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Elimination of ibuprofen and diclofenac by biofiltration on an organic support made from coconut fibers and husks

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Abstract: A biofiltration process using coconut fibers and husks as packing was developed for the removal of diclofenac and ibuprofen. The performance of a filter bed made up of coconut fibers and husks for the removal of diclofenac and ibuprofen was studied. Specifically, hydrostatic and hydrodynamic characterization of the filter bed, colonization of the filter bed and monitoring of the degradation rate of model compounds in the filter bed were carried out. The hydrostatic study was carried out by determining porosity, dynamic and static liquids and solid retention. The hydrodynamic study was carried out using the residence time distribution method. Measurement of the chemical oxygen demand (COD) at the inlet and outlet of the recirculated effluent filter bed over time was used to monitor colonization of the filter bed. The elimination of model compounds was monitored by measuring samples taken at the inlet and outlet of the filter bed at 380 nm for diclofenac and 224 nm for ibuprofen using a UV-visible spectrophotometer. The fibers and shells prepared have a porosity of over 50%. The bio-filter can be described as a J cascade reactor model. The filter bed encouraged the development and maturation of a purifying biomass. Removal efficiencies of over 80% were achieved for diclofenac and ibuprofen. The rate of elimination of analytes varies with the thickness of the fiber layer and the type of effluent. Biofiltration of diclofenac and ibuprofen on a bed of fibers and shells is feasible.

1. Introduction

Many organic micropollutants present in wastewater are poorly eliminated in conventional wastewater treatment plants (WWTPs) before being discharged into the receiving environment, because WWTPs are not designed for optimal treatment of these micropollutants (Castro, 2020). So, to obtain better elimination rates for organic pollutants, additional treatments are required (Margot et

al., 2013). These complementary treatments include adsorption on activated carbon, which can retain almost all organic contaminants; however, the elimination capacity is limited by the contact time, competition with natural organic matter, the solubility of the contaminants and the type of carbon (Deghles et al., 2019; Snyder *et al.*, 2007; Ternes *et al.*, 2002; Yoon *et al.*, 2003). Oxidation processes such as chlorination and ozonisation are also effective in reducing the concentrations of several types of micropollutants, but the elimination efficiency depends on the structure of the contaminant and the dose of the oxidant (Salem *et al.*, 2015; Melliti *et al.*, 2013; Huber *et al.*, 2005; Pinkston and Sedlak, 2004; Ternes *et al.*, 2003). In view of the inadequacies of the above-mentioned treatment methods, physico-chemical or biological systems have been set up to reduce the effect of contamination by micropollutants. But most of them are costly or require high technology and, as a result, cannot be applied at all scales (Gao *et al.*, 2010). As a result, biotechnological applications have emerged. Applications using bacteria or fungi to biodegrade micropollutants appear to be a promising strategy for mitigating the impact of micropollutants on the environment (Rodríguez-Rodríguez *et al.*, 2011; Loukili *et al.*, 2022). Biofiltration is a biological treatment technique that involves passing a polluted influent through a porous packing onto which purifying micro-organisms are attached. This process eliminates both suspended solids and a large proportion of organic and inorganic pollution (Rocher *et al.*, 2008). Originally, biofilters were developed using rock as a filter medium. Nowadays, several types and forms of media are used, with different materials including biological materials (Chaudhary *et al.*, 2003). Coconut residues have been used as a bio-sorbent for the removal of pollutants such as pharmaceuticals, personal care products, detergents, biocides and pesticides discharged into the aquatic environment (Bhatnagar *et al.*, 2010; Sousa *et al.*, 2010; Vidal *et al.*, 2011; Salghi *et al.*, 2012). The use of coconut residues as a filter medium for the elimination of drug residues was the subject of this study. These residues constitute abundant waste in tropical countries, particularly in Côte d'Ivoire. Their use has two advantages. The first is to achieve low-cost treated water and the second is to manage to use biomaterials considered as waste (Gbamele *et al.*, 2016). The model compounds selected for the study are diclofenac and ibuprofen (Figure 1a and 1b). They are non-steroidal anti-inflammatory drugs (NSAIDs) that treat pain, fever and inflammation (Monteiro and Boxall, 2010). They have been found in surface water (Kasprzyk-Hordern *et al.*, 2008), in wastewater near pharmaceutical plants (Alighardashi *et al.*, 2008), in hospital effluents (Langford and Thomas, 2009), in groundwater and in drinking water (Kumar *et al.*, 2010).

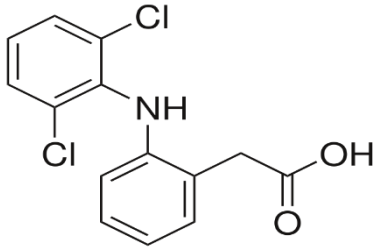

Figure 1a : Molecular structure of diclofenac

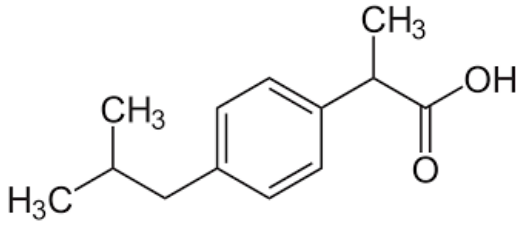

Figure 1b : Molecular structure of ibuprofen

2. Materials and methods

2.1 Materials

The study material consisted of coconut husks and flocks (**Figure 2a and Figure 2b**) harvested from coconut trees at the Institut National Polytechnique Houphouët Boigny (INPHB) and then dried at room temperature. These residues are abundant waste products in tropical countries, particularly Côte d'Ivoire. The technical equipment consisted mainly of a plant material shredder. For sieving, 5 mm and 2 mm mesh sieves were used, as well as an oven.

Figure 2a: Coconut stuffing

Figure 2b: Coconut shells

2.2. Methods

2.2.1. Preparation and treatment of the filter medium

Coconut flocks and husks were harvested and then dried at room temperature. After drying, they were ground using a plant material grinder. The resulting grindings were sieved using 5 mm and 2 mm sieves. Hull pellets of sizes between 2 and 5 mm were then obtained (**Figure 3**). The fiber fragments (**Figure 4**) obtained were larger than 2 mm. The sieved fractions were macerated in hot water for a week in order to eliminate the mineral salts likely to increase electrical conductivity and the phenolic compounds (tannins). The operation was repeated twice during the maceration period. At the end of this maceration phase, the interstitial liquid turned from brick red to clear (Martine, 2011). Next, the fibers and hulls were immersed in an 8% potassium hydroxide solution (mass by volume) for 24 hours and then rinsed with distilled water to remove excess potassium hydroxide (Christine *et al.*, 2018). This step is used to extract lignin, hemicellulose and any other extractable materials by dissolution. These compounds are likely to affect biofilter efficiency by increasing total COD and conductivity (Martine, 2011). After treatment, these fractions were oven-dried at 105°C for 24 hours.

Figure 3 : Fragments of coconut coconut shells

Figure 4 : Fragments of coconut coconut fibers

2.2.2 Biofilter construction and hydrodynamic study

2.2.2.1 Determination of porosity

The porosity (n) of the fiber and shell fragments was determined by saturating each material with water. The volume of water required to saturate a given volume of material is noted. Particular care was taken to ensure that no gas was trapped during immersion. The tests were carried out in triplicate (3 tests) using three 500 mL graduated test tubes (Molle, 2003). The porosity (n) is established as follows, **Eqn.1**, (Molle, 2003):

$$n = \frac{Volume\ of\ water\ required\ for\ saturation * 100}{Volume\ of\ saturated\ material} \quad \textbf{(Eqn.1)}$$

2.2.2.2 Determining retentions

Solid retention (Ɛs), gaseous retention (Ɛg) and liquid retention (Ɛl), which is subdivided into static liquid retention (Ɛls) and dynamic liquid retention (Ɛld), were determined using the method described by Martineau (1999). The different retentions were determined in submerged mode of the fiber fraction and new hulls. Six (6) 500mL graduated tubes (Vtotal) were filled with fiber and hull samples up to the gauge line, three tubes for each type of material, then saturated with a known volume of water (Vwater). After resting for three days, the liquid contained in the test tubes was drained and the volume of water collected (Vdrained) was noted. From these measurements, the various retentions were calculated from **Eqn.2**, **Eqn.3** and Eqn.4 according to the following formulae (Martineau, 1999):

$$Ɛ Ls = \frac{Vwater - Vdrained}{Vtotal} \quad \textbf{(Eqn.2)}$$

$$Ɛ Ld = Ɛ g = \frac{Vdrained}{Vtotal} \quad \textbf{(Eqn.3)}$$

$$Ɛ Ld + Ɛ Ls + Ɛ s = 1 \quad \textbf{(Eqn.4)}$$

2.2.3 Biofilter construction and hydrodynamic study

2.2.3.1 Biofilter design

The biofilters were created by installing a filter bed within the columns. The columns used during the bio-filtration tests were made of PVC. Two identical columns were used for the laboratory experiments. The columns have a total height of 100 cm and an internal diameter (D) of 10 cm. The height of the bed in the columns is 88 cm, giving a useful volume (Vu) of 6.908 L. The method for setting up the filter medium described by Gilbert (2006) and Aubry (2008) was used to create the biofilters. The two columns were filled with four successive layers. The top layer (5cm thick) is made up of coarse gravel, followed respectively by a layer of shell, a layer of fiber and finally a new layer of coarse gravel. This arrangement during filling is designed to prevent clogging and facilitate fluid flow. The two biofilters differ in the thickness of the shell and fiber layers. The first biofilter (biofilter A) (**Figure 5a**) is characterized by identical thicknesses (39 cm thick) in the shell layer and the fiber layer, whereas for the second biofilter (biofilter B) (**Figure 5b**), the thickness of the shell layer (26 cm thick) is half that of the fiber layer (52 cm thick). The layers of fibers and shells were laid in succession by lightly moistening each layer with water and compressing the said layers slightly close to the walls with a rod. This maneuver is designed to avoid the creation of preferential paths for the passage of gases and/or liquids, especially near the walls. The various layers were separated from each other by fine-diameter grids.

2.2.3.2 Hydrodynamic study

In order to study the hydrodynamic properties of the biofilter, chloride ion tracer tests were carried out as described by Maldonado (2005). Sodium chloride (NaCl) was used as the tracer. A solution of NaCl (4.16 g/L) was prepared by dissolving 2.08 g of NaCl in 500 mL of distilled water (Figure 6). Five (5) mL of this solution was injected using a syringe for a very short time of less than one hundredth of the transit time (τ) (Dirac injection, (less than 0.01τ) at the column inlet). Samples (10 mL) were taken at

the biofilter outlet in 5 min time steps for a time equivalent to 3 times the theoretical passage time (Charlou, 2014; Martineau, 1999).

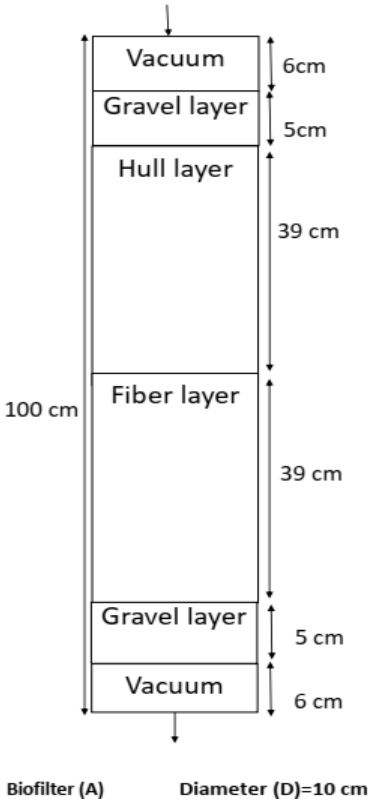

Figure 5a : Diagram of the biofilter A

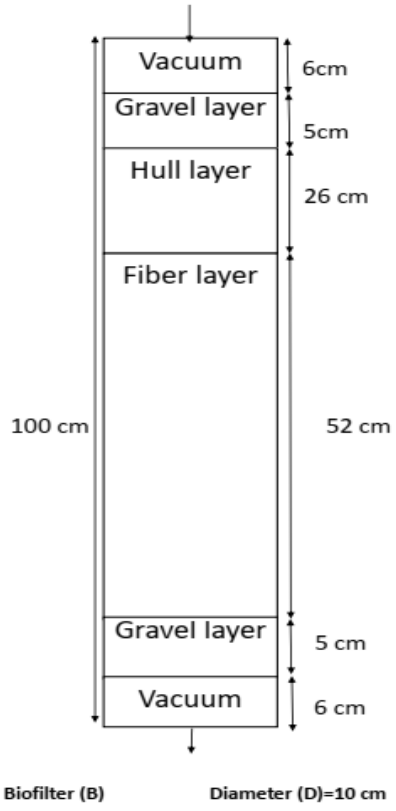

Figure 5b : Diagram of the biofilter B

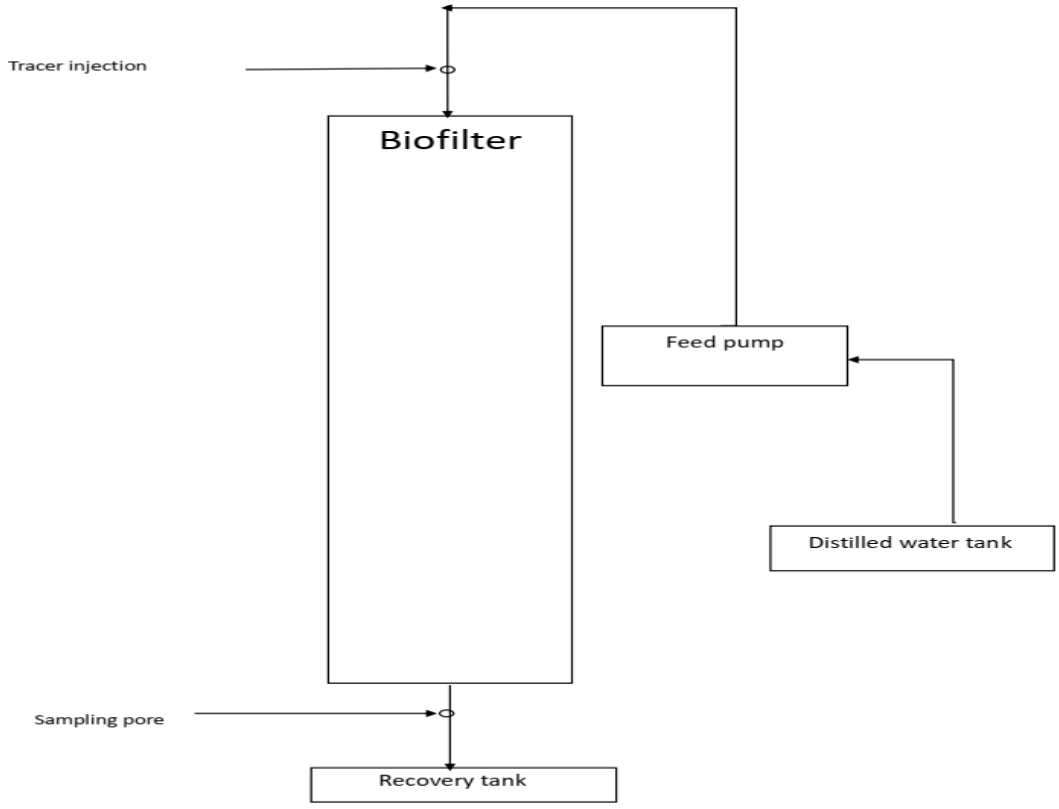

Figure 6 : Diagram of the study set-up

The conductivity measurement provided access to the residence time distribution function E(t) and the reduced residence time distribution function E(θ). The conductivity meter was calibrated using NaCl solutions (0.208, 0.166, 0.083, 0.042 and 0.021 g/L) made from the stock solution. These solutions were obtained by diluting with distilled water respectively 10 mL, 8 mL, 4 mL, 2 mL and 1 mL in a 100 mL volumetric flask. To carry out the laboratory tests, the biofilter was integrated into an experimental set-up allowing, among other things, water to be supplied, tracer to be injected at the injection port and measurements to be taken at the sampling port. A diagram of the experimental set-up is shown in Figure 6. During these tests, a peristaltic pump (Masterflex® L/S® Easy-Load® II) with a standard head was used to feed the biofilter. This allowed the feed rate to be varied. Three different flow rates 90.91, 145.63 and 231.56 mL/min were selected for the study, low, medium and high flow respectively, in order to study its effect on mean residence time. The tracer tests were carried out in triplicate. The conductivity of the various samples was used to establish the concentrations using the calibration curve. The residence time distribution (SDD) curves were evaluated using the residence time distribution function E(t), defined as the distribution of tracer residence times as a function of time and represented by Eqn.5 (Charlou, 2014):

$$E(\boldsymbol{t}) = \frac{\boldsymbol{C(t)}}{\int_0^\infty \boldsymbol{C(t)dt}} \qquad \textbf{(Eqn.5)}$$

Where C(t) represents the concentration of the species measured at time t in mol.m^{-3}. The mean residence time ($\bar{t}$) corresponding to the moment of order n=1 representing the statistical mean of the function E(t) was determined according to **Eqn.6** (Levenspiel, 1999):

$$\bar{\boldsymbol{t}} = \frac{\sum \boldsymbol{ti.Ci}}{\sum \boldsymbol{Ci}} \qquad \textbf{(Eqn.6)}$$

Where Ci, represents the concentration of the tracer measured at a discrete number of times ti. The second-order centered moment (σ2), also called the variance corresponding to the spread of the curve of the function E(t), was determined according to **Eqn.7** (Levenspiel, 1999) :

$$\boldsymbol{\sigma^2} = \frac{\sum \boldsymbol{t_i^2 Ci}}{\sum \boldsymbol{Ci}} - \bar{\boldsymbol{t}}^{\boldsymbol{2}} \qquad \textbf{(Eqn.7)}$$

The reduced time (θ) and reduced residence time distribution function (Eθ) were determined by **Eqn.8** and **Eqn.9** (Levenspiel, 1999):

$$\boldsymbol{\theta = t/\bar{t}} \qquad \textbf{(Eqn.8)}$$

$$\boldsymbol{E_\theta = E.\bar{t}} \qquad \textbf{(Eqn.9)}$$

The reduced centered variance (VarC) representing the ratio of variance and the square of the mean residence time giving an indication of the deviation from plug flow (VarC=0) or flow through a perfectly stirred reactor (VarC=1) was determined according to **Eqn.10** (Levenspiel, 1999):

$$\boldsymbol{VarC} = \frac{\boldsymbol{\sigma^2}}{\bar{\boldsymbol{t}}^{\boldsymbol{2}}} \qquad \textbf{(Eqn.10)}$$

2.2.3.3 Modelling residence time distribution curves

The axial dispersion piston reactor model associated with the Peclet number (Pe) is used to describe non-ideal piston reactors. The Peclet number (Pe) was determined from the following equation **Eqn.11** (Levenspiel, 1999):

$$\sigma_\theta^2 = VarC = \frac{\sigma^2}{\bar{t}^2} = \frac{2uL}{D} = \frac{2}{P_e} \qquad \textbf{(Eqn.11)}$$

D (m2/s) represents the coefficient of dispersion, L, the length of the reactor (m) and, u, the flow velocity (m/s).

$\sigma_\theta^2 = VarC$; represents the reduced centered variance.

When D/uL tends towards 0, there is little or no dispersion (ideal RP flow). Conversely, when D/uL tends towards infinity, there is a lot of dispersion (RPA flow).

When Pe tends towards infinity, there is little or no dispersion (ideal piston reactor (PR)). Conversely, when Pe tends towards 0, dispersion is high (perfectly stirred reactor (RPA)).

The perfectly stirred reactor in series model, which allows a given reactor to be represented by a set of small perfectly stirred reactors (RPA), is associated with the number of small reactors J. The number J is determined from equation **Eqn.12** (Levenspiel, 1999) defined as follows:

$$J = \frac{\bar{t}^2}{\sigma^2} \qquad \textbf{(Eqn.12)}$$

2.2.3.4 Study of flow anomalies

The mean residence time was compared with the theoretical passage time (τ), for the study of anomalies (Villermaux, 1993). The theoretical residence time (τ) was determined by Eqn.13 (Levenspiel, 1999):

$$\tau = \frac{Vu}{Q} \qquad \textbf{(Eqn.13)}$$

Vu is the useful volume and Q is the volume flow rate of product entering the reactor.

When :

$\bar{t} > \tau$, a short-circuit phenomenon in the biofilter is observed;

$\bar{t} < \tau$, the biofilter has stagnant or dead volumes or recirculation zones and,

$\bar{t} = \tau$, the biofilter has no operating anomalies reflecting an ideal reactor (RP or RPA) (Villermaux, 1993).

2.2.4 Development of biofilter purifying biomass

Colonisation was carried out by recirculating wastewater from a wastewater treatment plant (WWTP) through the biofilter. The effluent used to colonise the biofilter was wastewater from the INPHB wastewater treatment plant. Exactly 20 L of this body of water was taken and placed in a PVC tank, after first filtering to remove the coarse elements. The tank was transported to the laboratory and stored for 24 hours before being incorporated into the biofilter colonisation device (**Figure 7**).

The effluent was fed into the downflow biofilter by a Masterflex peristaltic pump with digital control. The test was carried out at ambient temperature. The biofilter was oxygenated from above using an aeration pump. Effluent and air flow co-currently through the pilots. Sampling ports were placed at the inlet and outlet of the biofilter. During operation of the pilot, the biofilter remained opaque to light. The portholes were closed with black plastic to encourage the development of heterotrophic micro-organisms. These use organic matter as both a source of energy and carbon. Aeration of the pilot plant is designed to promote an aerobic heterotrophic purifying biomass within the biofilter. Aerobic heterotrophic microorganisms are mainly involved in the biodegradation of organic matter (OM). The recirculation flow rate (Q) is 3 L. J-1. The low water and air flow rates result in minimal pressure drops (Zidane et al., 2006). The hydraulic retention time (HRT) and hydraulic head (HL) are 2 days and 0.38 $m.D^{-1}$ respectively. This biofilter colonisation phase took place from February 2022 to April 2022.

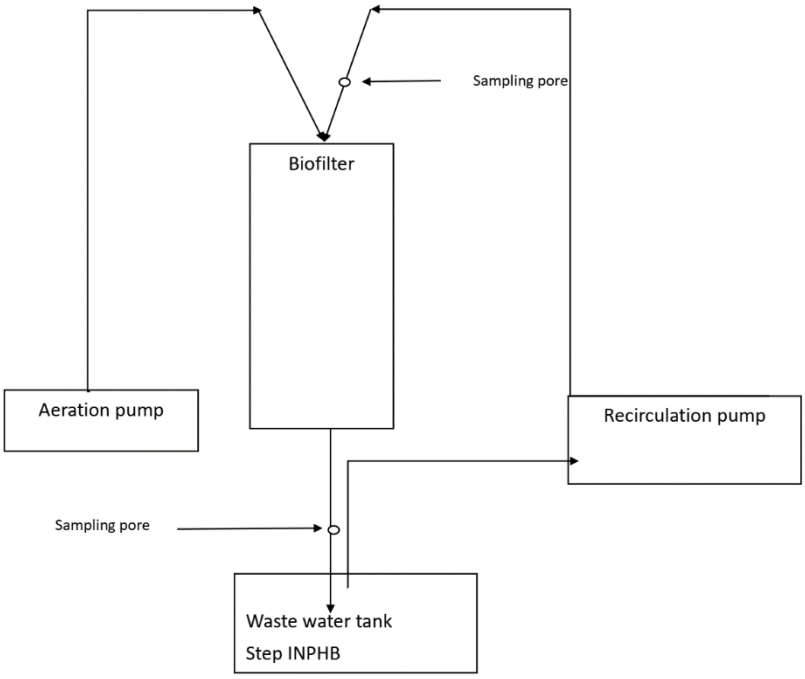

Figure 7: Diagram of the colonization system

2.2.5 Study of the removal of model compounds

2.2.5.1 Validation of the analytical method

The analytical validation approach described by (Saley, 2013) was followed in our study. The linearity study was carried out using the active ingredient alone. For this, we prepared a calibration range without matrix (calibration standards) which was used to calculate the method's response function. This calibration range covers a minimum of 5 concentration levels, representing the concentration range to be studied.

2.2.5.2 Preparation of calibration standards

Diclofenac sodium calibration standards were prepared according to the protocol described by Derraji *et al*. (2015) and Matin *et al.* (2005). The 1mg/mL stock solution was made by dissolving 100mg of diclofenac sodium in distilled water in a 100mL volumetric flask. Ten (10) mL of the stock solution was diluted in a 100 mL volumetric flask to prepare an intermediate solution of 100µg/mL. This intermediate solution was used to prepare five standard solutions of different concentrations (20, 15, 10, 5 and 1 µg/mL) by diluting 20, 15, 10, 5 and 1 mL respectively with distilled water in 100-mL volumetric flasks. The ibuprofen calibration standards were prepared according to the protocol described by Alkhafaji and Mahood (2019). The ibuprofen stock solution (100 µg/mL) was prepared by weighing 10 mg of pure ibuprofen, dissolving it in 25 mL of 95% ethanol, transferring it to a 100 mL volumetric flask and making up to the mark with a 0.1 M NaOH solution (0.4 g in 100 mL of distilled water).

This solution was used to prepare five standard solutions of different concentrations (15, 10, 8, 5 and 1 µg/ mL) by diluting 15, 10, 8, 5 and 1 mL respectively with distilled water in 100 mL volumetric flasks.

2.2.6 Determination of analytes

Determination of analytes the determination of diclofenac sodium in standard solutions was carried out according to the protocol described by Matin *et al*. (2005). Two (2) mL of standard solution containing the appropriate amount of diclofenac sodium were pipetted into a 10 mL volumetric flask and 1 mL of nitric acid (63% w/v) was added. The resulting yellowish solution was made up to the mark with distilled water. The absorbance of the coloured solution (yellow) was measured against a test blank (distilled water) at 380 nm. The corresponding calibration curve was linear over the range 1 to 30 mgL-1. The determination of ibuprofen in standard solutions was performed according to the protocol described by Alkhafaji and Mahood (2019). The absorbance of the standard solutions was measured at 220 nm against a test blank (mixture of 25 mL 95% ethanol and 75 mL 0.1M NaOH). The corresponding calibration curve is linear over the range 1-15 µg/mL.

2.2.7 Preparation of synthetic solutions

Synthetic solutions of diclofenac and ibuprofen were obtained by dilution in 20L tanks of standard solutions of diclofenac (300mg/L) and ibuprofen (200mg/L), respectively. The standard solutions of diclofenac (300mg/L) and ibuprofen (200mg/L) were prepared according to the protocols described by Derraji *et al.* (2015) and Matin *et al.* (2005) for diclofenac and by Alkhafaji and Mahood (2019) for ibuprofen.

To prepare the synthetic diclofenac solution, 1L of the standard diclofenac solution was transferred to the 20L tank and made up to the mark with distilled water. The same procedure was followed to prepare the synthetic ibuprofen solution.

To promote biodegradation, the C/N/P ratio (100/5/1) required for bacterial growth (Behra, 2013; Sawadogo, 2018) was maintained by adding ammonium chloride salt (NH_4Cl) and dipotassium hydrogen phosphate (K_2HPO_4). In addition, the pH was brought to neutral using a sodium hydroxide solution (NaOH, 2M).

2.2.8 Preparation of doped municipal effluent

To prepare the municipal effluent spiked with diclofenac, 1L of the standard diclofenac solution was transferred to the 20L tank and topped up to the gauge line using municipal wastewater from the INPHB-Yamoussoukro water treatment plant. The same procedure was followed for the preparation of municipal effluent spiked with ibuprofen.

2.2.9 Preparation of doped municipal effluent

After the colonization phase in pilots A and B, each pilot was subjected to a series of four biodegradation trials depending on the characteristics of the effluent to be treated (synthetic solutions (SS) and municipal water spiked (EUD) with diclofenac sodium or ibuprofen). The trials took place from June 2022 to February 2023. Each trial lasted 21 days.

The feed rate (Q) to the pilots was 3 L.D-1 and the hydraulic retention time (HRT) was 2.3 days. A long residence time gives more time for the effluent to be treated in the biofilter (Green *et al.*, 2005; Lopera, 2017). The hydraulic head (CH) remains 0.38 m.J-1. Similarly, the volume loads (Cv) of diclofenac sodium and ibuprofen are 6.51 and 4.34 g.m-3. J-1. Effluent and air flow co-currently from top to bottom in the pilots (**Figure 8a and 8b**). The biofilters had to be washed to prevent clogging as a result of biofilm development. Washing was carried out once a week. The first step was to empty the columns of liquid, then fill them in counter-current (from the bottom up) with tap water. Air was then injected to clean the bed thoroughly. On average, stirring takes between 10 and 15 minutes. The wash

water is then emptied and normal operations are repeated with the water to be treated (Garcia *et al.*, 2019).

Periodic sampling (2-day intervals) was carried out at the sampling ports of the devices. Glass vials with a capacity of 50mL were used for sampling. The bottles were filled to the brim and then the cap was screwed on to prevent any gas exchange with the atmosphere. Samples were either sent for analysis or stored at 4oC for later analysis.

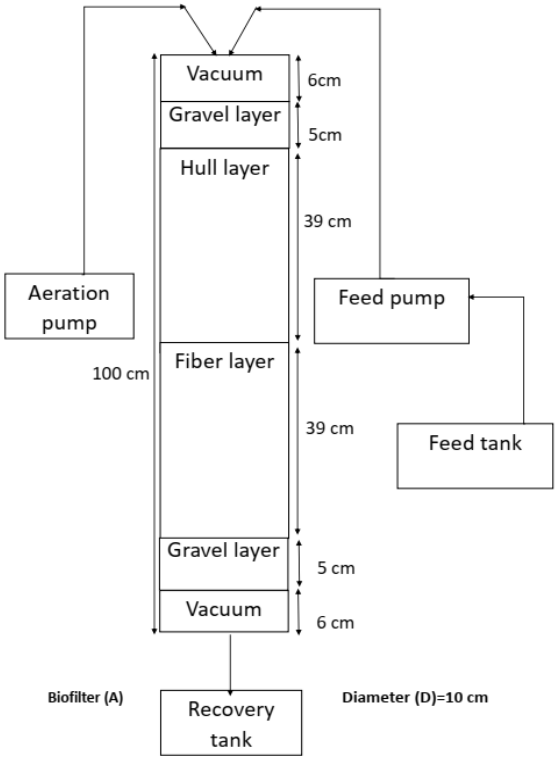

Figure 8a : Biofilter A operating diagram

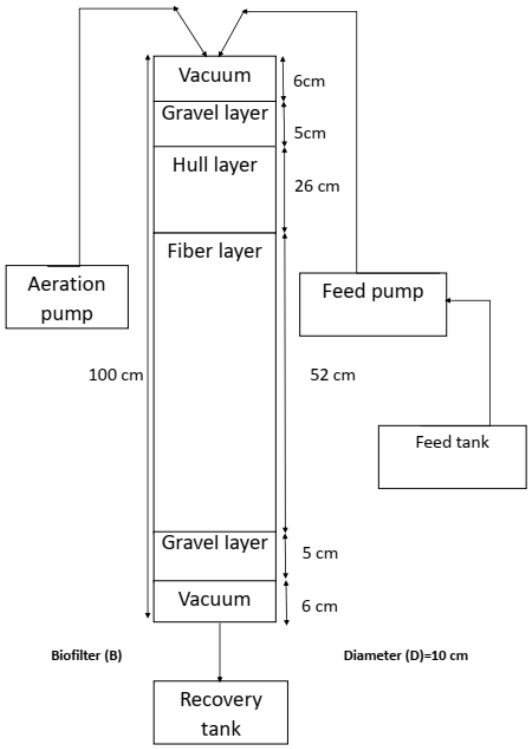

Figure 8b : Biofilter B operating diagram

2.2.10 Data processing

2.2.10.1 Calculation of parameter yields

The purification efficiency (R (%)) of the various parameters was determined using equation **Eqn.14** below, formulated by (Soupramanien, 2012):

$$R = \frac{Ce - Cs}{Ce} * 100 \qquad \textbf{(Eqn.14)}$$

R: is the treatment efficiency (%); Ce: is the influent concentration for the parameter concerned; Cs: is the effluent concentration for the parameter concerned.

2.2.10.2 Calculation of detection and quantification limits for analytical methods

The limits of detection (LOD) and quantification (LOQ) were calculated from equations **Eqn.15 and Eqn.16** (Saley, 2013) :

$$LD = \frac{3{,}3.\sigma}{S} \qquad \textbf{(Eqn.15)}$$

$$LQ = \frac{10.\sigma}{S} \qquad \textbf{(Eqn.16)}$$

σ: standard deviation of the response; S: slope of the calibration curve.

2.2.10.3 Statistical processing of data

The data collected were entered into an Excel spreadsheet and analysed using Statistica version 7.1 software. The normality of the data in each group was examined using the Shapiro-Wilk test. The Mann-Whitney test for comparing the medians of two independent groups was used to compare the median values of the porosity of the fibre fractions and that of the shell within the biofilters, respectively. It was also used to compare the median values of analyte removal rates as a function of biofilters (A and B) and effluent type, respectively. The Cochran test was used to study the homogeneity of the variances of the dependent variables (conductivity and absorbance) for each concentration level of NaCl, diclofenac and ibuprofen. The minimum threshold of 5% ($p < 0.05$) was used to judge the significance of the differences.

3. Results and Discussion

3.1 Hydrostatic characteristics of fibres and hulls

Table 1 shows the porosity, solid retention (Ɛs), gas retention (Ɛg) and liquid retention (Ɛl) values subdivided into static liquid retention (Ɛls) and dynamic liquid retention (Ɛld) of the fibre and shell fractions. A significant difference in porosity was observed between the fibre and shell fractions ($p < 0.05$, Mann-Whitney test). The porosity values obtained indicate that the fibres and shells obtained are extremely porous. A material has excellent porosity when its porosity is greater than 30% (Mouhous, 2016). Also, a significant difference between the static liquid retention (Ɛls) of the fibre and shell fractions was observed. The difference in porosity between the fibre and shell fractions could be explained by the non-uniformity of the mixture aggregates in the shell fraction and by the difference in density between the two types of material. The more distributed and non-uniform the mixture of grains, the lower the porosity (Benalia and Boukria, 2022; Kabagire, 2013; Marolf *et al*., 2004). Porosity is also very important in the case of lightweight aggregates (Ranarivelo, 2008).

Table 1: Hydrostatic characteristics of the biofilter

parameters	Fibers	Hull
Porosity (n%)	89,27± 0,87*	53,3± 0,70**
Retentions (average over 3 trials)		
Static liquid ($Ɛ_{Ls}$%)	28,20± 0,52	12,00± 0,89
Dynamic liquid (ƐLd%)	61,07± 0,40	41,30± 0,61
Solid retention (Ɛs%)	10,73± 0,87	46,70± 0,70
Total (%)	100	100

*: Significant difference in porosity between fibres and shells

3.2 Hydrodynamic characterisation of the filter medium

3.2.1 Validation of the assay method

The distribution of electrical conductivity values followed a normal distribution ($p > 0.05$; Shapiro and Wilk test) and the variances were homogeneous (Ccalculated < Ctabulated, $p < 0.05$; Cochran test). The linear regression between electrical conductivity and sodium chloride (NaCl) concentration showed a strong correlation (R2=0.998) (Figure 9). The linear regression shows a significant slope (Fcalculated > Ftabulated (0.05; 1; 13), $p< 0.05$; Fisher test). The chloride ion tracing method can be used to conduct the hydrodynamic study. The respective limits of detection (LOD) and quantification (LOQ) are 0.0053g/l and 0.01619g/l.

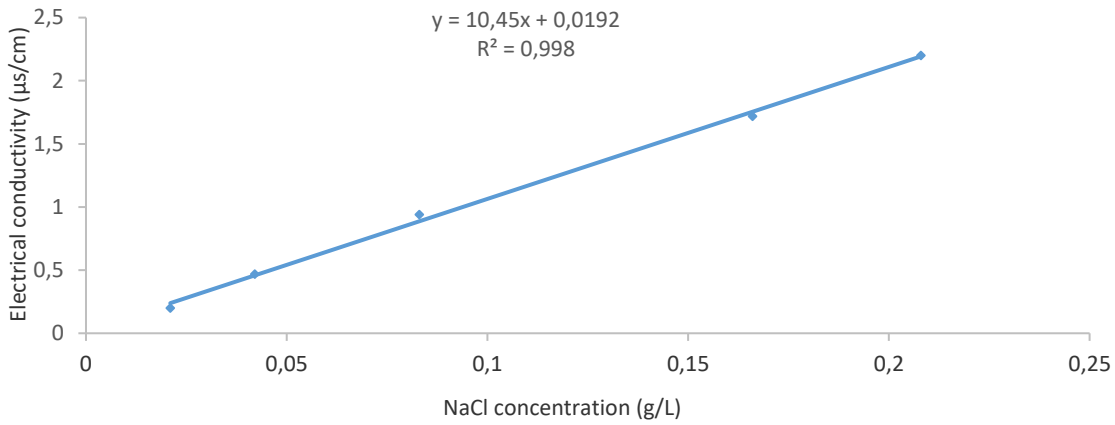

Figure 9 : Linear regression between electrical conductivity and sodium chloride (NaCl) concentration

3.2.2 Evolution of the residence time distribution function as a function of flow rate

Figure 10 shows the evolution of the residence time distribution function E(t) as a function of time for the three flow rates (Q) selected (minimum, average and maximum: 90.91, 145.63 and 231.56 mL/min). The experimental curves obtained at the different flow rates are characterised by the presence of drag. These trails indicate the existence of dead volume or short-circuiting in the biofilter during liquid flow. This can be explained by the fact that the tracer penetrates by diffusion into the dead zones or recirculation zones before leaving (Charlou, 2014; Villermaux, 1993; Yennoune, 2012). However, no peaks characteristic of a short circuit were observed on the various experimental curves obtained. The shape of the residence time distribution curve (E(t)) varies with the flow rate (Q). A peak appears on the curve as the flow rate increases. The peak becomes more pronounced at very high flow rates and tends to disappear at very low flow rates. These same observations have been reported by (Boskovic and Loebbecke, 2008; Pons and Potier, 2002; Yennoune, 2012) and this result is thought to be linked to the speed at which the particles making up the tracer move. At low flow rates, the speed at which fluid particles move becomes less important. As a result, the particles making up the tracer take longer to cross the filter bed and tend to have different exit times, resulting in a wider and more extended curve. At high flow rates, the drag tends to fade because the tracer does not have time to penetrate by diffusion into the dead zones or recirculation zones and takes preferential paths through (Boskovic and Loebbecke, 2008; Pons and Potier, 2002; Yennoune, 2012).

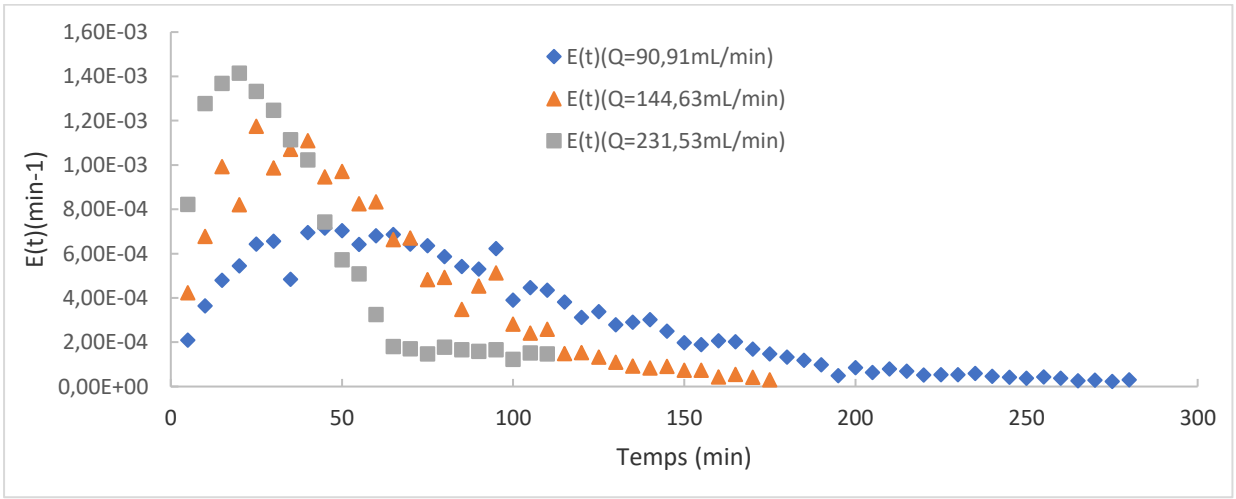

Figure 10 : evolution of the residence time distribution function E(t) as a function of time

3.2.3 Hydrodynamic characteristics

Table 2 shows the influence of the liquid feed rate on the hydrodynamic parameters. Analysis of the table shows that the passage time (τ) and mean residence time ($\overline{(t)}$) vary from 91.53 to 35.93 and from 85.65±0.01 to 34.75±0.06 respectively with the feed rate. These values decrease as the flow rate increases. (Charlou, 2014; Dabaliz, 2002) highlighted the same trend in their work. The passage time (τ) has a value greater than that of the mean residence time ($\overline{t}$) whatever the flow rate. According to (Villermaux, 1993), such an observation is related to the presence of dead zones or recirculation in the biofilter and would confirm the presence of drag at the level of the experimental curves of the residence time distribution function. Calculation of the number of cascade reactors (J) from the experimental results gave low values. When the flow rate increases, the number of reactors (J) tends to decrease from 3.541 to 2.436. (Lieto, 2008; Yennoune, 2012) explain this fact by the type of residence time distribution function curves obtained. The variation in flow rate leads to a variation in the number of cascade reactors. An increase in flow rate leads to a decrease in the number of cascade reactors(J). The same observation was reported by (Alkhaddar *et al.*, 2001) who linked the decrease in the number of cascade reactors (J) to an increase in agitation due to the increase in flow rate. Calculation of the Peclet number (Pe) from experimental results gives values of less than 100. For (Lieto, 2008), these values indicate a flow that is very close to a piston flow. According to (Maldonado, 2005), the low values of the cascade reactor number (J) and the Peclet number (Pe) obtained are linked to greater mixing of the liquid phase and the high porosity of the filter bed. The fact that the number of cascade reactors (J) and the Peclet number (Pe) decrease when the flow rate increases would be attributable to a significant mixing effect of the liquid, or even its uniformisation inside the biofilter (Maldonado, 2005). Also, according to (Villermaux, 1993), this evolution can be explained by the turbulence of the liquid phase leading to a uniform mixture. The liquid flow in the biofilter could easily be described by a J cascade reactor model, as the reduced centred variances (VarC) are all different from 1 and the values of the cascade reactor number (J) and the Peclet number (Pe) obtained are low (Levenspiel, 1999).

Table 2: Hydrodynamic characteristics of the biofilter

Flow rate (mL/min)	Passage time (τ)	Average residence time ($\overline{t}$)	Variance (Var)	Reduced centred variance ($\sigma_\theta^2 = VarC$)	Number of Peclet (Pe)	Number of cascade reactors (J)
90,91	91,53	85,65±0,01	2071,44±22,81	0,28±0,00	7,08±0,08	3,54±0,04
145,63	57,14	54,32±0,03	894,83±1,86	0,30±0,00…	6,59±0,01	3,29±0,01
231,56	35,93	34,75±0,06	495,80±11,68	0,41±0,01	4,87±0,13	2,44±0,06

3.2.4 Monitoring pilot colonisation

Figure 11 shows the evolution of the gross chemical oxygen demand (gCOD) at the pilot plant outlet over time, during recirculation. At the start of recirculation, the value of gross COD is around 200 mg/L. At the end of the 20th day of operation, this value fell below 100 mg/L, decreasing rapidly. After 30 days of operation, the value fell below 50 mg/L and stabilized at around 35 mg/L after 70 days of operation. In terms of monitoring the colonization of the pilot plant, the decrease in the gross chemical oxygen demand (gCOD) at the pilot plant outlet over time, reflected in the shape of the curve, could

be explained by the establishment and development of the purifying biomass. Micro-organisms use sources of carbon, nitrogen, phosphorus, etc. as nutrients for their growth, transforming soluble matter into biomass (Abu-Baker *et al.*, 2014; Hodkinson *et al.*, 1999; Metcalf and Eddy, 2003). The curve has three parts, namely a zone of slight decrease observed between the first and eighth day, a zone of sharp decrease observed between the eighth and thirty-fifth day and a zone of stabilization of the COD observed after the thirty-fifth day. These observations can be explained by the phases of adaptation, exponential growth and maturation of the biomass within the filter bed, corresponding respectively to the zones of slight decrease, strong decrease and a zone of stabilization of the COD (Metahri, 2012). During this adaptation phase, the cell synthesizes the enzymes needed to metabolize the substrate without forming new cells, which would justify a slight decrease in COD. The exponential growth corresponding to rapid cell reproduction would explain the sharp drop in COD. During the maturation phase, growth stops, even though the cells retain a certain amount of metabolic activity, which could reflect a stabilization of the COD value (Touafek, 2012). The stabilization of the COD, which would correspond to the maturation of the purifying biomass, was observed after 10 weeks of operation of the device. This time was reported by (Garcia et al., 2019; Menoret, 2001) for the establishment of a mature purifying biomass in a bio-filtration system.

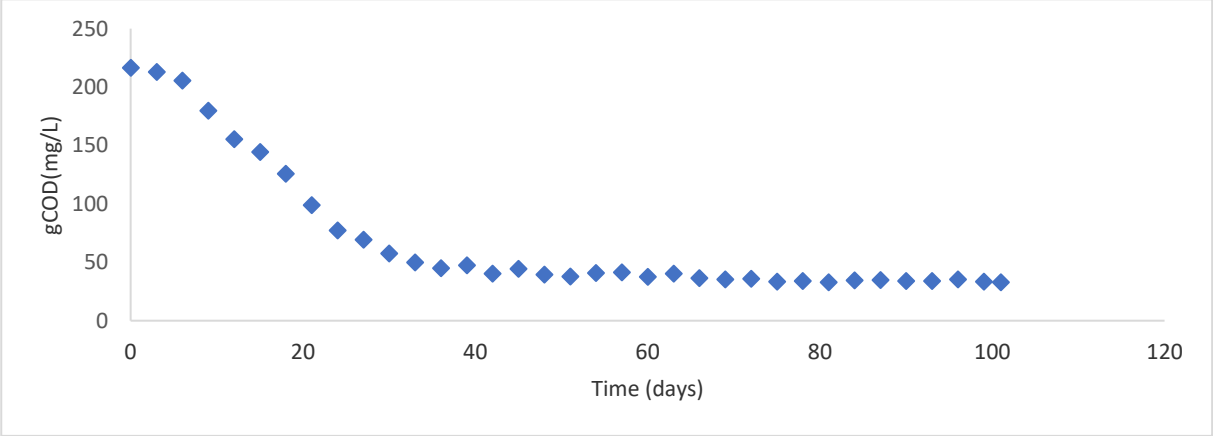

Figure 11 : Changes in gross chemical oxygen demand (gCOD) at the pilot plant outlet over time.

3.3 Monitoring the removal of model compounds in synthetic and doped municipal effluents

3.3.1 Validation of the assay method for model compounds

The distribution of absorbance values followed a normal distribution ($p > 0.05$; Shapiro and Wilk test) and the variances were homogeneous (Ccalculated < Ctabulated, $p < 0.05$; Cochran test). Linear regressions between absorbance and concentrations of diclofenac (DIC) and ibuprofen (IBU) showed a strong correlation (R^2=0.99) (**Figure 12a and 12b**). The linear regressions show significant slopes (Fcalculated > Ftabulated (0.05; 1; 13), $p< 0.05$; Fisher test). The detection limit (DL) and quantification limit (LQ) are 0.7328 and 2.2206 µg/mL for diclofenac and 0.4467 and 1.3537 µg/mL for ibuprofen, respectively.

3.3.2 Abatement of analytes as a function of model compounds

The evolution of the elimination rate as a function of the model compounds (diclofenac (DIC) and ibuprofen (IBU)) is shown in **Figure 13**. The evolution of the removal rates of the two analytes showed no significant difference ($p >0.05$, Mann-Whitney test). The removal rates obtained for diclofenac at the end of the experiments are much higher than those presented in the work of (Petrie *et al.*, 2013;

Verlicchi *et al.*, 2012; Ziylan and Ince, 2011) for activated sludge treatment and also higher than the results obtained by (Altmann *et al.*, 2014; Mailler et al., 2016) for tertiary treatment with activated carbon.

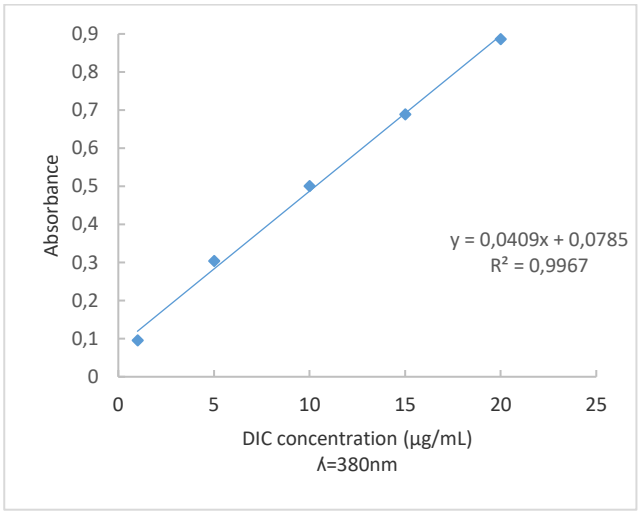

Figure 12a : linear regression between absorbance and diclofenac concentration (DIC)

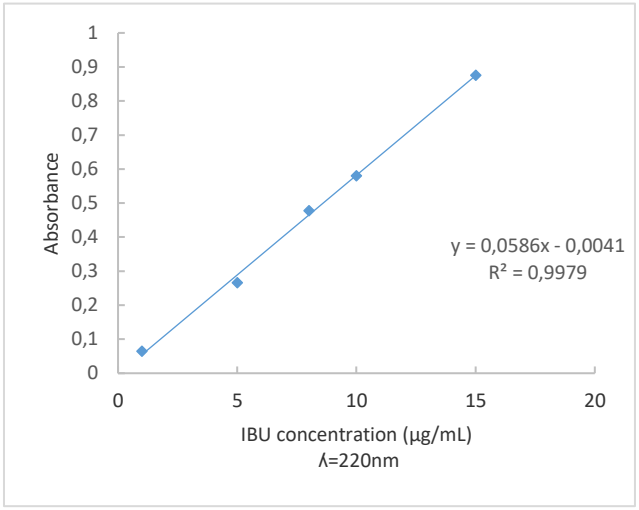

Figure 12b :linear regression between absorbance and ibuprofen concentration (IBU)

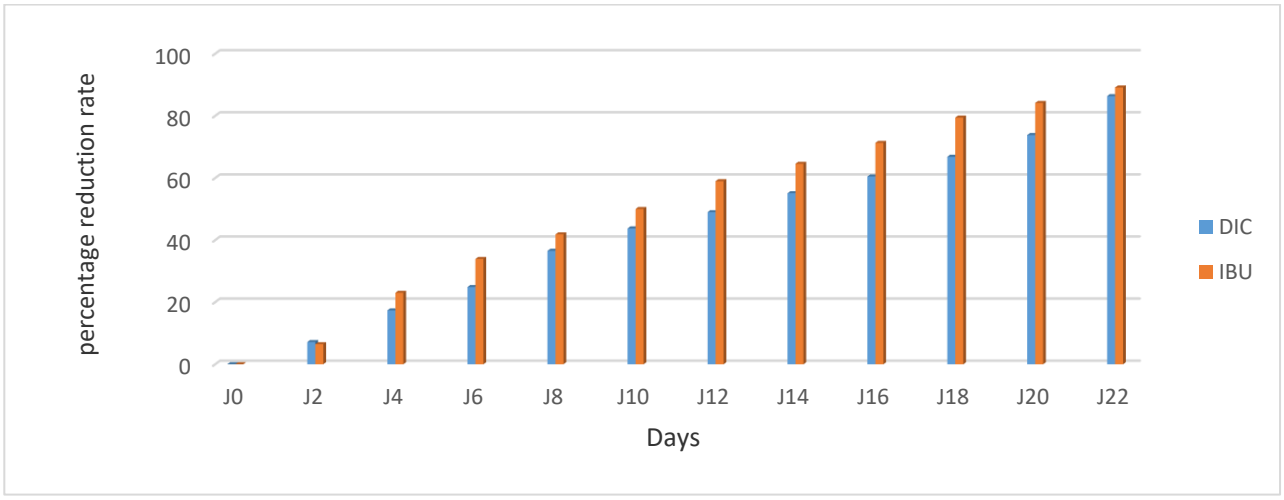

Figure 13 : Changes in elimination rates as a function of model compounds diclofenac (DIC) and ibuprofen (IBU).

Our values are close to those reported by (Altmann *et al.*, 2014; Schaar *et al.*, 2010) for ozonation treatment and lower than those obtained by (Lloret *et al.*, 2010; Samer, 2014; Tran *et al.*, 2010; Zhang *et al.*, 2008) for treatment with ligninolytic fungi (CLL). Similarly, the removal rates obtained in the case of ibuprofen are much higher than those obtained by (Carballa *et al.*, 2005; Kanda *et al.*, 2003; Rodríguez-Rodríguez *et al.*, 2011) during biological filtration of wastewater and activated sludge treatment. This reduction is in line with the elimination efficiencies of ibuprofen during activated sludge treatment presented in the work of (Kanda *et al.*, 2003; Kreuzinger *et al.*, 2004; Ternes, 1998). The satisfactory purification performance obtained is linked to the treatment process used. In fact, biofilters make it possible to ensure a high biomass load per unit reactor volume and to provide higher biodegradation rates (aerobic, anoxic and anaerobic biofilm zones) (Sonawane *et al.*, 2022). In

addition, fixed bacterial cultures are more resistant and resilient in the event of environmental stresses, toxic shocks or drastic variations in nutrient availability (Chen *et al*., 2006; Metcalf and Eddy, 2004). The nature of the material used as a lining support also influences the purification performance observed. The main characteristics, such as specific surface area and porosity, improve the exchange surface between the gas and liquid phases and increase the possibility of micro-niches (Oliver et al., 2016). In addition, organic materials enable an optimum pH to be maintained for the development of microorganisms and for the biodegradation of model compounds (Prado et al., 2006).
Hydrodynamic conditions also influence purification performance. A low flow rate of water and air results in minimal pressure drop and encourages a long contact time between the analytes to be degraded and the purifying biomass (Samb *et al*., 1996; Zidane *et al*., 2006).

3.3.3 Abatement of analytes as a function of biofilters Abatement of analytes as a function of effluents

The evolution of the removal rate of model compounds during three weeks of operation of biofilters A and B is shown in **Figure 14**. The change in analyte removal rates was significantly greater in biofilter B than in biofilter A ($p < 0.05$, Mann-Whitney test).
The height of the fiber layer in the biofilter would strongly influence the analyte removal rate. The fiber fraction has significantly high total porosity and microporosity. An increase in fiber height leads to an increase in void volume and particularly in the number of micropores. This leads to an increase in the specific and exchange surface area. This improves purification performance (Couillard, 1994; Ranarivelo, 2008).

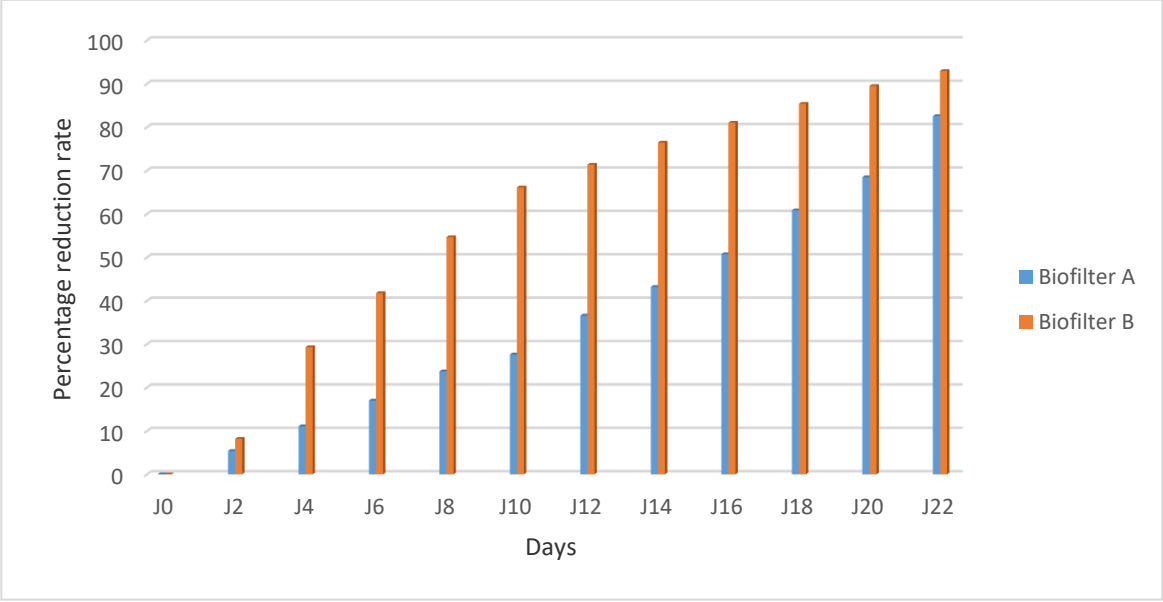

Figure 14 : Evolution of the rate of elimination of compounds as a function of biofilters A and B

3.3.4 Abatement of analytes as a function of effluents

The evolution of the removal rate of model compounds during three weeks of effluent operation (synthetic solution (SS) and doped waste water (DWW)) is shown in Figure 15. Changes in analyte removal rates were significantly greater in the doped waste water (DWW) than in the synthetic solution (SS) ($p < 0.05$, Mann-Whitney test). The type of effluent would influence the rate of analyte removal. The prior presence of purifying microorganisms in the spiked wastewater would have helped the rapid

start-up and enhanced biodegradation of compounds during operation. However, it should be noted that the synthetic solution has no such microorganisms. According to (Martineau, 1999), with natural effluent, there is no lag time and the mineralization rate is maximal. This improvement can be attributed to the presence of microbial flora in the natural effluent. This population, already adapted, will have had the effect of cancelling or reducing the lag time associated with the acclimatization of microorganisms (Sturman et al., 1995).

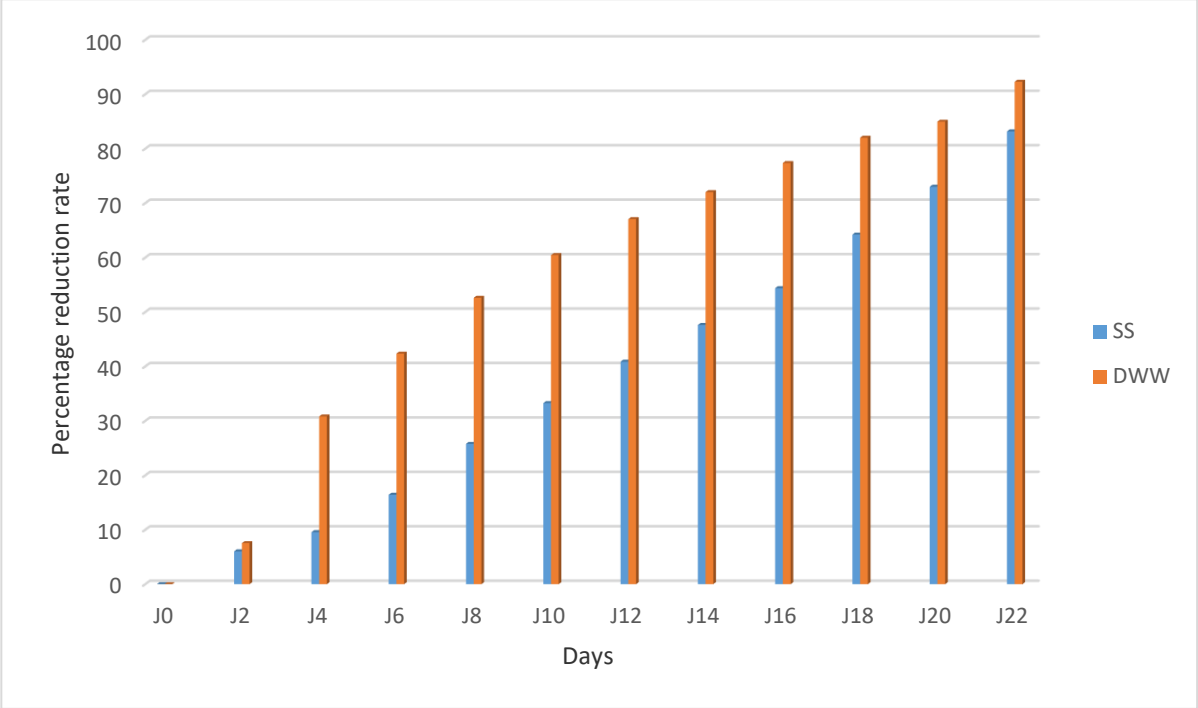

Figure 15 : Evolution of the elimination rate of compounds as a function of the effluents (synthetic solution (SS) and doped waste water (DWW))

Conclusion

The fibers and shells prepared have a porosity of over 50%, facilitating liquid percolation. The biofilter can be described as a J cascade reactor model. The filter bed formed encouraged the development and maturation of a purifying biomass. As a result of this study, biofiltration on a bed of fibers and shells was a very effective treatment process for removing diclofenac and ibuprofen from spiked wastewater, due to the rapid adaptation of the microbial flora already present in the medium. The rate of elimination of diclofenac and ibuprofen increases with the height of the fiber layer in the biofilter. The rate of elimination of diclofenac and ibuprofen also depends on the type of effluent.

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Disclosure statement: *Conflict of Interest:* The authors declare that there are no conflicts of interest.
Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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