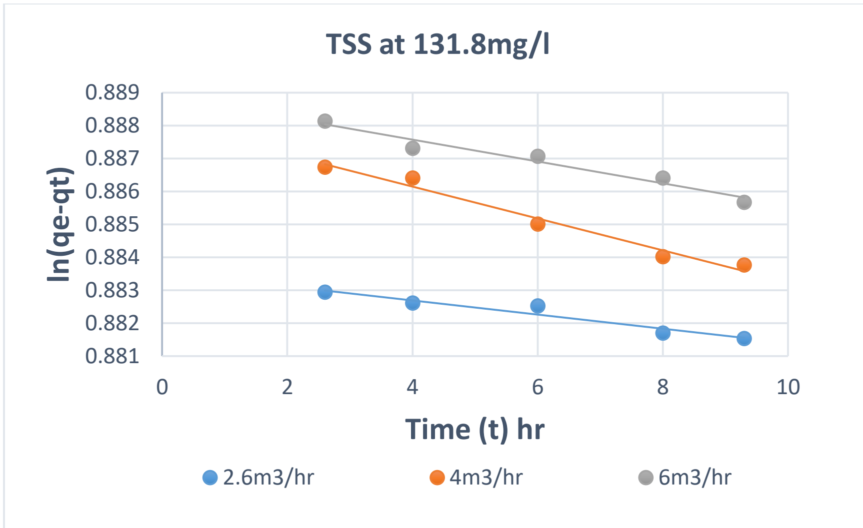
	131.8mg/l		
TDS Pseudo-first-order model	**2.6m3/hr**	**4m3/hr**	**6m3/hr**
Qt	**2.21**	**2.93**	**3.39**
K1	**-0.000115**	**-0.000115**	**-0.000115**
R^2	**0.9875**	**0.9575**	**0.9623**
TDS Pseudo-second-order model			
Qt	**0.051**	**0.055**	**0.054**

K1	**0.0076**	**0.0068**	**0.0058**
R^2	**0.9988**	**0.9988**	**0.9972**
TDS Intraparticle Diffusion model			
Qt	**1.067**	**1.375**	**1.741**
Kdiff	**0.0052**	**0.0052**	**0.0058**
R^2	**0.9958**	**0.9923**	**0.9725**
Elovich kinetic model			
Qt	**0.2355**	**0.2631**	**0.2711**
A	**0.1238**	**0.1201**	**0.1149**
R^2	**0.9673**	**0.9504**	**0.9155**

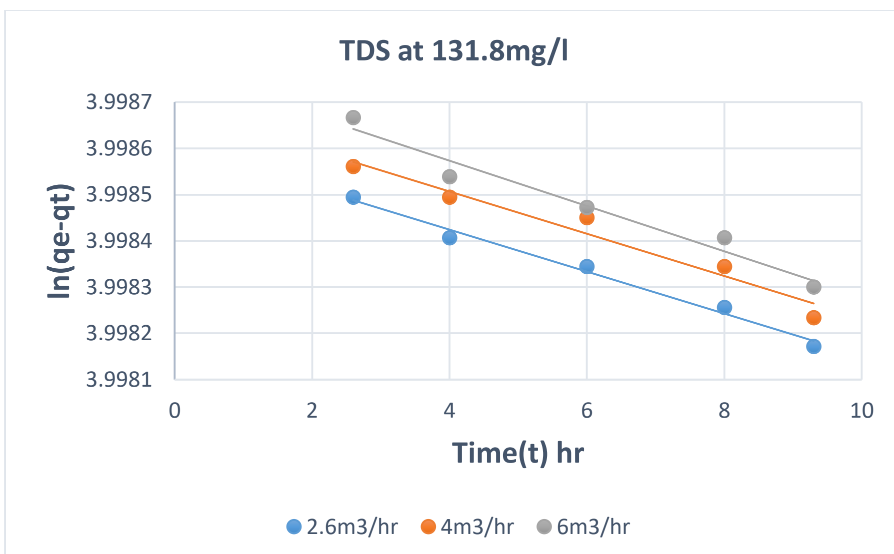
Table 3c: BOD Linear Kinetic Parameters for the removal of Ciprofloxacin from Simulated CIP Pharmaceutical Wastewater by Application of Modified Palm Fruit Fiber at 131.8mg/l, 200mg/l and 300mg/l

	131.8mg/l		
BOD Pseudo-first order	**2.6m3/hr**	**4m3/hr**	**6m3/hr**
Qt	**1.184**	**1.570**	**1.373**
K1	**-0.00016**	**-0.000115**	**-0.000115**

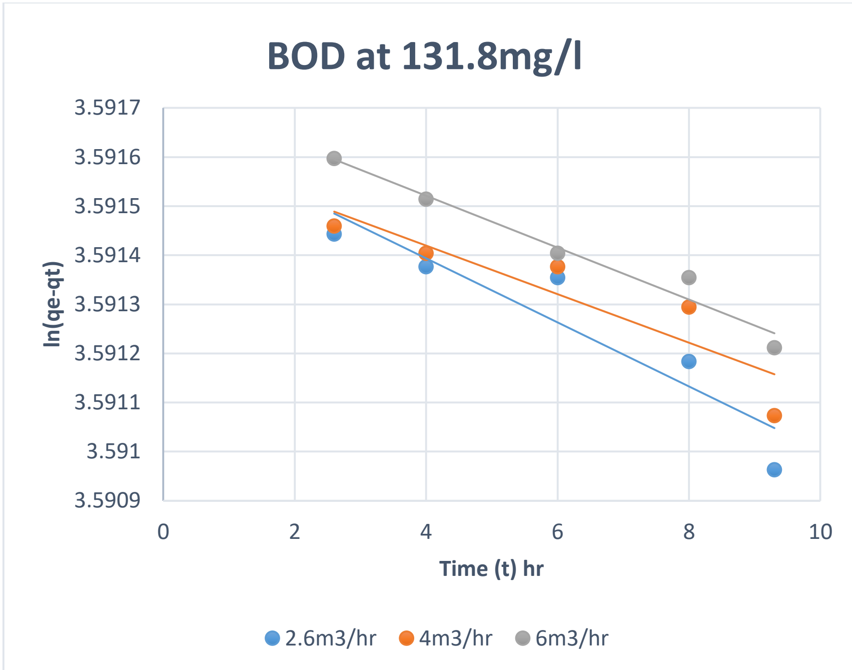
R^2	**0.8651**	**0.8189**	**0.9652**
BOD Pseudo-second order			
Qt	**0.012**	**0.015**	**0.015**
K2	**0.0023**	**0.0026**	**0.0024**
R^2	**0.9894**	**0.9918**	**0.9973**
BOD Intra particle diffusion			
Qt	**0.939**	**0.958**	**1.150**
Kdiff	**0.0047**	**0.0036**	**0.0038**
R^2	**0.8651**	**0.8189**	**0.9652**
Elovich kinetic model			
Qt	**0.168**	**0.196**	**0.199**
A	**0.087**	**0.09**	**0.085**
R^2	**0.7536**	**0.712**	**0.9302**


TSS at 131.8mg/l
ln(qe-qt)
0.889
0.888
0.887
0.886
0.885
0.884
0.883
0.882
0.881
0
2
4
6
8
10
Time (t) hr
2.6m3/hr
4m3/hr
6m3/hr

(a)

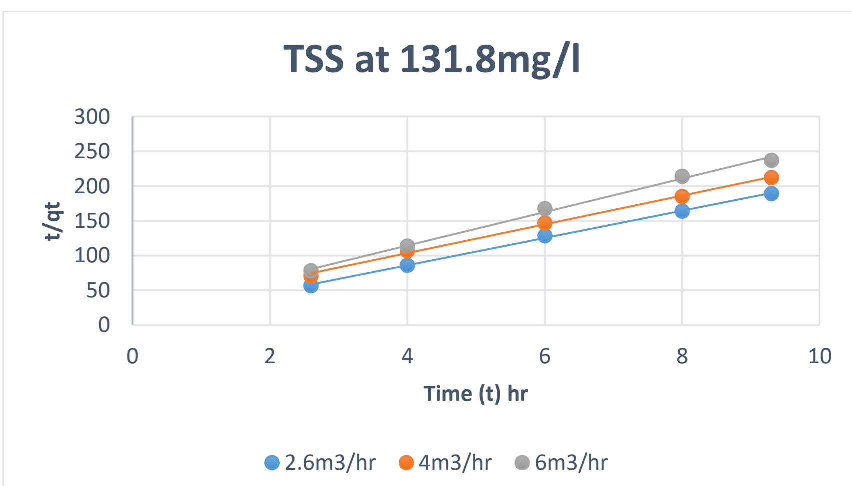

TDS at 131.8mg/l
ln(qe-qt)
3.9987
3.9986
3.9985
3.9984
3.9983
3.9982
3.9981
0
2
4
6
8
10
Time(t) hr
2.6m3/hr
4m3/hr
6m3/hr

(b)

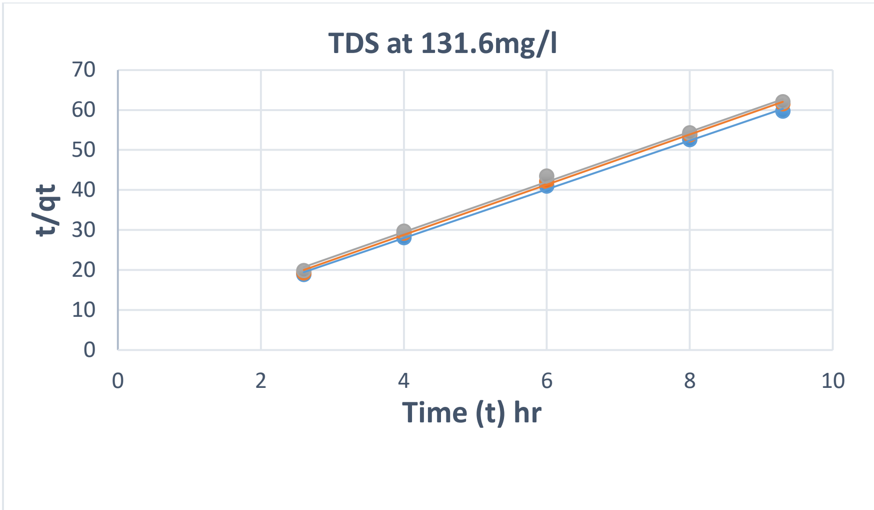


c

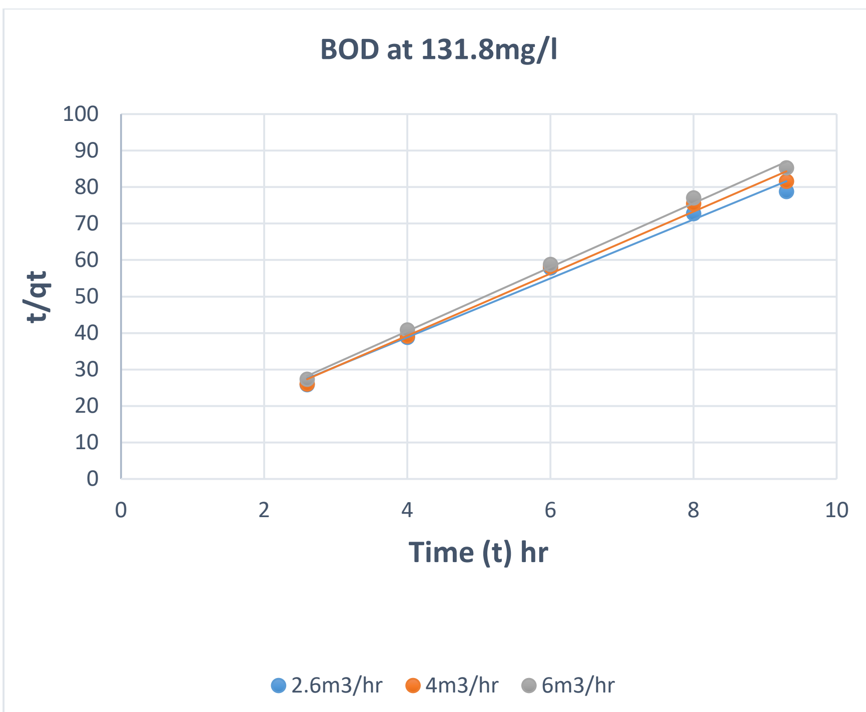
Fig 9 (a-c) TSS and TDS Biodegradation Pseudo-first order Kinetic Model of Treatment of Simulated Pharmaceutical Wastewater on Modified Palm Fruit Fiber at optimum Flow rates.



(a)

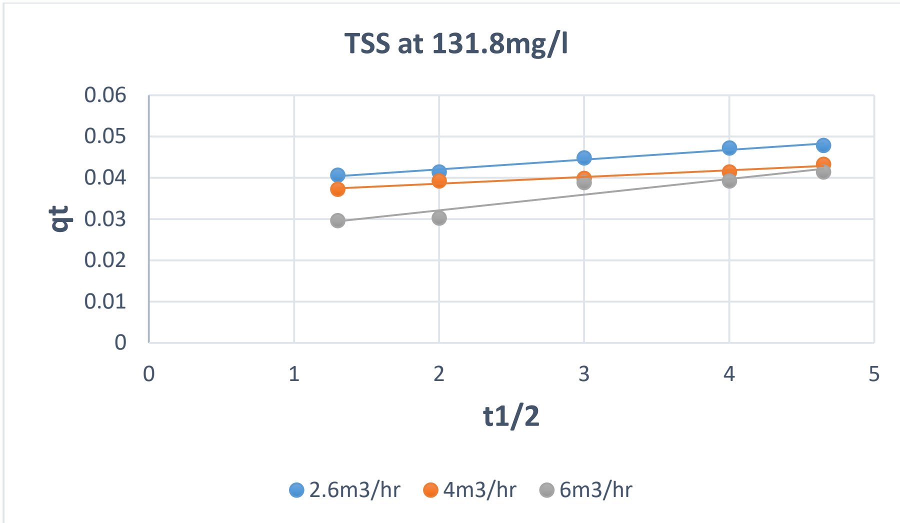


(b)

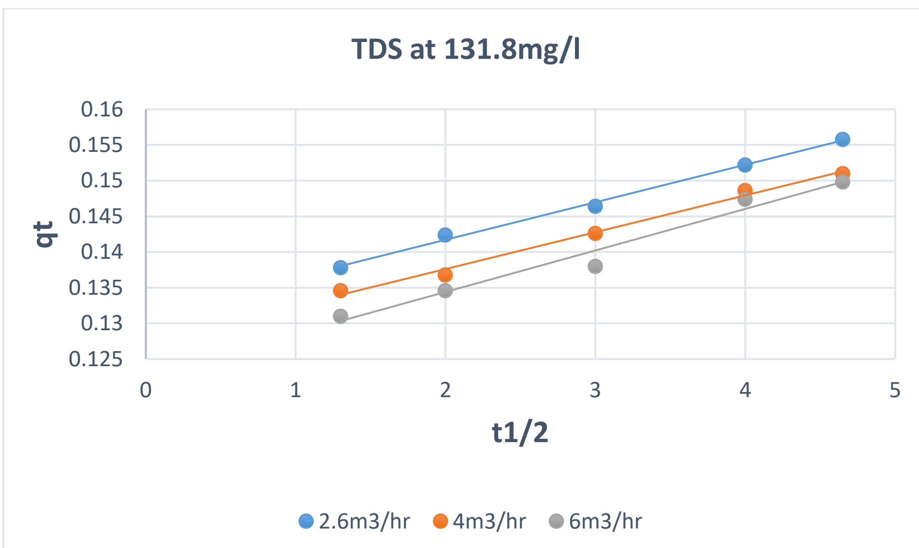


(c)

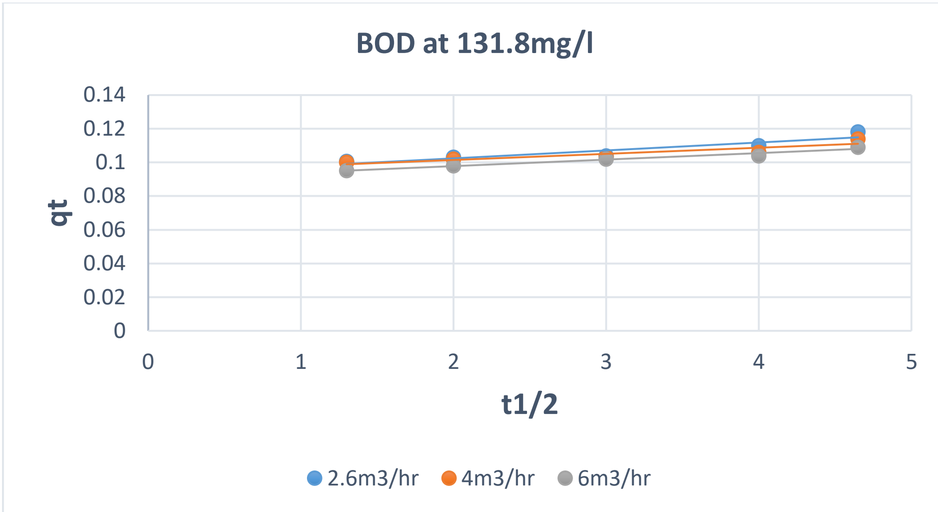
Fig 10 (a-b) TSS, TDS and BOD Biodegradation Pseudo-second order Kinetic Model of Treatment of Simulated Pharmaceutical Wastewater on Modified Palm Fruit Fiber at optimum Flow rates


TSS at 131.8mg/l
0.06
0.05
0.04
0.03
0.02
0.01
0
qt
0
1
2
3
4
5
t1/2
2.6m3/hr
4m3/hr
6m3/hr

a

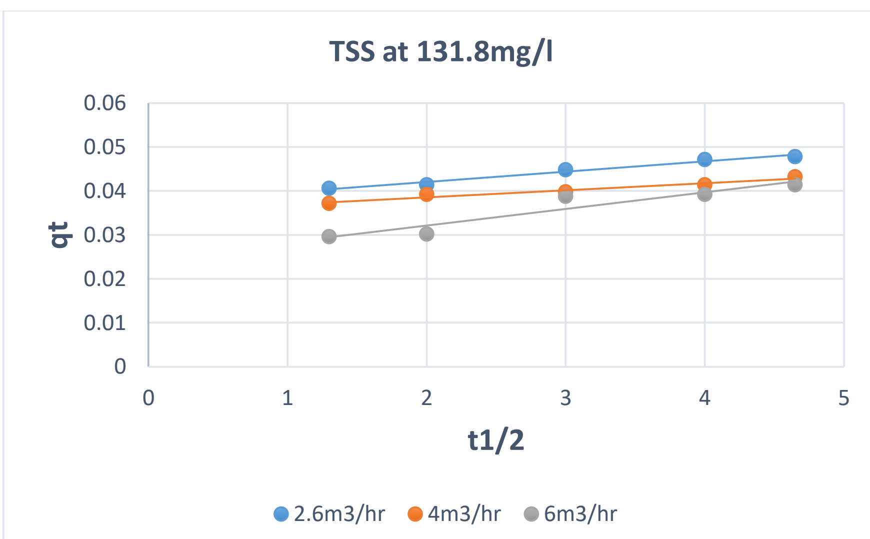

TDS at 131.8mg/l
0.16
0.155
0.15
0.145
0.14
0.135
0.13
0.125
qt
0
1
2
3
4
5
t1/2
2.6m3/hr
4m3/hr
6m3/hr

b

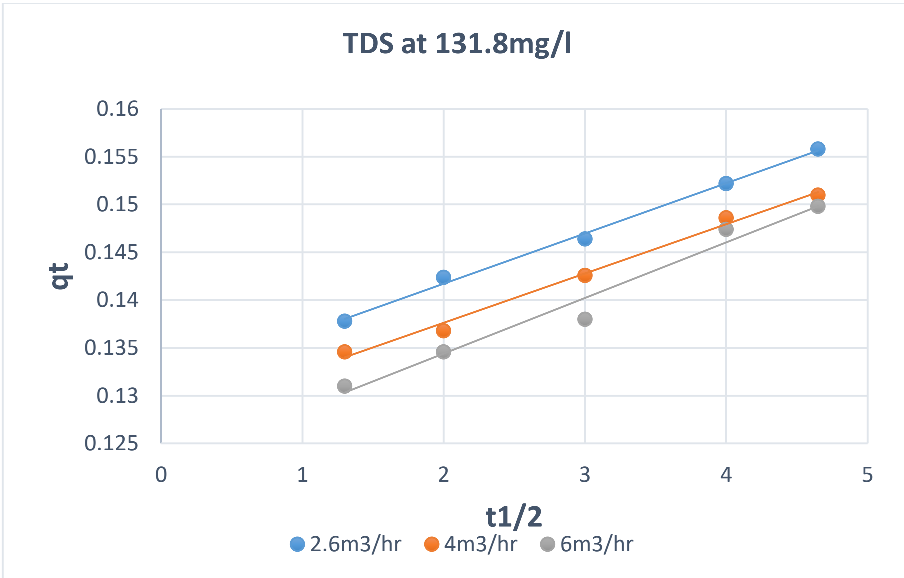


c

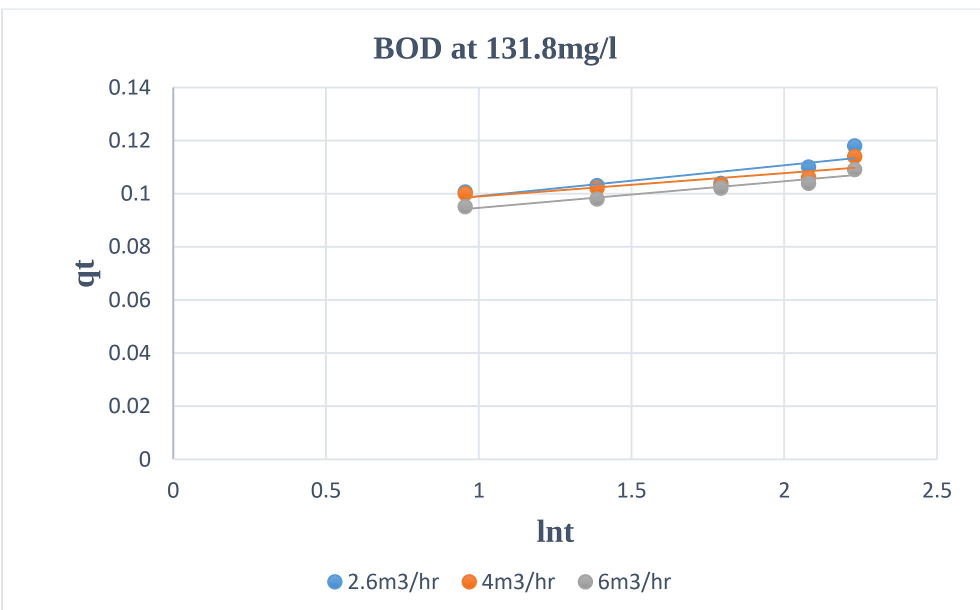
Fig 11 (a-c) TSS, TDS and BOD Biodegradation Intra particle Diffussion Kinetic Model of Treatment of Simulated Pharmaceutical Wastewater on Modified Palm Fruit Fiber at optimum Flow rates



(a)



b



c

Fig 12 (a-c) TSS, TDS and BOD Biodegradation Elovich Kinetic Model of Treatment of Simulated Pharmaceutical Wastewater on Modified Palm Fruit Fiber at optimum Flow rates

3.7 Comparison with Synthetic Media

Modified palm fruit fiber showed comparable pollutant removal efficiency to synthetic media, with the added advantages of biodegradation, lower cost, and reduced environmental impact. That makes it a sustainable alternative for regions with abundant palm fruit fiber waste.

4. CONCLUSION

The study demonstrates the potential of modified palm fruit fiber as a cost-effective and sustainable packing materials for the removal of ciprofloxacin in trickling filter systems. The system showed high removal efficiencies for CIP, TSS and TDS and slight lower of BOD, suggesting its viability for treating pharmaceutical-laden wastewater. Future studies should focus on scaling up the system and investigating the long-term stability of modified palm fruit fiber.

DISCLAIMER

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COMPETING INTERESTS DISCLAIMER:
Authors have declared that they have no known competing financial interests OR non-financial interests OR personal relationships that could have appeared to influence the work reported in this paper.

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