



## Empirical models of kinetic rate for river treatment analysis of cellulosic materials



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### ABSTRACT

The utilisation of cellulosic fibre in removing organic and nutrients pollutants in polluted river is becoming an increasingly popular alternative cost-effective and sustainable option. However, the related empirical models are yet to be fully comprehensive to study the adsorption mechanisms of natural adsorbents. This paper discusses developed empirical model used to estimate the mass transfer of organic pollutants into two natural fibres – coconut fibres and oil palm fibres to filter pollutant molecules in water. An empirical model was developed to estimate the mass transfer of organic pollutants in water onto the fibres in a fabricated physical model. The mass transfer relations were derived based on the substrates loading rates and the predicted accumulation rates of substrates in fibres along with the percentage of outflows. Matching empirical results with experimental results showed that the modified model was able to accurately predict the mass transfer rate. The higher adsorption rate of CF (91.02% COD) depicted greater global mass transfer rate ( $1.3696 \text{ d}^{-1}$ ) than OPF (82.35% COD) which only had  $1.2768 \text{ d}^{-1}$  of global mass transfer rate in 3% of COD outflow. The contribution of internal diffusion mechanism was significant due to the physical (porosity) and chemical (lignin and cellulosic content) characteristics of both CF and OPF. The study concluded that the performance of biological adsorption using CF and OPF is promising.

### 1. Introduction

River has been the source of life since billions of years ago. Early human civilization had mainly flourished at riverbanks, such as Egypt's Nile River, Indus River valley, and along major rivers in China. River forms a vital part of our ecosystem, providing food and shelter to many organisms, not to forget a mean of transportation for human [1]. In order to preserve its sustainability, it is important that river water bodies and riparian zones are maintained clean so that the delicate life balance is not disrupted. Ironically, as human civilization progresses by leaps and bounds throughout history, we are also stressing our river bodies through the tremendous amount of wastes generated. Many of these wastes are disposed irresponsibly into our river systems, overloading the rivers with excessive amount of nutrients that has resulted in harmful algal blooms, dead zones and fish killed [2].

The worsening pollution, fortunately, has also triggered vast amount of research being conducted on water treatment technologies and materials. However, the application of the water and wastewater treatment materials like alum, polymer flocculants, ferric chloride, and coal-prepared activated carbon remains a major challenge for the industry and agricultural sectors due to the high cost involved and the scarcity of equipment [3]. In order to reduce the treatment cost, efforts are now poured into exploring new and novel adsorbents. A notable example is the recycling of readily available agricultural and industrial by-products. These include fly ash bagasse [4], walnut shell [5], waste tires [6], and rice husk [7].

In this regard, coconut fibre (CF) and oil palm fibre (OPF) are natural residual products abundantly available as by-products from the agricultural industry, especially in Malaysia [8,9]. According to the Food and Agriculture Organization of the United Nations (FAU) in year

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**Nomenclature**

$C_o$	Initial concentration of organic pollutant (mg/L)
$C_t$	Concentration of organic pollutant in a day (mg/L)
$k_{BA}$	Adams-Bohart model's constant (L/mg d)
$N_o$	Sorption capacity (mg/L)
$v$	Linear flow velocity of water (m/d)
$H$	Bed depth (m)
$q_t$	Amount of adsorbed adsorbate into adsorbent at time (mg/g)
$Q$	Flow rate of water (L/s)

$\rho$	Density of adsorbents (g/L)
$q_{t \text{ acc}}$	Accumulation of organic pollutant adsorbed per mass of cellulosic fibres (CF and OPF) (g/g)
$k_f$	Film mass transfer factor or external mass transfer factor ( $d^{-1}$ )
$k_g$	Global mass transfer ( $d^{-1}$ )
$\beta$	Elovich coefficient of desorption constant (g/mg)
$k_d$	Porous diffusion factor or internal mass transfer factor ( $d^{-1}$ )
VLR	Volumetric loading rate (mg/Ls)

2013, the worldwide annual production of CF is approximately 650,000 t. This is mainly from India, Sri Lanka, Thailand, Indonesia, Malaysia, Vietnam, and the Philippines. In terms of OPF, approximately 29,091,000 t is being generated as waste annually in Malaysia [9]. The waste amounts are continuously increasing, but its utilization is marginal and yet to be fully tapped [10]. In fact, lignin and cellulose properties of coconut fibre are actively involved in chemical bonding and responsible for typical cation exchange characteristics [11]. It was discovered from previous findings that CF and OPF are expected in the direction of heavy metal ions, phenol and dye removal [12,13]. The examples of heavy metal ions and dyes removal using CF and OPF are such as chromium (VI), nickel (II), zinc (II), Copper (II), and Lead (II) ions [14–17]. While for the dyes and phenols that common been removed by CF and OPF are such as Methylene blue, Malachite green blue, Cationic methylene blue, Anionic phenol red, Methylene Blue, Acid orange 7, Methylene blue, and *p*-chlorophenol [18–21].

However, overall observations are less comprehensive for research studies on natural organic matter and nutrients pollutants adsorption from water bodies using CF and OPF. Most of the time they were used as a precursor for activated carbon in contaminated water [22–25]. In fact, the natural adsorption properties of fibres is needed to further investigate especially on organic matter and nutrients removal. In view of this, this paper aims to present a potential utilization of both CF and OPF to remove organic matters (OM) from river water.

Other than the adsorption capacity of fibres, the existing literature has shown that the establishment of an appropriate adsorption correlation is essential prior to the application of the fibres as water treatment medium; this is to give reliable prediction of related parameters and adsorbents behaviour under various experimental conditions [26]. A variety of mathematical models have been developed for this reason to determine and describe the equilibrium isotherm, the adsorption kinetic isotherm, and the column dynamic behaviour. All the mathematical models are quite different in nature. In fact, the models are

always constructed on the three basic consecutive steps that are external diffusion, internal diffusion and mass action [27]. However, most are restricted for activated carbon, chemical reaction kinetics and single solute applications only. The resistance of mass transfer during adsorption processes to remove pollutants from water using natural organic materials has by far been neglected. For example, pseudo-second-order rate equation was developed based on the chemical adsorption and not suitable to describe the physical organic pollutants adsorption by nonpolar adsorbents [28]. Therefore, it is significant to understand their boundary conditions and improve the current research on the adsorption kinetic modelling especially in organic pollutant adsorption by natural adsorbents.

With respect to this, this study had been conducted to focus on: (1) the physical and chemical characteristics of cellulosic fibres (CF and OPF); (2) its performance evaluation in treating OM from river water using a fabricated column model (FCM); and (3) the mass transfer resistance of OM through these fibres as predicted by a modified empirical model.

## 2. Methodology

### 2.1. Sampling location

The water sample was collected from a river located at one of the river catchments at Skudai, Johor Bahru, Malaysia. This river is severely polluted by domestic effluent discharged from four cells of oxidation ponds nearby. Other pollution sources include the discharge from residential and gardening areas and the surface runoff from rainy days. During the time of this study, fish kills and algal bloom have been observed even with the full operation of the waste stabilization pond nearby (see Fig. 1).



Fig. 1. Algal bloom and fish kills observed in river.

## 2.2. Material preparation

The major materials used in this study were the coconut fibres and the oil palm fibres, as shown in Fig. 2. The CF were industrial wastes generated from the process of separating the outer husk of coconuts (also called coconut coir) from the inner portion. On the other hand, the OPF refers to the empty fruit bunch from palm oil extraction.

The coconut fibres were pre-treated by physical washing and soaking in distilled water for 24 h. This was to remove water soluble residue and dust particles on the surface. The OPF were also washed, but with the aid of citrus lemon (lemon) before being soaked in distilled water to remove surface oil residue and dirt. Both fibres were then collected and dried. This procedure was repeated twice.

## 2.3. Physical and chemical characteristics of the adsorbents

Electron Probe Micro-Analysis (EPMA) was conducted to study the physical characteristics of both fibres in view that it is a standard technique for the analysis of porous textures. The EPMA machine operated at 5 kV under 500 times magnification (see Fig. 3 for setup). In order to obtain better results, caution was exercised during polishing and coating of samples with a layer of carbon to avoid sample damage and contamination.

The lignin, cellulose and hemicellulose content of both cellulosic fibres were determined according to the Association of Official Agricultural Chemists (AOAC) Official Method [29]. The tests carried out included the Acid Detergent Fibre (ADF) test, the Neutral Detergent Fibre (NDF) test and the Acid Detergent Lignin (ADL) test. Ash test was also conducted to identify the basic components of both CF and OPF.

## 2.4. Fabricated column model (FCM)

The Fabricated Column Model (FCM; patent number: 2013701675) used in this study consisted of a storage tank, two water pumps and three prefabricated cylindrical columns sufficient to contain both fibres. The polluted river water sample was collected and stored in a storage tank with an approximate volume of 0.2 m<sup>3</sup>. The adsorbents were then equally divided into three portions and installed in each of the three cylindrical columns measuring 51 mm in diameter. The water was consistently circulated using the defragmented pump for eight days, which was the total testing period for both CF (86 g) and OPF (60 g) respectively. Fig. 4 shows the concept and the design of the proposed system on site.

## 2.5. Data monitoring and analytical method

The river water quality was monitored and tested every day for seven consecutive days to gauge the adsorbents-to-adsorbates adsorption performance. The specific parameter gauged here is the chemical oxygen demand (COD) since it is more reliable, quicker and easier than the measurement of biological oxygen demand (BOD) and total organic carbon (TOC). The COD test conducted conformed to the Standard Method 5220D published by the American Public Health Association (APHA) Standard Methods procedure [30].

## 2.6. Empirical model development

The empirical model proposed in this study was modified from some existing models as summarized in Table 1. These include the Adams-Bohart model [31], the Wolborska model [32] and the Fulazzaky model [33]. This model was used describe the adsorption dynamics of fibres (CF and OPF) during OM removal.

Several assumptions and considerations were made on some factors while developing the empirical model. These included factors like driving force and affinity of adsorbate/adsorbent. It was also assumed that  $q_t = \ln q_t \text{ acc}$ , i.e., the accumulation of mass pollutants to CF and

OPF due to the circulation of water in FCM is pursuant to  $t = \ln t$ .

## 3. Result and discussion

### 3.1. Physical and chemical characteristics of the cellulosic fibres (CF and OPF)

The porosity and surface texture of both cellulosic fibres are shown in Fig. 5, which generally indicated the presence of small pores on the surface. These pores are normally covered with dust particles and contaminants, but the washing and soaking processes had clearly cleansed the pores. However, this did not affect the lignin and cellulose content in the cell walls.

From the results, both CF and OPF were characterized as having a rough and uneven surface. Principally, the shape of the pores affects the diffusion of pollutant molecules by the fibres (see Fig. 6) [34].

As shown in Fig. 6, the adsorption reaction of pollutant molecules is highly dependent on the presence of physical hindrances in the fibres. This refers to the pore width and architecture (which is sometimes called geometrical structure) of the fibres [35,36]. Essentially, high surface area and high porosity positively contribute to the adsorption performance during OM removal, though these are not the only affecting factors [37]. Alternatively, the surface area of CF and OPF have also been carried out as OPF is 5.63 m<sup>2</sup>/g and CF is 2.68 m<sup>2</sup>/g [38]. Another factor is the elemental composition of fibres (CF and OPF); this was investigated through chemical composition tests for both fibres (see Table 2 for results).

From Table 2, it can be seen that CF exhibited slightly higher lignin (5.19%) and cellulose (6.05%) content compared to OPF. Based on existing literature, the lignin content in CF and OPF may vary from 21.2% to 59.4% and 32.65% to 43.75%, respectively. Furthermore, the cellulose content for both fibres may differ from 11% to 65%. The differences are attributed to the species, the organs, the climate conditions and the harvest stages [39–42]. The lignocellulose matrix of both fibres also plays an essential role in biomass binding in which the existing polar functional groups such as carboxyl groups (–COOH) and phenolic hydroxyl groups (–OH) are vital chemical bonding agents [43]. High lignin and cellulose content in plant fibre results in a tougher and stiffer fibre composition which cannot be easily degraded by microbial action, but it also makes it an interesting adsorbent for pollutant adsorption [44,45]. As such, this significant and positive feature had been further analysed for the decomposition of OM via mass transfer analysis.



Fig. 2. The coconut fibres (CF, on the right) and oil palm fibres (OPF, on the left) used.



Fig. 3. Overview of the EPMA setup.

3.2. Treatment effect on OM using CF and OPF

The chemical oxygen demand of river water is linked to biological oxygen demand when identifying the total amount of oxygen needed for all organic compounds to oxidize completely [46]. In this study, the COD was taken as the main indicator of the efficiency of cellulosic fibres (CF and OPF) in filtering the OM; the results are as shown in Fig. 7. The authors are aware that TOC results as a better alternative to present the complete oxidization of organics compound. As of that, it has been carried out and is currently under the consideration for publication in another manuscript.

From Fig. 7, an exceptionally high adsorption rate of both fibres is observed within the first two days of the experiment. Within seven days of the experiment, a maximum adsorption of 91.02% in COD for CF and 82.35% in COD for OPF were recorded. The removal rate gradually decreased with time; this was generally attributed to a reduction in OM content in the water sample, but could also be caused by a deteriorating adsorption ability of the fibres. In addition, the accumulation of pollutant molecules on the solid surface of both fibres was attributed to the physical and chemical bonding between adsorbate and adsorbent. To be more specific, OM containing functional groups such as –OH, –CO, or –COO– stretching vibration tend to occupy the lignocellulose matrix of fibres by interacting with the cellulose acetate group in the fibres during the adsorption process [47,48]. However, a point to note is that the quality of the water sample also affects the adsorption rate using both fibres even when the volume is fixed and subjected to constant

Table 1

The development of empirical model in this study based on list of existing models.

	Equations:
From Adams-Bohart model:	(1)
	$\ln\left(\frac{C_0}{C_t} - 1\right) = k_{BA}N_0\frac{H}{v} - k_{BA}C_0t$
From mass balance equation:	(2)
	$q_t = \frac{(C_0 - C_t) \times Q \times t}{m} = \frac{N_0}{\rho}$
Substitute Eqs. (1) into (2):	(3)
	$q_t = \frac{C_0 \times v}{H \times \rho} \times t - \frac{\ln\left(\frac{C_t}{C_0 - C_t}\right) \times v}{H \times k_{BA} \times \rho}$
Apply logarithm for both sides:	(4)
	$\ln q_{t,acc} = \frac{C_0 \times v}{H \times \rho} \times \ln(t) - \frac{\ln\left(\frac{C_t}{C_0 - C_t}\right) \times v}{H \times k_{BA} \times \rho}$
From Wolborska model:	(5)
	$\ln\left(\frac{C_t}{C_0}\right) = \frac{k_f \times C_0}{N_0} t - \frac{k_f H}{v}$
Substitute Eqs. (4) into (3):	(6)
	$k_f = -\frac{\ln\left(\frac{C_t}{C_0}\right) \times k_{BA} \times N_0}{\ln\left(\frac{C_0}{C_t} - 1\right)}$
From Fulazzaky model:	(7)
	$\ln q_{t,acc} = \frac{1}{\beta} \ln(t) + \frac{\ln(k_g) - \ln\{\ln\left(\frac{C_0}{C_t}\right)\}}{\beta}$
Relationship of $K_g$ and $K_f$ :	(8)
	$\ln(k_g) = \frac{\ln\left(\frac{C_t}{C_0 - C_t}\right) \times \ln\left(\frac{C_t}{C_0}\right) \times N_0}{C_0 \times \ln\left(\frac{C_0}{C_t} - 1\right) \times k_f} + \ln\{\ln\left(\frac{C_0}{C_t}\right)\}$
Relationship of $K_g$ , $K_d$ and $K_f$ :	(9)
	$k_d = k_g - k_f$

flow rate. This was obvious in the daily COD reading of CF in which it consistently remained higher than that of OPF. Therefore, the mass transfer resistance of OM was analysed to give a more comprehensive picture on the performance of the cellulosic fibres in removing OM.

3.3. Performance of CF and OPF based on accumulation rate

This section discusses the ability of the cellulosic fibres in the

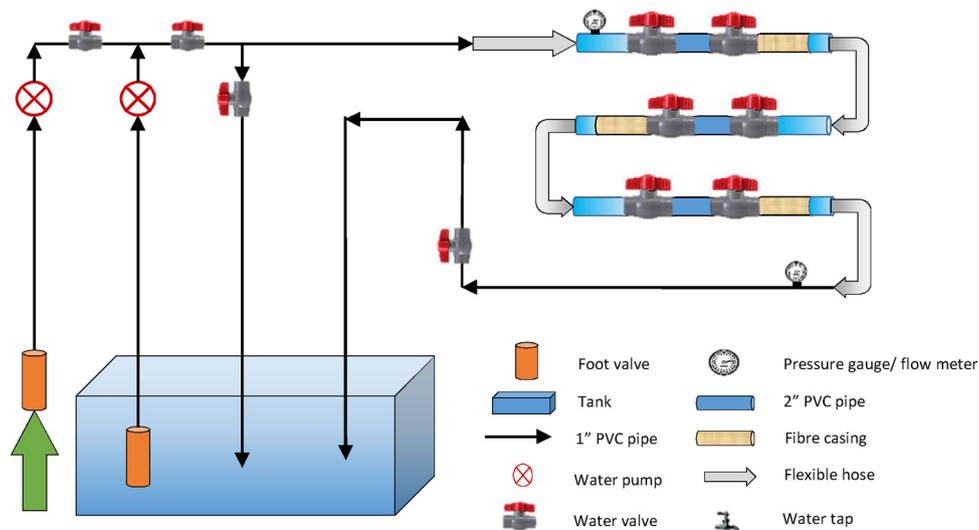


Fig. 4. A schematic diagram of the fabricated column model.

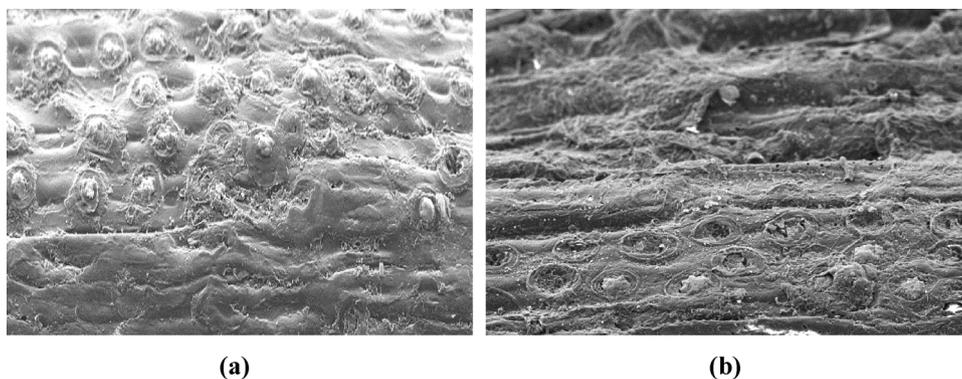


Fig. 5. EPMA photographs of (a) CF and (b) OPF under 500X magnification.

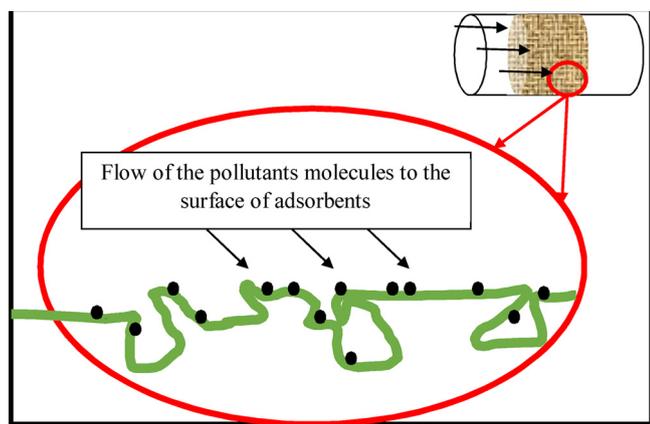


Fig. 6. Mass transfer resistance due to the physical hindrances of CF and OPF.

Table 2  
Chemical characteristics of CF and OPF.

Properties	CF (%)	OPF (%)
Acid Detergent Fibre (ADF)	79.32	68.08
Neutral Detergent Fibre (NDF)	92.22	92.76
Lignin content (%)	40.70	35.51
Cellulose content (%)	38.62	32.57
Hemicellulose content (%)	12.90	24.68
Ash content (%)	1.07	0.96

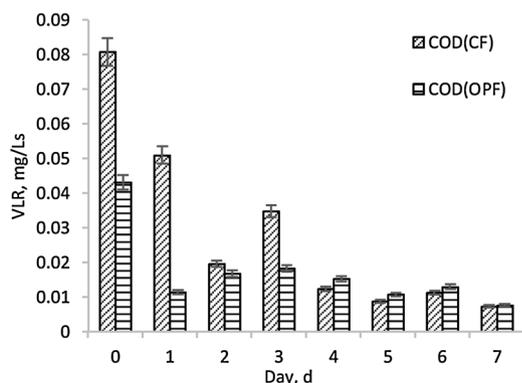


Fig. 7. Relationship between organic matter (OM) loading rate vs. time (d).

Fabricated Column Method to collect a wide range of organic and nutrient contaminants through continuous filtration and adsorption. Examination was also made to the OM accumulated and attached to the fibres. The total mass of the accumulated OM onto CF and OPF per day ( $\ln q_t$  acc) was calculated based on Eq. (4). The performance of the new

modified mass transfer model was gauged by plotting a graph of  $\ln q_t$  acc versus  $\ln t$ , as shown in Fig. 8. All the result in the figures are using the experimental data and trendline represents the model predicted. This yielded a straight line intercepted at  $\frac{\ln\left(\frac{C_t}{C_0 - C_t}\right)^{xv}}{H \times k_{BA} \times \rho}$  and with a gradient of  $\frac{C_0 \times v}{H \times k_p}$ .

Fig. 8 showed that the correlation of all parameters are strong ( $R^2 > 0.9$ ), indicating that the linear regression analysis of using the new modified model (Eq. (4)) is feasible to study the adsorption mechanisms of OM onto CF and OPF. The adsorption capacities of the CF and OPF are 8.105 mg/g and 5.5476 mg/g respectively. The coefficient of gradient and intercept of the graphs has reasonably scrutinized the mass transfer potential, the adsorbate-adsorbent affinity and the influence of river water flow rate on CF and OPF. The gradient of the plot in Fig. 8 is the affinity of adsorbate-adsorbent related to molecular weight, molecular structure, solubility/polarity, flow rate, and properties of adsorbent; the intercept is the inverse of the potential mass transfer related to the driving force of pollutant concentration in water to the adsorbent due to physical, chemical, and biological processes [49]. It was found that the gradient value (2.0799) and intercept value (1.9548) of COD adsorption for CF was higher than those for OPF (gradient = 1.7072 and intercept = 1.7249). Also, it was clear that the circulation of water in the FCM had promoted the biodegradability of OM in polluted water. Both CF and OPF were assumed to have served as a base medium for biological growth which consequentially developed a microbial film that had utilized all organic and nutrients contaminants as food sources [50,51]. Principally, adhesion of microorganisms does not happen on a ‘clean’ surface, but fuelled by the presence of organic carbon compounds such as carboxylic acids, proteins and polysaccharides with glucose as food source [52–54]. This had been studied by Christenson in 2011 whereby he proved that a natural medium based on cellulose performed better in biofilm growth compared to other synthetic polymers [55]. This contributed to the slightly higher ratio of biodegradable OM in the water for CF compared to OPF, which then induced a greater gradient. On the other hand, the smaller intercept value of OPF indicated a stronger C–C\* bond due to higher potential mass transfer of OM to OPF [49].

Comparison between the pollutants adsorption of CF and OPF is in strong agreement with the empirical results of the newly developed mathematical model for all examined ranges. As such, the model was applied in the simulation of breakthrough curves to depict the percentages of outflows in the system and ultimately, the mass transfer resistance for the OM to adsorb onto CF and OPF.

### 3.4. Mass transfer evaluation on cellulosic fibres

The rate in which OM is transported across the cellulosic fibres is strongly related to the effect of mass transfer resistance. The related mass transfer equation was established using a mathematical empirical

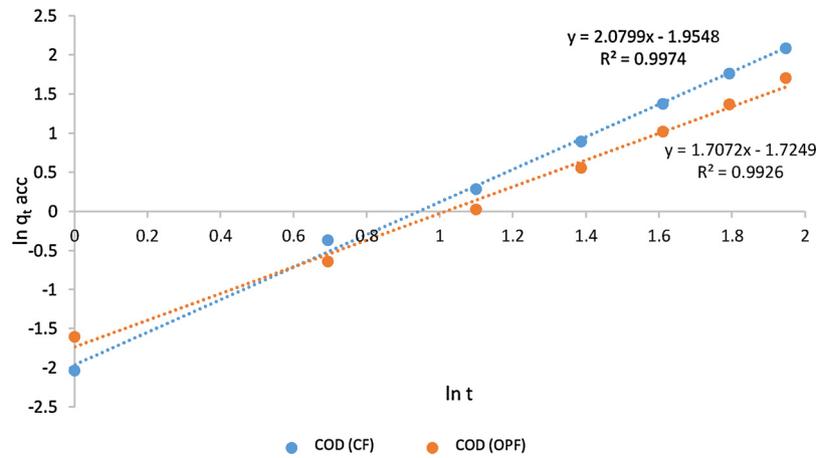


Fig. 8. Plot of  $\ln q_t, \text{acc}$  vs.  $\ln t$  for mass accumulation of OM onto CF and OPF.

model to describe the adsorption dynamics of the cellulosic fibres when removing OM. The plots of mass transfer factor versus percentage outflow are shown in Fig. 9.

The experimental results in Fig. 9 showed a unified picture of the mass transfer factors; the global mass transfer factor ( $k_g$ ) curves and internal mass transfer factor ( $k_d$ ) curves are all hyperbolic concave while all external mass transfer factor ( $k_f$ ) curves are convex. The hyperbolic concave  $k_g$  and  $k_d$  curves indicated that both rates of internal mass transfer and global mass transfer had decreased and reached a minimum at the end of the outflow. In contrary, the convex  $k_f$  suggested that the film mass transfer rate of the adsorbents increased and peaked at the end of outflow. It was noticed that all curves eventually converged close to zero mass transfer. This showed that the mass transfer had decreased with increasing repulsion force which in turn affected the adsorbate-adsorbent affinity.

The mass transfer coefficient is useful in predicting the behaviour of adsorbate diffusivities in the porous adsorbent, which is a prerequisite knowledge in the adsorption process. Theoretically,  $k_g$  is the sum of  $k_f$  and  $k_d$ . This is an important relation to understand the interface concentration of adsorbate to the adsorbent since sample testing on the interface of adsorbent for concentration of pollutants is impossible. The internal mass transfer factor,  $k_d$ , is commonly used in the simulation of adsorption kinetics of pollutants in water onto activated carbon or any ion exchangeable reactors [56,57]. This factor is also used in describing and assuming the non-equilibrium transport of adsorbate to adsorbent

due to the porosity diffusion resistance [58]. Another function of this factor is to predict the behaviour of adsorbate diffusivities in the porous adsorbent. On the other hand, the external mass transfer factor,  $k_f$ , is widely used for engineering purposes to describe the effect of additionally induced bulk flow. The effects of concentration, hydrodynamic condition, and surface area of adsorbent on  $k_f$  is important to describe the adsorption process. Table 2 shows the experimental data validation on the value of  $k_g$ ,  $k_f$  and  $k_d$ .

Table 3 showed that the value of global mass transfer factor,  $k_g$ , is consistently higher for coconut fibres than oil palm fibres; the mass transfer rate for OM was significantly higher in CF. The lower rate in OPF was attributed to the lower initial concentration of COD in water sample. A close relationship was also foreseen between biodegradability and mass transfer due to the circulation of water in the FCM; a better circulation was expected to promote attachment of microorganisms onto the fibres surface [59] to create an obvious gradient in the concentration of adsorbed pollutants and unadsorbed pollutants with respect to time [60]. When considered together with a higher lignin and cellulose content, this would give even higher  $k_g$ . In this regard, Paul Singh [61] had previously concluded from their experiment that the significant reduction in COD was due to attachment of naturally occurring microorganisms onto cellulosic fibres to produce biofilms [61].

Table 3 also depicted higher  $k_d$  values for coconut fibres. Again, this was imputed to a higher initial COD concentration in the water sample with CF. A similar remark was also made by Viorica and Cucu-Man

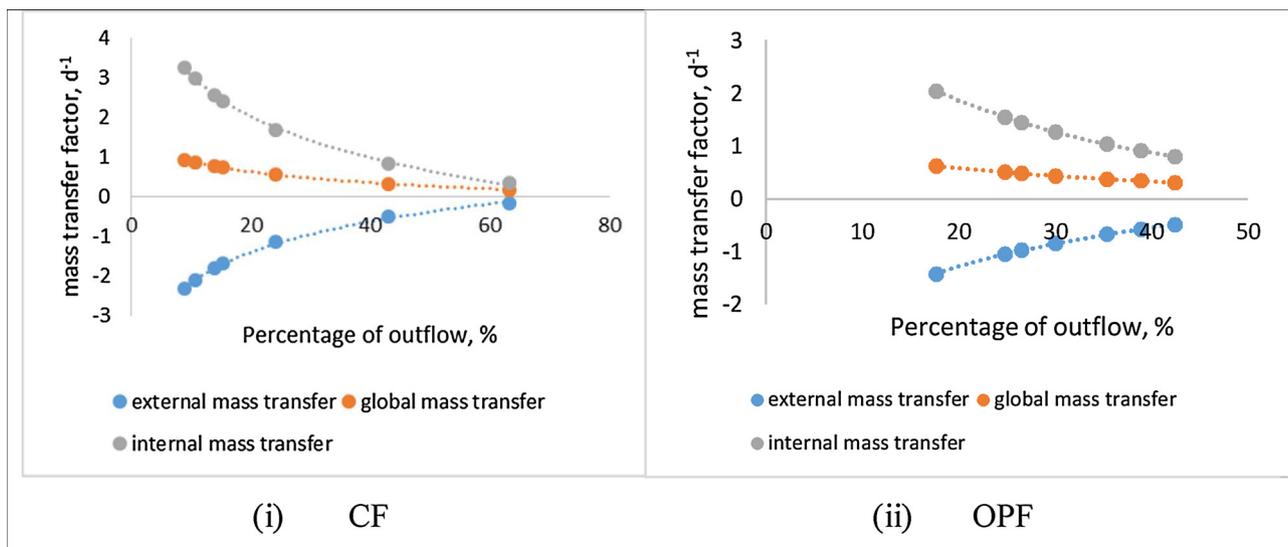


Fig. 9. The variation of global, internal and external mass transfer factor pursuant to the percentage of outflow for the adsorption of OM onto CF and OPF.

**Table 3**  
Percentage of COD outflow by CF and OPF in FCM.

Adsorbent	Percentage of outflow (%)					
	3	5	8	10	20	50
$k_g$ ( $d^{-1}$ )						
CF	1.3696	1.1699	0.9861	0.8989	0.6279	0.2696
OPF	1.2768	1.0909	0.9198	0.8386	0.5863	0.2527
$k_d$ ( $d^{-1}$ )						
CF	4.8988	4.1280	3.4187	3.0820	2.0360	0.6534
OPF	4.5490	3.8236	3.1562	2.8393	1.8551	0.5539
$k_f$ ( $d^{-1}$ )						
CF	-3.5286	-2.9572	-2.4315	-2.1820	-1.4067	-0.3818
OPF	-2.4066	-2.2504	-2.0281	-1.8879	-1.2829	-0.4279

where increased initial concentration of pollutants in water would increase  $k_d$  [62]. On another note, the particle size of natural OM between 15 nm to 0.1  $\mu\text{m}$ , which means that it can easily adhere to the cellulosic fibre pores [63,64]. When the adsorbate molecules rapidly move towards the porous active zone of adsorbents, the smaller particle size promotes its adsorption onto the cellulosic fibres; this could have contributed to the high  $k_d$  value as well.

The external mass transfer factor,  $k_f$ , was the major factor that had inhibited the overall mass transfer. This is because the mass transfer resistance has been largely controlled by external diffusion. Table 2 showed a negative  $k_f$  at the early point of outflow. The negative sign in external mass transfer factor indicates the flux is actually in the direction of decreasing [65]. More exactly, the external mass transfer resistance has been taken into account. This is translated to a longer movement time for the adsorbate to reach the external surface of adsorbents compared to its diffusion from external surface to reach the pores of the cellulosic fibres. The fierce competition among the pollutants molecules eventually impeded the overall mobility and resulted in an even longer time taken to reach the inner active surface of CF and OPF. This had been proven in previous studies in which the competition amongst the solubility of pollutant molecules and the different physical as well as the chemical properties of these pollutants had affected and governed simultaneous adsorption [66,67], resulting in different  $k_f$  values. In addition, from Table 3, the minor increment in film diffusion and the reduction of internal mass transfer rate observed were the consequence of attractive forces and gradual reduction of impregnated character of adsorbate molecules onto adsorbent. This was caused by a saturation of adsorbate molecules on the porous surface of the adsorbent. Furthermore, the higher concentration might have induced repulsion and thus, increased the film mass transfer resistance during the adsorption process [62,68]. Hence, it can be concluded that the OM concentration in the circulated system greatly influences the film diffusion of pollutant molecules to the adsorbent surface. The higher  $k_f$  value for CF showed that it was more difficult for the pollutant molecules to make contact with the adsorbent surface when the initial OM concentration was higher.

#### 4. Conclusion

The present study has demonstrated both CF and OPF as effective adsorbents for the removal of organic matter from polluted river water. The recorded removal rates were up to 91.02% and 82.35% in term of COD measured within seven days for CF (8.105 mg/g) and OPF (5.5476 mg/g), respectively. The OM adsorption was also studied through the mass transfer analysis based on organic utilization rate. It was found that the rate was higher for CF than OPF due to higher initial OM concentration in the river water sample and higher lignocellulose content in CF. From the empirical model, The  $k_g$ ,  $k_f$ , and  $k_d$  pursuant to the percentage of outflow were traced separately to evaluate the properties of adsorbent and adsorbate in consideration of the molecular

size, the concentration and the polarity of the adsorbate. The internal mass transfer analysis showed effective diffusivity of pollutants to cellulosic fibres, but this reduced with a decreased concentration gradient in the water. Besides organic loading rate of the sample water, there were also other factors identified as having major influence on the adsorption rate of CF and OPF. These include the presence of living organisms and the competition to molecular adsorption in water. However, these additional analyses are not covered in this paper. It can be concluded at this point that the CF and OPF have excellent adsorption capacity when used as a low cost alternative treatment medium to replace the costly activated carbon in removing OM from polluted river water.

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