INSTITUTO POLITÉCNICO DE BRAGANÇA
Escola Superior de Tecnologia e Gestão

Biosorption of pharmaceuticals from wastewater using Moringa *oleífera* as biosorbent

De Olivera Agustina Raquel

Thesis report submitted to

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Supervisors:

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A mi querida abuela, mi “BABA”.

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ABSTRACT

Pharmaceuticals as emerging contaminants have become one of the most controversial environmental issues at global scale. Over the years, there has increased the presence of antibiotics and anti-inflammatory drugs inside rivers, lakes, oceans and even inside drinking water streams. The waste-water treatment plants (WWTPs) lack the necessary technology to remove a concentration between the range ng/l-mg/l and therefore, the need to develop new methods able to remove contaminants in an effective, low cost and environmental friendly way arises. The term "Biosorption" appears as a possible solution. It is a separation process inside the area of Chemical Engineering that follows the same fundaments of adsorption with the only difference that uses biodegradable materials as adsorbent (biosorbent). The present work focuses on studying the potential adsorption capacity of Moringa *oleífera* (MO) to remove Diclofenac (DCF) and Oxytetracycline (OTC) from waste-water.

After different experiments, it was found that in both cases (DCF and OTC) the adsorption processes present high pH dependence, the first one governed by the mechanism of chemisorption while the second one could be controlled by diffusion of the particles between both surfaces. Equilibrium isotherms were determined by Langmuir, Freundlich, and Sips models. In both cases, the adsorption process was best described by the Freundlich model (R^2>0.97). Kinetics essays were described by pseudo-first-order, pseudo-second-order, and Intraparticle diffusion models. The experimental data of OTC and DCF removal were best fitted by Intraparticle Diffusion (R^2>0.95) and pseudo-second-order (R^2>0.93) model respectively. It was possible to obtain a removal percentage of 88% for DCF at a pH of 2 and 50% for OTC at a pH of 10, indicating that MO represents a viable option for the removal of drugs present in contaminated water.

Keywords: Pharmaceuticals, adsorption, biosorption, Moringa *oleífera*, biosorbent, Diclofenac, Oxytetracycline.

RESUMEN

Los fármacos en su papel de contaminantes emergentes, se han convertido en uno de los problemas ambientales más preocupantes a escala global. Con el pasar de los años, la presencia de antibióticos y antiinflamatorios dentro de ríos, lagos, océanos e inclusive en corrientes de agua potable, ha ido aumentado. Las plantas de tratamiento de aguas residuales (ETARs) aún no cuentan con los métodos adecuados para remover concentraciones dentro del rango de ng/l-mg/l y por ello, surge la necesidad de desarrollar nuevas tecnologías que sean efectivas, de bajo costo y amigables con el medio ambiente. Como posible solución nace el término de "biosorción". La biosorción es un proceso de separación dentro del área de Ingeniería Química que sigue los mismos fundamentos de la técnica de adsorción, con la única diferencia que utiliza materiales biodegradables como adsorbentes, conocidos como "biosorbentes".

Es de gran interés en el presente trabajo, estudiar las características, principales propiedades y capacidad de adsorción que posee las cáscaras de la planta Moringa *oleífera* (MO) para la remoción de Oxitetraciclina (OTC) y Diclofenac (DCF) presentes en aguas residuales. MO es reconocida mundialmente debido a sus propiedades anti-microbiales, nutricionales y coagulantes, mientras que DCF y OTC son considerados dos de los fármacos con mayor contribución a la contaminación del medioambiente.

A través de diferentes ensayos, se encontró que en ambos casos (DCF y OTC) se trata de procesos altamente dependientes de pH con la diferencia que el primero es gobernado por el mecanismo de quimisorción mientras que el segundo es controlado bajo la difusión de partículas entre ambas superficies.El modelo de Freundlich (R^2>0.98) ha logrado, en ambos casos, el mejor ajuste de los datos empíricos. Mientras que, en modelos de cinética de adsorción, el modelo de Difusión Intraparticular presentó el mejor ajuste para el proceso de remoción de OTC (R^2>0.95) y el modelo Pseudo-Segundo-orden, para la adsorción de DCF (R^2>0.93). Se ha logrado remover hasta un 88% de DCF a un pH de 2 y hasta 50% de OTC a un pH de 10, indicando que MO representa una opción viable para la remoción de fármacos presentes en aguas contaminadas.

Palabras claves: fármacos, adsorción, biosorción, Moringa *oleífera*, biosorbente, Diclofenac, Oxitetraciclina.

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INTRODUCTION

2 INTRODUCTION

Over the years, the water surfaces have been used for drinking water, food production, industrial maintenance, energy, hygiene, and recreation. They are considered one of the main sources of humans and animal's living [1]. Water surfaces pollution has become a worldwide issue. Since the industrial revolution, the factories began to throw chemical waste inside rivers, lakes, and streams [2].

Until now, "emerging contaminants", especially pesticides and pharmaceuticals, are the residues with the biggest environmental impact. The pharmaceuticals, particularly antibiotics and anti-inflammatory drugs, are the ones which have caught more attention. Due to its increasing sales, consumption and potentially adverse effect on aquatic surfaces, they have been included inside the "watch list" of the emerging pollutants in water by UNESCO in 2017 [3].

The present work focuses on the removal of the antibiotic Oxytetracycline (OTC) and the anti-inflammatory Diclofenac (DCF). The first one considered the most used antibiotic in the veterinary area and the second one, the most common pharmaceutical to relieve human pain. Even though they are found at trace levels, it is enough to harm human and animal health. However, as it is a recent issue compared to other types of pollutants, official documents from the government that specify the contaminant's limit values are not yet available.

In order to minimize their concentration, there is a long list of non-conventional methods that achieves acceptable results, such as adsorption, membrane technologies, and advanced oxidation process, [1]. However, it is the lack of advanced technologies and methods to remove the pollutants which makes the theme a new challenge for the scientific community.

The adsorption is the most common separation process; it is a low cost and simple operation but is not environmental friendly. For this reason, it has been created the term "biosorption". It is a removal process that follows the same fundaments of the conventional adsorption process with the only difference that uses biodegradable material as adsorbent [4].

The main purpose of the work is to perform the biosorption process to remove Oxytetracycline and Diclofenac from water using Moringa *oleífera's* shells as biosorbent.

3 GENERAL OBJECTIVE

Evaluate Moringa *oleífera*'s shells capacity as a possible biosorbent to remove Oxytetracycline and Diclofenac from water through the biosorption process.

4 SPECIFIC OBJECTIVES

- Characterize the main functional groups of Moringa *oleífera* shells before and after adsorption.
- Characterize the pH dependence of the pharmaceuticals (DCF and OTC).
- Evaluate the optimal conditions of the adsorption process (temperature, pH and initial concentrations).
- Find the equilibrium isotherm model (Langmuir, Freundlich, and Sips) which presents the best fit of the empirical data.
- Study the adsorption kinetics of the process through different models (Pseudo-first-order, pseudo-second-order and Intraparticle Diffusion model).
- Define the adsorption mechanism for every pharmaceutical removal process.

5 STRUCTURE OF THE WORK

Basically, the work is divided into five chapters. The first one tries to summarize the main problem in question and the possible solution to it through a brief introduction, general and specific objectives. In the second chapter is developed the state of art, all related to the background of water surface's pollution, the pharmaceutical contribution, the principal characteristics of the adsorbates (Diclofenac and Oxytetracycline), the conventional treatments used until now, the removal process purposed (biosorption) and the main properties of the Moringa *oleífera.*

The third chapter presents the material and the methods used in the laboratory to achieve the objective of the work.

The fourth chapter contains the results and the main conclusion obtained from the analytical work. It includes the characterization of the adsorbent and adsorbates, the study of every condition (pH, temperature, concentrations and stirring speed) and the adjustment of empirical data to the different models.

In the fifth and last chapter, there is the conclusion obtained from the results of the fourth chapter as well as some recommendations for future research.

STATE OF THE ART

6 STATE OF THE ART

6.1 Water surface pollution by emerging contaminants

The water pollution became a worldwide problem that has led to develop new and advanced technologies to detect the presence of emerging contaminants. The emerging contaminants are defined as unknown pollutants that were not recognized as a threat to the environment. This new term involves all those products or compounds which their presence is not new, they are of daily use but its toxicity was not taken into account until now [5], some examples are, drugs of abuse, heavy metals, pharmaceuticals, chloroalkanes, polar pesticides, brominated flame retardants, detergents and metabolites of degradation products [1].Due to its high production level and consume, its presence in the environment grows as the water surfaces pollution does. The main contamination sources are the effluents from industries, homes, commercial, hospitals, livestock and agricultural area. Figure 1 shows how all the residues from the pollution focus finish in the wastewater treatment plant (WWTP) and then into the water surfaces such as lakes, rivers, oceans and also to the drinking water streams [6].

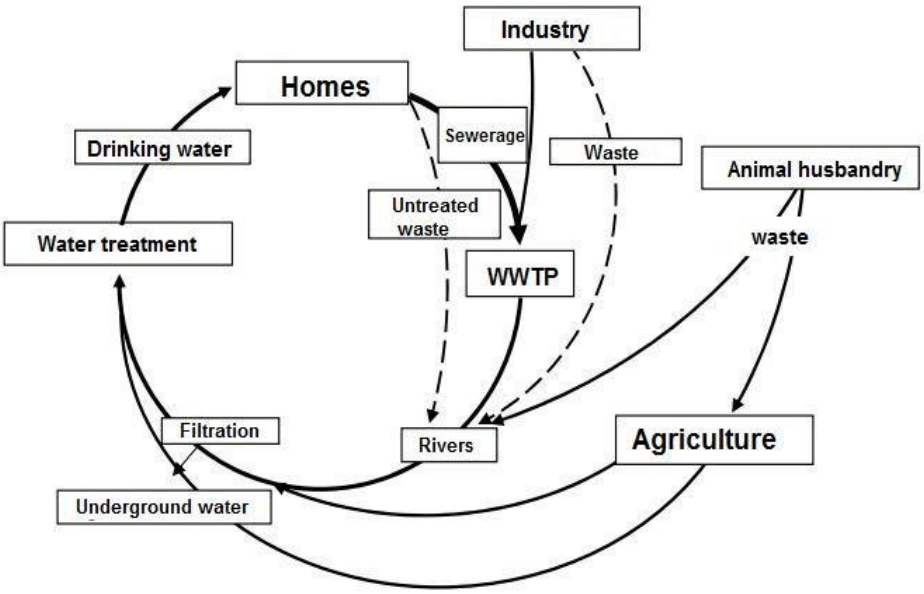

Figure 1 Water Cycle. Main sources of water pollution.

Montes Perales, J. (2016). Design of an installation for antibiotic recovery of a process stream by ultrafiltration. Valencia, España.

6.2 Pharmaceuticals as water surface contaminants

Pharmaceuticals are synthetic or natural chemical compounds used for diagnosis, treatment or prevention in human and animal diseases [7]. The pharmaceuticals are considered big molecules with complex chemistry properties, structure, functions, and high pH dependence, thus they can be neutral, charged negatively, positively or be under zwitterions form, making its comprehension more difficult compared to the other emerging contaminants. Within them, are found the antibiotics, analgesics, anti-inflammatories, B-blockers, cytostatics agents, hormones steroids and lipid regulators (Table 1) [1].

Table 1 Most found pharmaceuticals into the environment [1].

PHARMACEUTICALS	**ANTIBIOTICS**	Penicillin Tetracyclines Trimethoprim Sulfamethoxazole Erythromycin
	ANALGESIC AND ANTI-INFLAMMATORIES	Aspirin Diclofenac Ibuprofen Paracetamol Naproxen Phenazone
	HORMONES AND STEROIDS	17B- Estradiol Estrona Dietiltilbestrol
	CYTOSTATIC AGENTS	Ciflofosfamide Ifosfamide
	DIURETICS	Furosemide
	ANTISEPTICS	Carbamazepine
	SEDATIVES	Diazepan
	LIPID REGULATORS	Benzyfibrate Phenofibrate Clofibric acid
	B-BLOCKERS	Atenolol Propranolol Metoprolol

It has been surprising how pharmaceuticals products have become one of the greatest contributions to environmental pollution. On a global scale, the European Union took second place of pharmaceutical sales with approximately 25% destined to human consumption, while 31% has been destined to the veterinary area [8]. In Portugal, according to the National Health Services in the year 2017, there has been a rise in the amount of consumption of medicament and an increase in the quantity in pharmacies [9]. It has also been shown that lipid regulators, anti-inflammatories and antibiotics were found in influents (1841.1, 1339.4 and 330.7 mg/day/100 inhab. respectively) and effluents (22.3, 15.0 and 68.6 mg/day/100 inhab. respectively) of Portuguese's WWTPs [8].

Near 3000 active pharmaceutical products are authorized in the EU market [8]. As consumption grows, its presence in the environment also does. Table 2 presents a list of the mean concentration values of the pharmaceutical most found in Europe's water surfaces.

Table 2 Concentrations of different pharmaceuticals in European water surfaces.

Pharmaceutical	Median concentration	Water Surface	Source
Diclofenac	424 ng/l	Sewage treatment plant	World Health Organization (2011)
Ibuprofen	3086 ng/l	Sewage treatment plant	
	826 ng/l	Stream or river water	
Trimethoprim	271 ng/l	Sewage treatment plant	
	9 ng/l	Stream or river water	
Meprobamate	40 ng/l	Drinking water	
Naproxen	450-1840 ng/l	WWTPs-STP	
	<0.3-1.46 ng/l	Freshwater-river canals	
Ketoprofen	225-954 ng/l	WWTPs-STP	Gavrilescu, M., (2014)
Carbamazepine	130-290 ng/l	WWTPs-STP	
Atenolol	1720 ng/l	WWTPs-STP	
	314 ng/l	Freshwater-river canals	

The pharmaceuticals have different routes to get into the environment; the majority of them are excreted by the urine and the feces of humans and animals, becoming the domestic,

agricultural and livestock area, three of the main sources of contamination. As can be observed in Figure 2 other two main sources are the effluents from the hospitals and the pharmaceutical industries ending in the WWTP which becomes the most important source of pollution. Due to its low efficiency to minimize the concentration of the solute, the resulting sludge after the treatment continues with high percentages of the drug's presence. The effluents of the plant are also discharged to water surfaces and drinking water streams, making it a cycle of contamination [10].

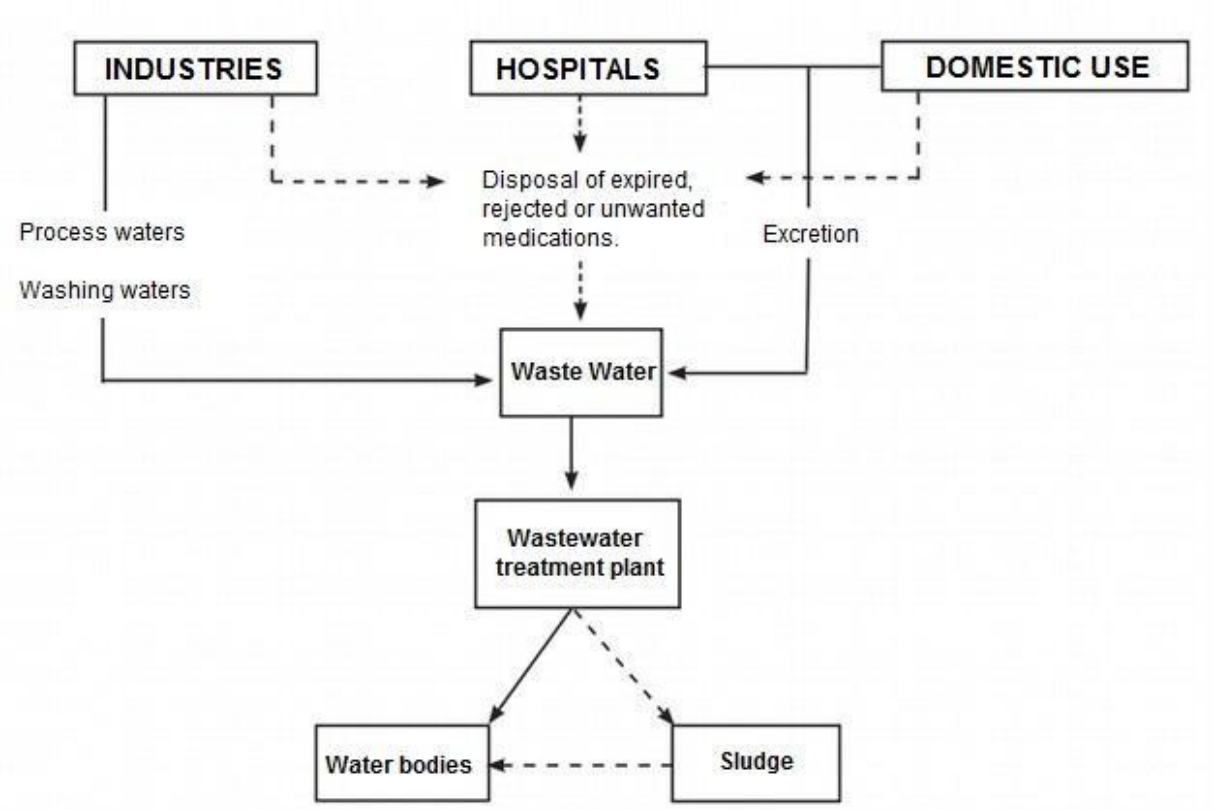

Figure 2 Diagram of the known pharmaceuticals contamination pathways [1].

In spite of the great concern that has been developed about the contribution of the pharmaceuticals into the environmental contamination, non-official documents have been developed by the government with the established limits of permitted concentration in the water surface.

6.3 Description of the pharmaceuticals

6.3.1 Tetracyclines

The tetracyclines are bacteriostatic, bactericidal agents of large spectrum and able to fight organisms such as Gram^{+} and Gram $^{-}$bacterias, mycoplasma, rickettsias, chlamydiae, and

protozoan parasites. Are considered the group of antibiotics most used in the area of agriculture and veterinary because of its effectiveness and low cost [11] [12].

The group of tetracyclines (Figure 3) is obtained by fermentation of the bacteria *Streptomyces aureofaciens* and *Streptomyces rimosus* (tetracycline, chlortetracycline (CTC) and oxytetracycline (OTC)), by semi-synthetic way (demeclocycline, rolitetracycline and methacycline) or by a pure synthetic process (doxycycline and minocycline) [13]. They are divided according to the duration of their activity, being able to be short, medium or long. They present similar antimicrobial properties but big differences in relation to the activities of absorption, metabolism, distribution, and excretion. They constitute an antibiotic family that inhibits the protein synthesis of microorganisms through the breaking of the binding of the transfer RNA to the ribosome [12] or also by its bactericidal potential, killing the bacteria [14].

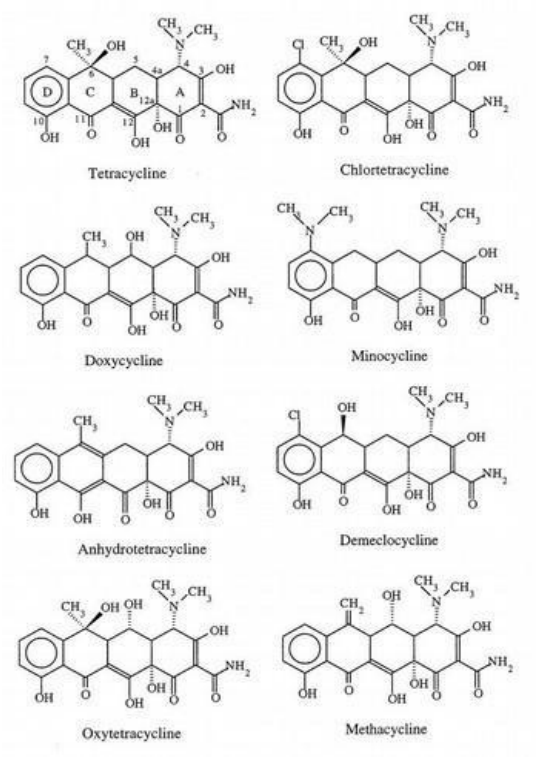

Figure 3 Structures of the group of Tetracyclines.

Vartanian, V.H., Goolsby, B. &Brodbelt, J.S. J Am Soc Mass Spectrom (1998) 9: 1089.

Over the years, it has been detected an increase of tetracycline's concentration in water streams and wastewater treatment plants (WWTP). Due to the fact that the antibiotics are used as a veterinary drug and it has a low absorption in animals, levels of OTC are

eliminated by them to the environment through their urine and fecal matter ending up in streams of water. Table 3 summarizes the environmental concentration values of the tetracycline family. Most of them are measured in μg/l [13].

Table 3 Concentration of the Tetracycline family in water surfaces of Europe. [14],[15],[16],[17].

Antibiotic	Mean concentration (ng/l)	Matrix	Country	Sources
Doxycycline	8100	Hospital effluent	Portugal	Barceló et al, 2012
	0,068 ug/l	Water surface	Ghana	Danner, Robertson, Behrends& Reiss, 2019
	0,047 ug/l		China	
Minocycline	531.700-3.177.900	Hospital effluent	Portugal	Barceló et al, 2012
	1,70 ng/l	Water surface (River)	China	Ying Li et al, 2018.
	12,96 ng/g	River's sediment	China	
Tetracycline	0,03 ug/l	Water surface	Ghana	Danner Marie C. et al, 2019
	0,114 ug/l		China	
	1 ng/l		UK	
	0,228 ug/l		Spain	
	0.008		Luxembourg	
	6-531,7 ug/l	Hospital effluent	Coimbra,Portugal.	Pena A. et al, 2010.
	95,8-915,3 ug/l	WWTP		

6.3.2 Oxytetracycline (OTC)

Within the tetracycline group, the most known and used one is the Oxytetracycline. The OTC or (4S, 4aR, 5S, 5aR, 6S, 12aS) -4- (Dimethylamino) - 3,5,6,10,11,12a-hexahydroxy-6-methyl-1,12-dioxo-1,4,4a, 5,5a, 6,12,12a-octa-hydro tetracene-2- carboxamide is an antibiotic produced from the fermentation of the bacteria *Streptomyces rimosus* (Figure 4*)* [19]. It is used in areas of agriculture, livestock, veterinary medicine, and aquaculture activities.

It can be found as Hydrochloride Oxytetracycline, Calcium Oxytetracycline or Agricultural Terramycin [20]. Table 4 summarizes the principal physicochemical characteristics of the Hydrochloride Oxytetracycline.

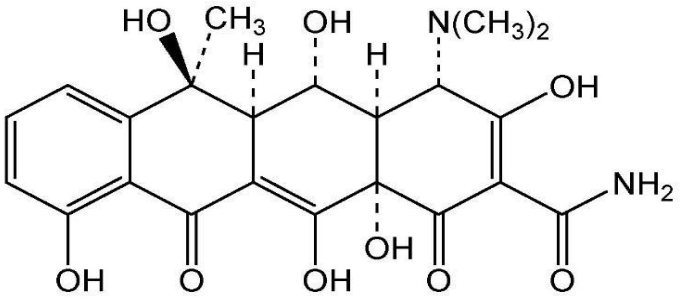

Figure 4 Chemical structure of Oxytetracycline.

Silva Oliveira, C. (2013). Estudo da degradação eletroquímica da oxitetraciclina (Mestrado). Universidade da Beira Interior Ciencias.

Table 4 Physicochemical properties of Oxytetracycline.

Physicochemical properties of Oxytetracycline	
Molecular formula	$C_{22}H_{24}N_2O_9.HCl$
Molecular weight	496,897 g/mol
Water solubility (25°C)	313 g/l
Melting point	180°C
Density (20°C)	1,634 g/cm3
Log $Kow_{(octanol/water)}$	-1.12
pKa	pka_1= 3,27; pka2= 7,32; pka3 = 9,11
Physical appearance	Yellow powder, odorless and bitter

Andrade Díaz, C. (2018). Removal of oxytetracycline present in aqueous solutions using rice husk ash (Master). Lieira, Portugal.

The OTC is an amphoteric molecule, constituted by a complex structure of four rings with different ionizable functional groups. Its structure as its chemical properties is strongly linked to the changes in pH. Theoretically, it has three pKa values and four ionization states (H_3OTC^+, H_2OTC^+, H_2OTC, and OTC^{-2}) (Figure 5) [19]. The molecule presents a positive charge when pH<pka_1, a negative charge when pH>pka_2 and two negative charges when pH>pka_3. In the pH range between pka_1 and pka_2, the OTC is found as a neutral molecule (Zwitterión) [19] [21].

Oxytetracycline is considered a complex molecule because, in addition to being pH-dependent, it is susceptible to photodegradation, it is unstable at alkaline medium and presents quelation power.

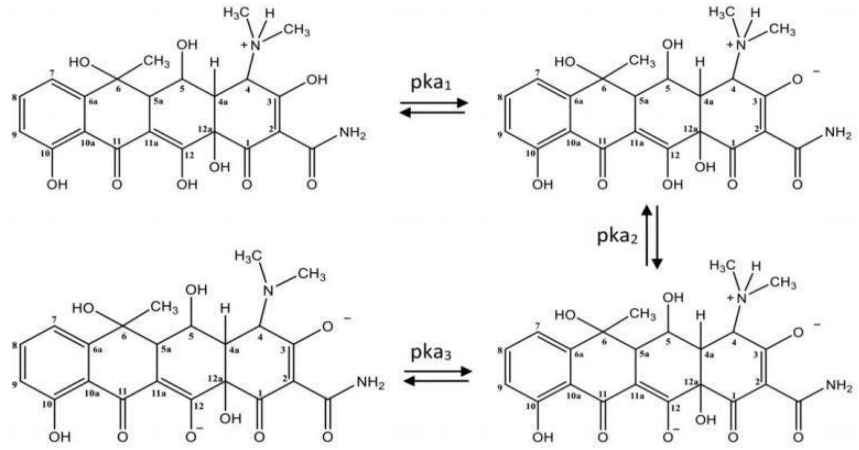

Figure 5 Ionization states of OTC [19].

6.3.2.1 Environmental effect of Oxytetracycline on water

This antibiotic can get into the aquatic environment through sewage system due to excretion by humans and by farm's residues, the OTC and other antibiotics are considered of low absorption inducing its liberation to the environment through the animals feces [11], another contamination source are the livestock residues, the OTC is highly demanded for growth promotion [11]. The majority of the residuals finish at the conventional WWTPs, which are not designed to remove the low concentration of antibiotics, becoming in this way, in another source of environmental pollution.

The presence of Oxytetracycline has been detected in soil, hospital residues, WWTPs, water surfaces (rivers and lakes) and even in drinking water around the world [19]. For example, in USA it was detected between the range of 0,07-1,34 µg/l from surfaces water and a mean concentration of 0,34 µg/l from natural water [13], in the UK it was found values higher than 0,34 µg/l from water surfaces and 0,5 µg/l from water streams [13]. In the river Weihe from China, it was measured a mean concentration of 16,13 ng/l into the water and 20,60 ng/g into the river's sediments [17]. In Asia, it was found a maximum value of 484 µg/l into the river Xiao [16]. In Ghana, a mean concentration of 0,026 µg/l and 0,68 µg/l, 0,43 µg/l and 0,007 µg/l from water surfaces of France, Croatia and Luxembourg respectively [16].

The Oxytetracycline has been declared as a toxic residue for aquatic organisms, humans and animal's health [22] [23], high amount of this antibiotic could have negative consequences on the gastrointestinal tract, skin, central nervous system and in accumulating calcium organs like as bones and teeth [23].

Until now, it has been developed many types of methods to remove the OTC from the water, such as Hybrid carbon membrane which reached almost 99% of removal [24], magnetic ion-exchange resin [25], Reverse Osmosis membrane with a removal percentage higher than 90% [26] and adsorption by activated charcoal, also showing a strong adsorption capacity [27].

6.3.3 Diclofenac

Diclofenac also known as (2 [(2,6-diclorophenyl) amino] phenylacetate) is a nonsteroidal anti-inflammatory drug (NSAID) (Figure 6). It is used to relieve pain, usually in the treatment of rheumatoid arthritis, osteoarthritis, musculoskeletal injuries and post-surgery analgesia for humans and animals [28].

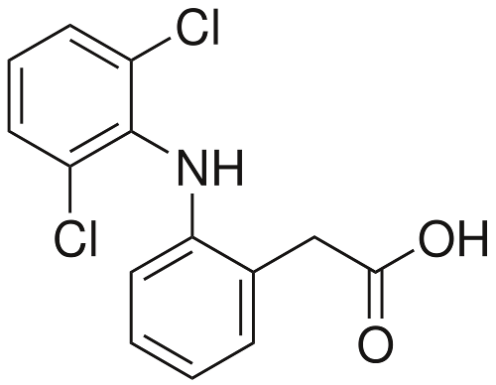

Figure 6 Chemical structure of Diclofenac.

Gazdová, K. (2017). Degradation of anti-inflammatory drug diclofenac in sewage water. ActaChimica Slovaca,10(1), pp 1-5

The most common way to find it is under the following names, Acoflam, Algosenac, Almiral, Ana-Flex, Antiflam, Arcanafenac, Arthrex, Arthrifen, Arthtotec, Diclabeta, Dicloabac, Diclodoc, Diclofenac-Ratiopharm, Diclofenbeta, Diclomex, Diclowal, Dicuno, Difen, Diklotab, Dolgit-Diclo, Eese, Effekton, Jutafenac, Monoflam, Motifene Dual, Sigafenac and Voltaren [29].

Usually, is commercialized as Diclofenac Sodium (DCFNa) or Diclofenac Potassium. Table 5 shows the principal physicochemical characteristics of DCFNa.

Table 5 Physicochemical properties of Diclofenac Sodium.

Physicochemical properties of Diclofenac Sodium	
Molecular formula	C14H10Cl2NNaO2
Molecular weight	318,13 g/mol
Water solubility (25°C)	50 mg/ ml (water); 7,4-5,15 mg/ml (PBS); 1,2-0,0012 mg/l (pH).
Melting point	275-277°C
Density (20°C)	1,634 g/cm3
pKa	Pka_1= 4,15
Physical appearance	White powder, odorless and bitter

Kaur, M,. (2014). Diclofenac Sodium Adsorption onto Montmorillonite: Adsorption Equilibrium Studies and Drug Release Kinetics. Adsorption Science & Technology. 32. pp.365-388

6.3.3.1 Environmental effect of Diclofenac on water

The anti-inflammatory drugs are one of the most used pharmaceuticals around the world and also one of the most detected in the environment at concentration values of ng/l-mg/l.

Within the group of the NSAIDs, the DCF is considered the most popular one. It has been found that about 940 tons/year of diclofenac is consumed at a global scale and could be a big possibility that the number has crossed the 1000 tons [30]. In Europe, especially in Portugal, DCF is established as the most sold anti-inflammatory drug [31]. The total consume for Europe is estimated at about 180 tons/year. Also, it has been published, in other countries, such as China, India and Brazil's consume more than 60 tons/year [30].

As much the DCF consumption increases, the probability to find it in water surfaces (lakes, rivers or ocean), sediments and sludge, too. A significant level of Diclofenac could be harmful to humans and animal's health causing cardiovascular problems [30] [31].

Although there is a great difficulty to establish the typical values of DCF concentration, some sources have published results from different studies to have an idea of the concentration values in the environment, for example, a DCF concentration range of 0,44

and 7,1 µg/l was found in municipal wastewater and a maximum of 6,88 µg/l in hospital wastewater and a value of 203 µg/l from pharmaceutical factories, all measured in South Korea [33]. In Pakistan's rivers, a concentration of 4900 ng/l and a maximum of 1030 ng/l in water surfaces in Germany have been detected. [30]. Nowadays, DCF residues are detected in almost all European countries and that is why the European Commission has established as maximum allowable concentration an annual average value of 0,1µg/l for inland surfaces waters (rivers, lakes and related artificial or modifies water bodies) and 0,01 ug/l for other surface waters [34].

Given the need to reduce DCF values below those established, advanced methods have been used, for example, membrane filtration, ozonation, oxidation and electro-dialysis, obtaining as results an acceptable percentage of removal but also, a high production cost and the formation of toxic sub-products [32].

6.4 NON-CONVENTIONAL REMOVAL METHODS

The challenge of removing low concentrations of pharmaceuticals from water surfaces has led to the development of numerous treatments, such as physicochemical, biological and advanced treatments [1].

Physicochemical treatments: within this group are the traditional removal methods, such as coagulation, flocculation, oxidation process by ozone, adsorption with activated carbon and chlorination. According to the bibliography, good removal percentages were obtained by the three last ones [1]. The oxidation process by ozone is considered an important technology to remove organic compounds like pharmaceutical and personal care products [35], because the hydroxyls (OH) groups released during the process, can react in a non-selectively way with the pharmaceuticals, allowing a better removal of those products that have a complex chemical structure. The chlorination is a simple and low-cost method to remove micro-pollutants from the water; it presents a good removal capacity. The main problem, also in the case of oxidation, is that both processes can produce sub-products with an unknown effect. These methods are recommended for the removal of organic compounds with a low percentage of carbon [36]. At least, it is the adsorption process by activated carbon which is considered the most effective physicochemical treatment, its only problem is that the adsorbent runs out fast and its regeneration is an expensive technique.

Biological treatments: they are considered the most suitable technology for wastewater treatment plants; however, they do not produce a complete removal of all the emerging contaminants. In this group can be found treatments such as biological filters and activated sludge systems [1] [36].

Advanced treatments: are considered the most adequate methods to remove emerging contaminants. It can be found the ultra-filtration, nano-filtration, reverse osmosis, membrane technologies, and oxidation processes [1].

The membrane process presents numerous advantages such as high separation efficiency, the ability to separate compounds that no other technique can, as being environmentally friendly and energy-efficient [37]. On the other hand, it is the oxidation process that has been named as one of the most effective methods to remove pharmaceuticals, like Diclofenac, Carbamazepine, and Ibuprofen [36]. Within the group, there is an advanced oxidation process by ozone with hydrogen peroxide (O_3/H_2O_2) and solar system combined with photocatalysis and TiO_2/H_2O_2 and O_3.

6.5 ADSORPTION PROCESS

Adsorption is a surface process and it occurs when molecules, atoms or ions from a gas or liquid zone travel and get stocked to the surface of a solid. This addition can be produced by physicals forces (physisorption) or by chemical bonds (chemisorption) [38] [39] [40]. The adsorbed solute (G or L) is known as adsorbate and the solid, as adsorbent (Figure 7).

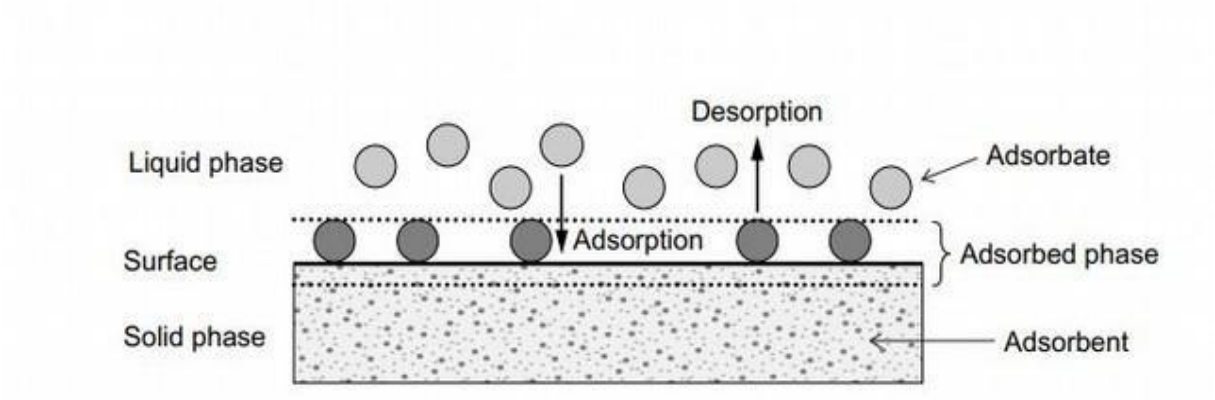

Figure 7 Description of the adsorption process

Worch, E. (2012). Adsorption Technology in Water Treatment. Dresden, Germany.

In this type of process, is necessary to analyze three different situations [40]:

1) Adsorption equilibrium, when the number of molecules arriving at the solid surface is the same as the number of molecules that are leaving.

2) Adsorption kinetics, to evaluate the velocity of the process.

3) Adsorption thermodynamics, to study the influence of the interfacial energy of the system at the equilibrium.

6.5.1 Factors that influence the adsorption process

Within the long list of factors that have influence in the adsorption process, it can be mentioned:

Type of adsorbent: to be considered a good sorbent, it should have high selectivity; favorable kinetic and transport properties for quickly adsorption; Chemical and thermal stability; strong mechanical properties to avoid erosion and crushing; capacity to be regenerated and low cost [39].

Nowadays, exists hundreds of commercial adsorbents but the most known ones are the zeolite, silica gel, activated carbon and alumina because of their high porosity and area/volume relation that allows them to obtain high removal percentages [41].

Adsorbent's granulometry: it was found that the effectiveness of the process increases when the size of the grain decrease and that is because there is an inverse proportionality between the size of the adsorbent and the load losses that they generate, it means that at a smaller size, the load losses increase and the effectiveness as well [40].

Temperature: the adsorption is considered an exothermic process, it means when the temperature increases, the adsorption capacity decrease. However, it does not happen in all the cases, when the process is governed by chemisorption, the system shows proportionality between the temperature and the efficiency [40].

Initial concentration of the adsorbate: as the initial adsorbate concentration increases, the adsorption capacity decrease and it is because the active sites of the adsorbent get saturated. It depends on the sorbent's nature to determine the maximum adsorbate concentration they can support [42].

Types of adsorption processes: It depends on the types of interactions between the solute and the adsorbate, the process of adsorption can be physical or chemical. If the adsorbate is attracted by weak Van der Waals forces (dipole-dipole interactions, dispersion and induction forces) towards the adsorbent, the process is known as physisorption, otherwise, it is considered as chemisorption because involves strong chemical bonds [43].

Table 6 summarizes the main differences between chemisorption and physisorption.

Table 6 Principal characteristics of Chemisorption and Physisorption mechanisms

CHEMISORPTION	PHYSISORPTION
The adsorption enthalpy is higher than 50 kJ/mol.	The adsorption enthalpy is lower than 50 kJ/mol.
Low temperatures	High temperatures
Weak interactions (dipole-dipole, Van der Waals)	Strong chemical interactions, as covalent bonds.
Adsorption takes place in monolayer or multilayer.	Adsorption takes place only in monolayer.
Low activation energy	High activation energy
Rapid, non-activated and reversible.	Reversible only at high temperatures.
No dissociation of adsorbed species.	Increase in electron density in the adsorbent-adsorbate interface.

Vesna V.,. (2013). Adsorption of azo dyes on polymer materials. Hemijska industrija.67(6) pp. 881–900.

6.5.2 Adsorption isotherms

An adsorption isotherm is defined by the equilibrium relationship between the concentration of the adsorbate adsorbed into the adsorbent surface (qe) and the concentration of the solute into the liquid phase (Ce) at a given condition [44].

The equilibrium isotherms are considered a powerful tool in the practical design and operations of adsorption processes. The most known and used are Langmuir, Freundlich, Sips, Tempkin, Toth, Dubinin-Radushkevich (D-R), Frumkin, Harkins-Jura, Smith, and Brunauer-Emmet-Teller (BET) [45] [41].

In this work, in order to analyze and fit the experimental data, it will be used the Langmuir, Freundlich, and Sips model.

6.5.2.1 Langmuir Isotherm

It was originally proposed by Langmuir in 1918. The model assumes the formation of a monolayer of the adsorbate on the homogenous adsorbent surface and it only takes place in a specific site within the adsorbent. Also assumes uniform energies of adsorption into the surface and no transmigration of adsorbate in the plane of the surface [41] [46].

The isotherm can be described by Equation 1:

$$q_e = \frac{qo \cdot KL \cdot Ce}{1 + KL \cdot Ce} \qquad \text{Equation 1}$$

Where q_e is the amount of adsorbate adsorbed per gram of adsorbent at the equilibrium (mg/g), C_e is the equilibrium concentration of adsorbate (mg/l), q_o is the maximum monolayer coverage capacity (mg/g) and K_L is the Langmuir isotherm constant (l/mg) related to the energy of adsorption.

The linear form of the Langmuir isotherm equation is given as:

$$\frac{1}{qe} = \frac{1}{qo} + \frac{1}{qo \cdot KL \cdot Ce} \qquad \text{Equation 2}$$

The values of qo and KL can be found through the slope and the intercept of the Langmuir plot of 1/qe vs. 1/Ce.

Also, there is another dimensionless constant separation factor R_L to determine the nature of the adsorption process.

$$R_L = \frac{1}{1 + KL \cdot Co} \qquad \text{Equation 3}$$

Where C_o is the initial concentration of the adsorbate and K_L is the Langmuir constant. $R_L>1$ indicates an unfavorable process, favorable if $0<R_L<1$ or irreversible if $R_L=0$[46].

6.5.2.2 Freundlich Isotherm

The Freundlich isotherm is considered the model for non-ideal adsorption because it assumes it occurs on heterogeneous surfaces. It has been especially used for organic compounds and high interactive species on activated carbon [47].

The model is described by Equation 4:

$$Qe = Kf \cdot Ce^{\frac{1}{n}} \qquad \text{Equation 4}$$

The linear form of the Freundlich isotherm equation is given as:

$$log(qe) = log(Kf) + \frac{1}{n} \cdot log(Ce) \qquad \text{Equation 5}$$

Where K_F ((mg/g) * (l/mg) (-1/n)) is a Freundlich constant related to the adsorption capacity and n related to the adsorption intensity. The relation 1/n belongs to the range of 0-1. The degree of heterogeneity of the surface increase when 1/n decreases and gets closer to 0. When 1/n =1 the adsorption is linear and when 1/n<1 indicates the process is chemisorption [47].

6.5.2.3 Sips Isotherm

The Sips isotherm is a mixture of Langmuir and Freundlich models. When the adsorbate concentration is low, it can be considered as Freundlich Isotherm and when C_e is higher, as Langmuir's model [48].

The linear Equation 6 of the model is given as:

$$\frac{1}{qe} \quad \frac{1}{Qmax \cdot Ks} \cdot 1/Ce^{1/n} + \frac{1}{Qmax} \qquad \text{Equation 6}$$

Where Ks (mg^{-1}) and Qmax (mg/g) are the Sips equilibrium constant and the maximum adsorption capacity; n is a dimensionless heterogeneity factor between the range of 0 and 1. When n=1, the Sips equation reduces to the Langmuir model.

6.5.3 Adsorption Kinetics:

The general mechanism which describes the kinetics of adsorption follows the next steps [40]:

- Transport from the inside of liquid zone to the liquid film that surrounds the adsorbent. The transfer is made by diffusion or convection.
- Transfer through the liquid film to the solid surface.
- Diffusion of the solute inside the adsorbent. This stage of the process is governed by the concentration gradient.
- Adsorption. It can be characterized by two types of interactions: Physical or chemical adsorption. In most of the cases, the first one seems to be the predominant.

Pseudo-first-order model: was proposed at the end of the 19th century by Lagergren. It is based on liquid-solid adsorption system and it is considered the most used model for systems with high initial concentration of adsorbate from an aqueous solution [52].

Equation 7 of the model is given as:

$$q_t = qe \times (1 - e^{-K1t}) \qquad \text{Equation 7}$$

Where q_t and q_e are the amount of antibiotic adsorbed per mass of adsorbent (MO) (mg/g) at any time and equilibrium, respectively, K_1 is the first-order adsorption rate constant (min^{-1}) [49].

Pseudo-second-order model: was introduced in the middle of the 80's and as long the time goes has become the most popular model to fit experimental data of adsorption kinetics [49].

This model assumes that the process is controlled by chemisorption, it means, the removal of the adsorbate is due to physicochemical interactions.

Equation 8 of the model is given as:

$$q_t = \frac{qe^2 \times K2 \cdot t}{1 + qe \cdot K2 \cdot t} \qquad \text{Equation 8}$$

Where K_2 is the adsorption rate constant (g/ mg*min) [49] [50].

Intraparticle diffusion model: It was proposed by Crank in 1975 and is used when the diffusion rate controls the sorption process, it means, depends on the speed in which the solute travels to the adsorbent. In practice, the equation should be applicable to a system with a large concentration of adsorbate to adsorb [51].

The model is described by Equation 9:

$$q_e = k3 \cdot t^{\frac{1}{2}} + c \qquad \text{Equation 9}$$

Where, k_3 is the rate constant of the intraparticle transport (g/mg/min) and c is the intercept. The empirical data can be fitted with a q_t vs. $t^{1/2}$ plot [51].

6.5.4 Thermodynamics considerations

The system can be described by the fundamental thermodynamic equation (Equation 10 and Equation 11) of Gibbs free energy (ΔG°) that at the same time is related to the enthalpy and entropy of the process.

$$\Delta G° = \Delta H° - T\Delta S° \qquad \text{Equation 10}$$

$$\Delta G° = -R\ T\ \ln K_c \qquad \text{Equation 11}$$

Where ΔH° is the enthalpy of the system, ΔS° is the entropy, T is the absolute temperature of the process in K, R is the universal gas constant (8.314J/mol*K) and Kc is the equilibrium constant which represents the effectiveness of the adsorbent [53]. To be considered a spontaneous process, the ΔG° should be negative. Also, through the sign of the enthalpy it is possible to determine when the process is exothermic (ΔH°<0) or endothermic (ΔH°>0) and through the value of the entropy, to characterizes the movement of the adsorbent, when it is immobilized, the disorder between the solute and the adsorbent decrease which mean the entropy is negative (ΔS°<0) [53].

6.6 BIOSORPTION, A NON- CONVENTIONAL ALTERNATIVE

Biosorption is defined as an environmentally friendly, low cost and simple process, able to remove pollutants by using biological material as adsorbent [4], mean reason why has become the new alternative to address the issue of conventional methods. The process

involves a solid (biosorbent) and a liquid phase which contains the pollutant. A great affinity is necessary between both phases since the pollutants should be attracted by the solid so as to be removed by different mechanisms [54]. It is important to consider that the process leads to high efficiency, a decrease in the use of chemical products and biological sludge, no addition of nutrients and the possibility to recover both, the contaminant and the biosorbent [55]. However, the adsorbent can be saturated quickly and the process is susceptible to variables such as temperature, pH and presence of other ions [54] [55]. One of the main and most important advantages presented by this method is the type of material used as an adsorbent. Biomass can be living or inert material. In the first group are involved materials such as algae, bacteria, fungi and yeasts, while in the second group, are found materials like biopolymers, agro-industrial residues, and plants [54] [55]. Table 7 illustrates the most important feature of each type of material.

Table 7 Advantages and disadvantages of using living and inert biomass.

Inert Biomass	Living Biomass
ADVANTAGES	
It does not need nutrients.	Can be saturated, the system is self-established due to growth.
The selection of the immobilization technique is not governed by toxicity limitations.	Economical way to achieve changes in the valence state or to degrade organometallic compounds.
Fast and efficient process, the biomass behaves like an ion exchange.	Two or more organisms can be used synergistically.
DISADVANTAGES	
Fast saturation	Nutrients are needed for growth.
The process is sensitive to pH. Organometallic species are not susceptible to degradation.	Only metals can be treated at low concentrations. Metabolic products can form complexes with them preventing precipitation,
The biological process is limited since cells do not produce metabolism. The production of the adsorbent occurs during the growth stage.	The modeling of the system presents mathematical difficulties.

Tejada Tovar, C., (2014). Adsorption of heavy metals in water using biological materials. Tecno Lógicas,18(34), pp.109-123.

By means of the comparison, it can be seen how inert biomass presents a greater number of advantages than living biomass. Through the use of inert material, economic and maintenance issues are avoided, it is needless to be concerned about inconveniences on toxicity and addition of nutrients to the environment [55]. Table 8 shows the most used and known, until now, biodegradable adsorbents.

Table 8 most used biosorbents [54], [55], [56].

Type of adsorbent	Biosorbent
Microorganisms	*Penicillium* *Aspergillus Rizopus* *Saccharomyces cerevisiae* *Aspergillus niger* *Mucorrouxi*
Agroindustrial waste.	Coconut Shell Lemon Shell Orange Shell Yuca Shell Tamarind shell
Biopolymers	Bentonite - Quitosano QuitosanoEpiclorhidrinatrifosfato
Activated carbon	Activated carbon from *Escherichia coli* Activated carbon from *Arthrobacter viscous.* Activated carbon from coconut and orange shell.
Other materials.	Sand, ashes, and zeolites. Bark and materials rich in tannins Lignin, quitosán. Crab carapace Material derived from maracuyá. Bagasse sugarcane Corn Moringa plant.

6.7 MORINGA *oleífera* Lam

Moringa *oleífera*, the best-known variety of the genus Moringacea, is a tree native to the southern foothills of the Himalayas, the north of India, Bangladesh, Afghanistan and Pakistan [57]. Nowadays, it can be found in Central and South America as it grows in tropical, semi-tropical and arid areas [58].

Moringa *oleífera* is recognized also, as Marango, Moringa resedá, Radish tree, Tree of drumsticks, Pearl tree, Angela, Asparagus tree, "Ben" tree, Life tree, Miracle tree, "Palo de jeringa", Drum stick, among others [58].

Such a variety of names accounts for the fact that it is considered one of the most famous plants worldwide. For more than thousands of years, practically all parts of the plant have been used: leaves, stems, pods and fruits. However, it was not long ago that the scientific community started to give it the attention it deserved. Recently numerous reports about its characteristics, benefits, origins and its uses have been launched. So far it is known that leaves are used as bio pesticide, forage, biogas and to fight malnutrition in children, while seeds are used for nutrition, medicine, sewage treatment, adsorption of toxic metals and as fertilizers. The stem is employed in the adsorption of toxic metals as well, in carpet and rope manufacturing and finally, the pods of seeds are used in the absorption of metal, activated coal production and ion exchangers [58].

Figure 8, Figure 9 and Figure 10 illustrate each of the above parts:

Figure 8 Moringa *oleífera* seeds. Source: Exportersindia.com

Figure 9 Moringa *oleífera* leaves. Source: Indiamart.com

Figure 10 Moringa *oleífera* plant. Source: Echonet.org

6.7.1 Applications of Moringa *oleífera*

Human and animal nutrition: as food, Moringa *oleífera* is highly nutritive, rich in vitamins, carbohydrates, dietary fiber, fats, proteins, minerals and amino acids (Figure 11) thus it is considered a powerful resource against children malnutrition [58].

According to most of bibliographic sources, fresh leaves have "more vitamin A than carrots, more vitamins C than oranges, more calcium than milk, more potassium than bananas, more iron than spinach, more proteins than any other vegetable" [6]. Besides, they

can be stored full, ground, fresh or dry. Moringa dirt can be kept intact without changing its properties for months [6].

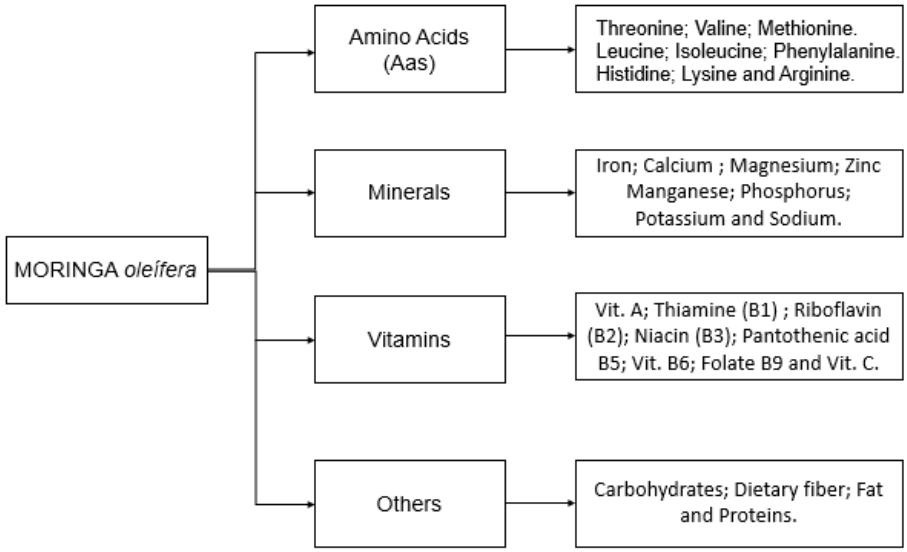

Figure 11 Chemical composition of Moringa *oleífera*.

Khalid Abbas, R., (2018). Nutritional Values of Moringa *oleífera*. Journal of Microbial and Biochemical Technology,10(2), pp 56-58.

Moringa leaves are important not only for human nutrition but also for animals. It has been found that the leaves contain amino acids such as arginine and histidine which are found in animal proteins [58]. The protein levels of the leaves are similar to soya beans and the number of digestible proteins in the intestine (PDI) is higher than food supplement (coconut, sesame, and bran peanut food), turning it into an option for livestock nutrition [59].

Medicinal use: for thousands of years it has been used as a medicament. Even though not all of its uses are backed up by scientists, Moringa *oleífera* is capable of fighting: anxiety, anemia, lack of breast milk, diabetes, articulation pain, and headache, impurities of blood, kidneys issues, and arterial hypertension, among others [58].

Waste-water treatment: Moringa *oleífera* is highly recognized in this area due to its coagulant and bactericidal properties. Using their seeds or dust from their ponds, it is possible to decrease the turbidity of the water, the presence of bacteria and achieve a high

percentage of removal of suspended solids [58]. The use of Moringa in waste-water treatments represents an economical and environmentally friendly option.

Adsorption of toxic metals: Represents a low cost and high-efficiency alternative, generates low sludge production and a high metal recovery. MO and other biological adsorbents have polar functional groups that form coordination complexes with metal ions in solution, thus allowing the removal of metals such as Cadmium (Cd), Nickel (Ni), Lead (Pb), Copper (Cu) and Mercury (Hg) [60].

MATERIALS AND METHODS

7 MATERIALS AND METHODS

7.1 CHEMICAL SOLUTION AND MATERIAL PREPARATION

The pharmaceuticals used in this work were Oxytetracycline hydrochloride (>95% crystalline) and Diclofenac Sodium, both obtained by Sigma-Aldrich Company (Figure 12). Also, were used solutions of NaOH (1M, 0,1M) and HNO_3 (1M, 0,1 M).

For all the experiences, it was prepared 1 mg/l solution of Oxytetracycline and Diclofenac, both diluted with distilled water.

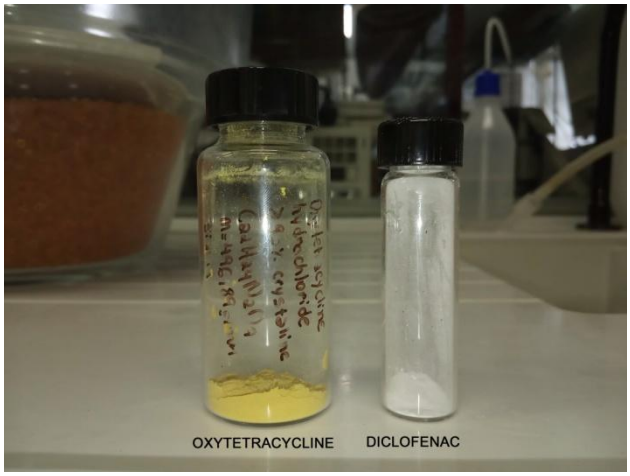

Figure 12 Oxytetracycline and Diclofenac obtained by Sigma-Aldrich Company.

7.2 Biosorbent preparation

The Moringa *oleífera* (MO) shell (Figure 13) was taken from Luanda, Ángola, África. It was dried in an oven at 30ºC for one day and pulverized into powder through IKA A11 basic analytical mill.

As seen in Figure 14, Moringa powder was separated according to the size of the grain through a series of sieves with different diameters (0,425 µm, 0,250 µm, 0,106 µm, 0,075 µm and lower than 0,075 µm) ordered in column.

The experiences were done with the granulometry $0{,}106 < \mu m < 0{,}205$.

Figure 13 Aspect of the Moringa oleífera shells used in the experiences.

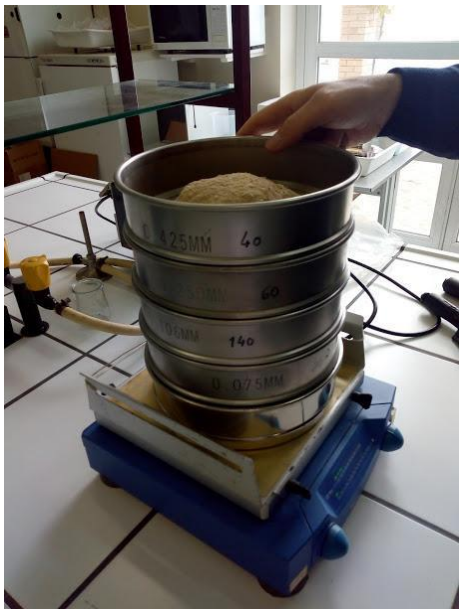

Figure 14 Different sieves used in the Granulometry essay.

7.3 Physicochemical characteristics of the Biosorbent

7.3.1 Characterization of biosorbent by FTIR

Fourier transform infrared spectroscopy (FTIR) was performed to determine the functional groups present in the Moringa and the effect of the interaction between the pharmaceuticals and the biosorbent. For this analysis, it was prepared KBr pellets, through the use of the SPECAC Hydraulic Press and it was used the UATR Two Perkin Elmer Spectrum FT-IR C112095. The transmittance spectra were obtained in a wavelength range between 4000-450 cm^{-1} and with a resolution of 4 cm^{-1}. The data were processed using Perkin Elmer Spectrum IR Software Version 10.6.1.

7.3.2 Determination of adsorbent's surface charge:

It was used 100 mg of MO and 50 ml of distilled water, under constant stirring (150 rpm) at 25°C in the Shaking Incubator of SHELL-LAB. To regulate the pH solution, it was used HCl 0.1 M and NaOH 0.1M, both measured by buret and a pH -meter of HANNA Instruments.

7.3.3 Total Organic Carbon analysis

The quantification of Total Organic Carbon (TOC) of the Moringa *oleífera* solution was performed by using a Shimadzu Equipment TOC-L CSH/CSN.

It was used 20 g of MO and 1 l of distilled water measured in Erlenmeyer. The experience was done under constant stirring, at 30°C for 5h in a VWR Advanced Digital Shaker VMS-

C7. After that, the solution was centrifuged for 10 min at 12000 rpm in the Eppendorf Centrifuge 5810 R and it was filtered through vacuum filtration using a qualitative filter paper of 70 mm and 47 mm, both of FILTER-LAB Company. The essays were performed six times.

7.4 SAMPLE ANALYSIS

7.4.1 UV-Vis analyses

In order to identify the specifics absorptions wavelengths for studying the results of the experiences, the UV-Vis spectrometer JASCO V-530 was used. A 1 mg/l solution of Oxytetracycicline (OTC) and Diclofenac (DCF) was prepared with distilled water and the spectra were taken in the range of 200-400 nm using quartz cells. The absorption peak occurred at 276 nm and 360 nm for DCF and OTC solution respectively.

7.4.2 HPLC-DAD analyses:

The determination of the concentration of pharmaceuticals was made by HPLC equipment of the Laboratory of Separation and Reaction Engineering (LSRE) of the Chemical Engineering Department, University of Porto (FEUP).

Figure 13 HPLC equipment. LSRE, Universitiy of Porto, Portugal.

7.4.2.1 HPLC-DAD detection methods

The detection methods were also proportioned by the LSRE of the FEUP.

The DAD wavelength was set at 276 nm for the DCF and at 360 nm for the OTC solution, as was discussed in the previous section.

7.4.2.2 Oxytetracycline detection method

OTC concentration was followed by HPLC using a VWR Hitachi ELITE LaChrom LC fitted with a Merck LiChrosorb® RP-18 (5 µm) LiChroCART® 125-4 column at 25 °C and a diode array detector (DAD). The equipment was operated in gradient mode using as mobile phase a mixture of acetonitrile/methanol/0.014M oxalic acid with ratios of 10:10:80 (v/v) from 0 to 3 min, 15:10:75 (v/v) from 3 to 5 min, 20:10:70 (v/v) from 5 to 7 min, and 10:10:80 (v/v) from 7 to 14 min. The flow rate was 0.8 ml/min. Samples of 20 µL were injected and the DAD was set at 354 nm. The retention time was 5.8 min and the limits of quantification and detection were 1.2 and 0.3 mg/lof OTC, respectively.

7.4.2.3 Diclofenac detection method

Diclofenac concentration was followed by HPLC using a VWR Hitachi ELITE LaChrom LC fitted with a Merck LiChrosorb® RP-18 (5 µm) LiChroCART® 125-4 column at 25 °C and a diode array detector (DAD). The equipment was operated in isocratic mode using as mobile phase a mixture of acetonitrile/0.014M oxalic acid with a ratio of 60:40 (v/v) during 7 min. The flow rate was 1.0 ml/min. Samples of 20 µL were injected and the DAD was set at 276 nm. The retention time was 4.0 min and the limits of quantification and detection were 0.04 and 0.01 mg/l of diclofenac, respectively.

7.5 Determination of Biosorption kinetic

A pre-equilibrium kinetic experiment was carried out to determinate the equilibrium time for batch reaction in order to study the sorption isotherms. For the study was used 1 l of Oxytetracycline hydrochloride solution (1 mg/l) with pH 3 and 2 mg/l of MO.

The experience was done with continuous stirring (150 rpm), at a constant temperature of 25°C. Samples were taken from the reactor at seven different times (5, 10, 20, 30, 60, 90

and 120 min) then they were centrifuged at 5000 rpm for 10 min and also filtrated with syringes and filters of 45 µm.

To Diclofenac's biosorption, the experience was done in Erlenmeyers of 50 ml of solution (1 mg/l of DCF) with 100 mg of adsorbent. The conditions were the same (continuous stirring 150 rpm, at a constant temperature of 25°C but at a pH of 2).

Samples were taken from the Erlenmeyers at seven different times (5, 10, 20, 30, 60, 90 and 120 min) then they were centrifuged at 5000 rpm for 10 min and also filtrated with syringes and filters of 45 µm. All essays were performed in duplicate.

The results were analyzed using high-performance liquid chromatography (HPLC-DAD) equipment to quantify the amount of pharmaceutical present in solution and thus to evaluate the biosorption efficiency removal.

The adsorption capacity of the MO, qt (mg/g) was obtained by Equation 12:

$$q_t = \frac{(Co - Ct) \times V}{m} \qquad \text{Equation 12}$$

Where Co is the initial pharmaceutical concentration (mg/l), Ct is the concentration of the pharmaceutical (mg/l) in solution at different times, V is the volume of the aqueous solution (ml) and m is the dry adsorbent mass (mg).

In this work, the pseudo-first-order, the pseudo-second-order and Intraparticle Diffusion models were used to adjust the experimental data.

Pseudo-first-order model was obtained by Equation 13:

$$q_t = qe \times (1 - e^{-K1t}) \qquad \text{Equation 13}$$

Where q_t and q_e are the amount of antibiotic adsorbed per mass of adsorbent (MO) (mg/g) at any time and equilibrium, respectively, K_1 is the first-order adsorption rate constant (min^{-1}) [61].

Pseudo-second-order model was obtained by Equation 14:

$$q_t = \frac{qe^2 \times K2 \cdot t}{1 + qe \cdot K2 \cdot t}$$ Equation 14

Where K_2 is the adsorption rate constant (g/ mg*min) [1].

Intraparticle diffusion model was defined using the Equation 15, below

$$q_e = k3 \cdot t^{\frac{1}{2}} + c$$ Equation 15

Where, k_3 is the rate constant of the intraparticle transport (g/mg/min) and c is the intercept. The empirical data can be fitted with a q_t vs. $t^{1/2}$ plot [62].

7.6 Determination of fundamental adsorption process conditions

7.6.1 Effect of initial antibiotic concentration

The initial pharmaceutical concentration in aqueous solution is considered one of the most important conditions to evaluate the removal efficiency. The Oxytetracycline and Diclofenac concentration's range was 0,2-1 mg/l while other parameters were maintained constant (V=50 ml of solution, at pH 2 (DCF) and pH 3 (OTC), adsorbent dosage of 2 g/l, stirring at 150 rpm and temperature at 25°C).

7.6.2 Effect of pH:

The effect of pH is another important condition in the biosorption process and it is not only because it changes the chemical properties of the pharmaceutical solution, but also controls the active sites of the adsorbent and thus its removal capacity. For the removal of Oxytetracycline, the study was carried out between the pH range of 3-10 (3, 5, 7 and 10) while keeping the other parameters constant (V=50 ml of solution, antibiotic initial concentration of 1 mg/l, adsorbent dosage of 2 g/l, stirring at 150 rpm and temperature at 25°C). Meanwhile, for the removal of Diclofenac, the pH range used was 2-10 (2, 5, 7, 8 and 10) and the same parameters previously mentioned.

7.6.3 Effect of the temperature

To analyze the influence of the temperature, it was changed from 20 to 40 °C (20, 30 and 40 °C) while other parameters were kept constant (V=50 ml of solution, antibiotic initial

concentration of 1 mg/l, adsorbent dosage of 2 g/l, at initial pH of OTC (7) and DCF (8) and stirring speed of 150 rpm).

7.6.4 Effect of total organic carbon of the adsorbent

The main objective of this essay is to evaluate if the carbon's amount of MO has any influence in its capacity of removal. For that, it was used one sample with Moringa's powder washed and another one with adsorbent without any previous treatment. The conditions were the same as they were mentioned before (V=50 ml of solution, antibiotic initial concentration of 1 mg/l, adsorbent dosage of 2 g/l, at initial pH of OTC (7) and DCF (8), stirring speed of 150 rpm and a temperature of 25°C).

RESULTS AND DISCUSSION

8 RESULTS AND DISCUSSION

8.1 Characterization of biosorbent by FTIR

The FTIR spectra of MO (Figure 16) shows the presence of many functional groups, indicating the complex nature of the biosorbent and the huge similarity with the already known structure of cellulose [63].

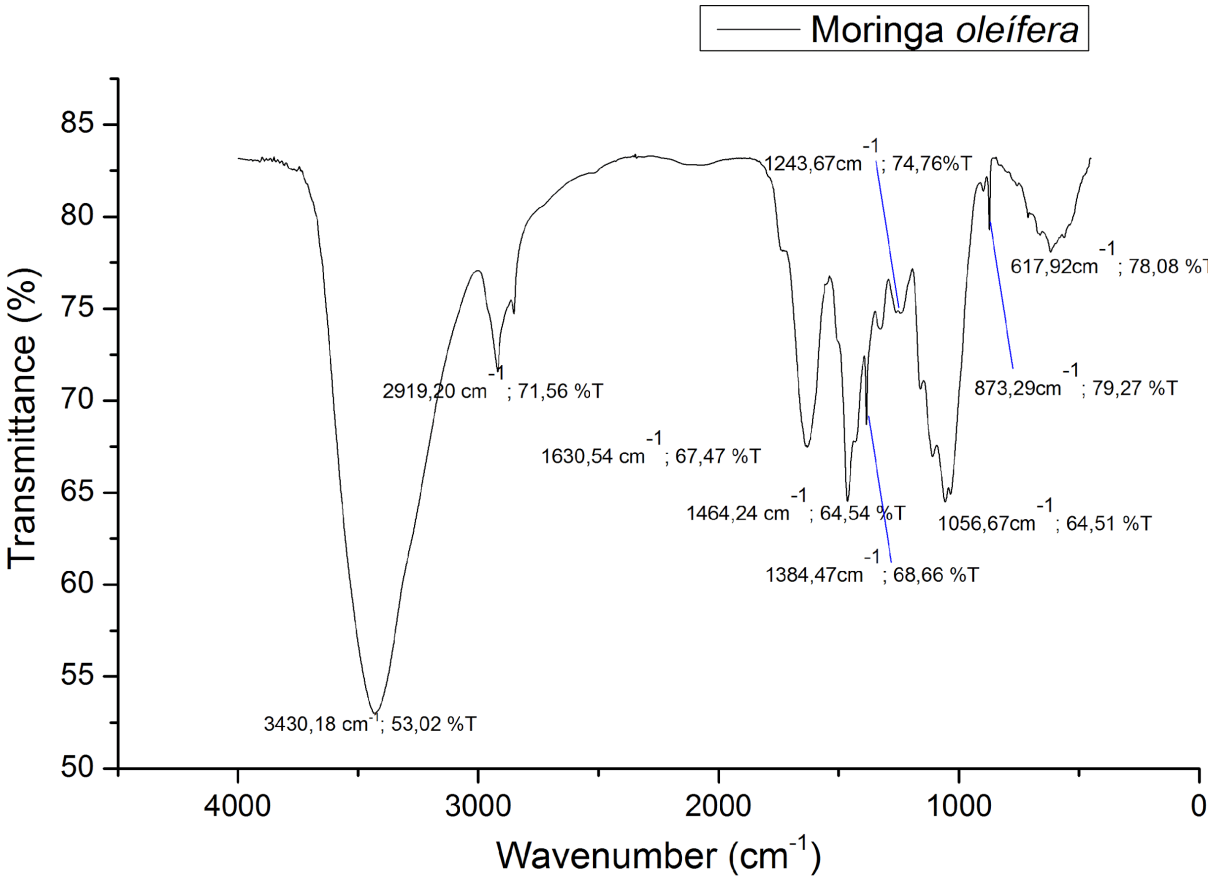

Figure 14 Main functional groups of Moringa oleífera by FTIR analysis.

A strong peak at 3430 cm^{-1} indicates the presence of the hydroxyl group (-OH) which could belong to the proteins, fatty acids, carbohydrates and phenol compounds. The peak at 2920 cm^{-1} indicates the presence of -C-H bond of the CH_2 group. The peak at 1630 cm^{-1} is due to the carbonyl group (-C=O) that could belong to the primary or secondary Amide compounds (NH_2CO). The band at 1464 cm^{-1} corresponds to the -C=C of Aromatics compounds. In the region of 1384-1243 cm^{-1}, it is found a series of weak peaks that could correspond to the presence of carboxylic acids. The strongest band is near to the

wavelength of 1056 cm^{-1} and is attributed to the -C-O bond, as a prove of the presence of phenols compounds, carboxylic acids and also shows the lignocellulosic structure of the biosorbent [64]. Finally, the weak bands between 873-618 cm^{-1} could correspond to the -C-H bond of aromatics compounds.

Table 9 summarizes the main functional groups found in the chemical structure of the adsorbent.

Table 9 Main peaks and functional groups of Moringa oleífera by FTIR analysis.

N°	cm^{-1}	Intensity range (%T)	Intensity	Group Assignment	Functional Group
1	3430.18	53	Strong	-OH	Alcohol
2	2920	71.56	Medium	-CH	Aromatic Compounds.
3	1630.54	67.47	Medium	-C=O	Carbonyl group
4	1464.24	64.54	Medium	-C=C	Aromatic Compounds.
5	1384.47	68.66	Medium	-COOH-	Carboxylic acid.
6	1243.67	74.75			
7	1056.67	64.51	Medium	-C-O	Phenols, Carboxylic acids.
8	873-618	78	Weak	-C-H	Aromatic Compounds.

As can be seen from Figure 17, after the adsorption process, the peak at 3430 cm^{-1}, which represents the -OH- group, the band at 1637 cm^{-1} (-C=O) and the peak at 1459 cm^{-1} (-C=C) have been changed. These changes indicate that the hydroxyl, carbonyl, and aromatic groups are the responsible for the DCF removal. Also, that could cause a strong interaction between the negative charges of the groups of the adsorbent with the positive charges of the amine group of the anti-inflammatory.

Also, two new peaks can be observed, the first one at 610 cm^{-1}, which belongs to the aromatic group (-C-Cl) of DCF and another one at 1506 cm^{-1} which confirms the presence of its aromatic ring [65].

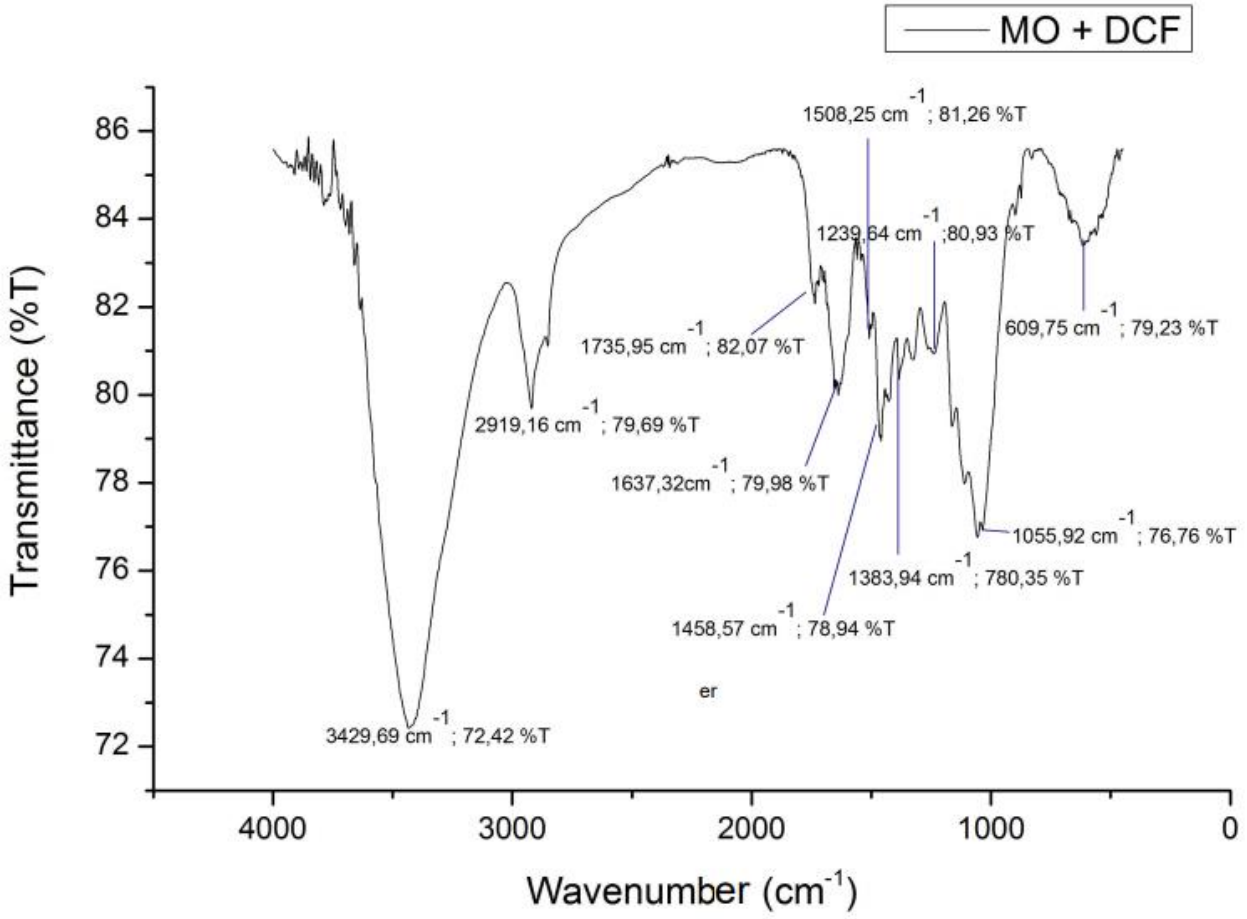

Figure 15 Moringa oleífera shells composition after the adsorption process of DCF from water.

Figure 18 illustrates the results of the adsorption process of Oxytetracycline solution. Knowing the complex composition of the antibiotic (amides, carbonyl, amines, hydroxyl and aromatic groups), the main differences can be seen at the following peaks: 3435 cm^{-1} (-OH), 1633 cm^{-1} (-C=O), 1465 cm^{-1} (-C=C), 1260 cm^{-1} and 1055 cm^{-1} of carboxyl acids, indicating that the compounds responsible for the adsorption, also in this case, are the hydroxyl, carbonyl and aromatic groups.

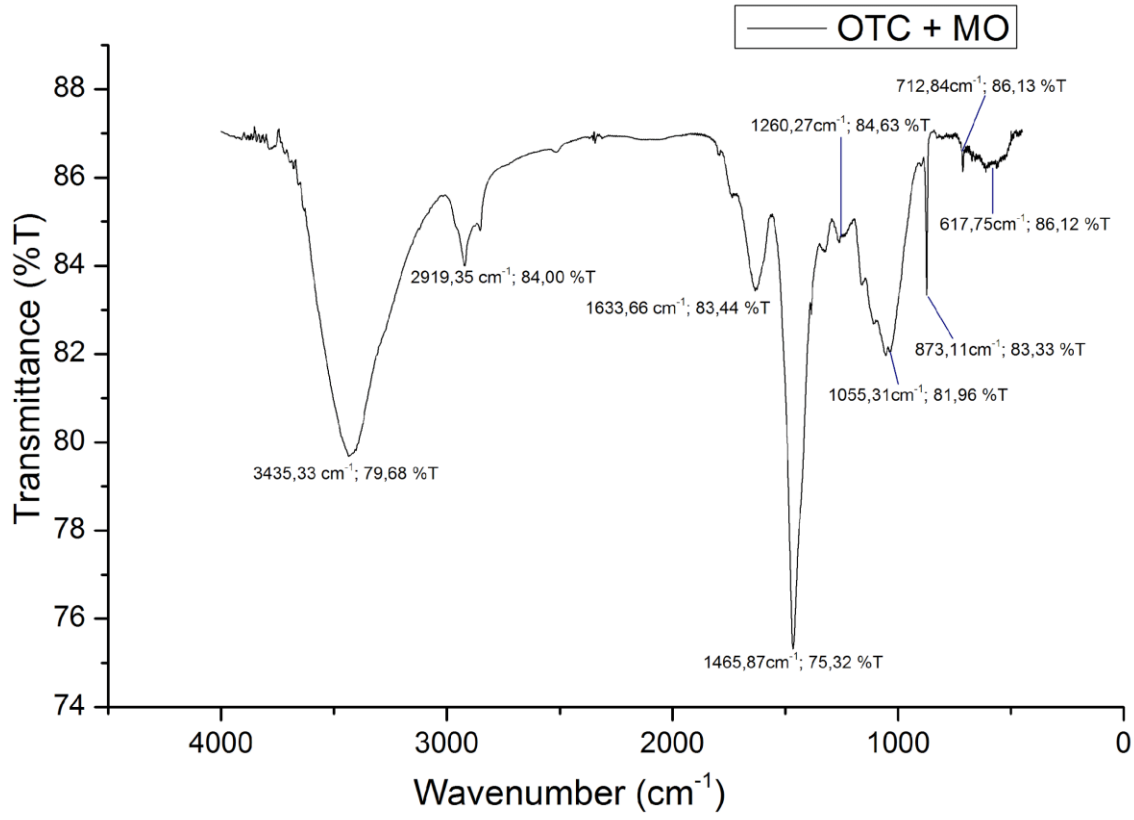

Figure 16 Moringa oleífera shells composition after the adsorption process of OTC from water.

The lower absorption at 3435 cm^{-1} could be related to hydrogen bonding between the functional groups of the adsorbent and the antibiotic. The peak at 712 cm^{-1}, could indicate the complex formation between the OTC and the adsorbent or maybe, the presence of aromatic group of the antibiotic [66].

8.2 Determination of adsorbent's surface charge

Determining the surface charge of the adsorbent enhance the understanding of the relationship between Moringa *oleífera* and the pharmaceuticals, at the tested pH values.

In Figure 19, it can be observed that the surface charge of the adsorbent at pH<6 is positive and for pH>6, negative, which improves the DCF adsorption but not necessarily for OTC.

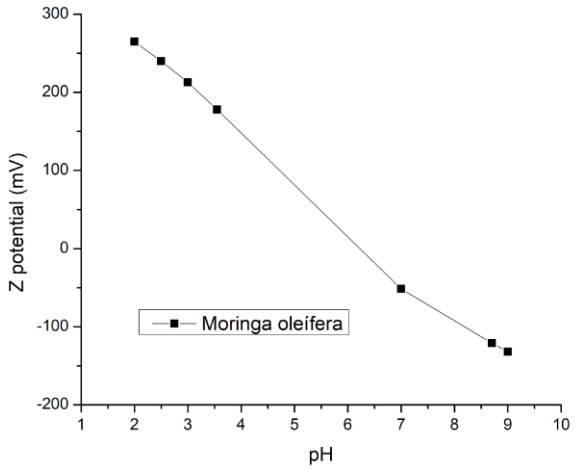

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Figure 17 Surface charges of Moringa oleífera shells between the pH range of 2-10.

It is known that the surface charge of the anti-inflammatory is negative [64]. It could indicate there is a strong electrostatic attraction between MO and DCF surfaces when the pH is lower than 6 and also, a significant electrostatic repulsion when the pH > 6.

In the case of DCF adsorption, the pH of interest is situated in the acid area, especially at pH 2 where it was measured the best percentage of removal. This could be one of the main reasons for the highest adsorbent's potential and the great affinity between the solute and the MO. At the initial pH of the adsorbent (pH=8) it was reached a removal percentage of approximately 10%, indicating the high influence of the pH in the adsorption process and the multiple interactions that could take place between both surfaces.

In the case of OTC adsorption, it is known the antibiotic presents a negative surface [67] which could indicate a high percentage of removal in the acid region but unlike the case of DCF adsorption, the OTC presents a complex composition and a high dependence with pH, so knowing the surface charge is not enough to explain its adsorption process.

8.3 Total Organic Carbon analysis (TOC)

The main objective of this analysis was to minimize the amount of MO's organic carbon that could contribute to the interactions with the pharmaceutical solution and after can affect UV-Vis spectrophotometer readings.

The experience was repeated six times to get the minimum possible value of organic carbon present in the MO. Once the test was finished, it was necessary to recover the adsorbent by filtration to use it in the following experiences.

As can be observed in Table 10 the high percentage of carbon, was confirmed [63]. Before washing, the TOC was approximately 2000 mg/l. After, it was almost totally eliminated (36, 32 mg/l). At the table, it is also exposed the Inorganic carbon amount (IC) in mg/l and the total carbon value (TC) that is the sum between the TOC and IC.

Also, twenty hours later, the TOC did not have any significant change. The equilibrium was reached at an average concentration of approximately 40 mg/l.

The slight unexpected increase in the last value may be due to some external contamination.

Table 10 Total organic carbon amount of Moringa oleífera shells after the washing process

WASH N°	t (h)	TOC (mg/l)	IC (mg/l)	TC (mg/l)
1	5	1226.4	38.208	1264.608
2	10	293.7	20.775	314.475
3	15	100.3	6.744	107.044
4	20	46.11	6.655	52.765
5	35	29.38	5.901	35.281
6	55	36.32	4.524	40.844

Figure 20 illustrates the decrease in Moringa *oleífera* carbon content over time after successive washes.

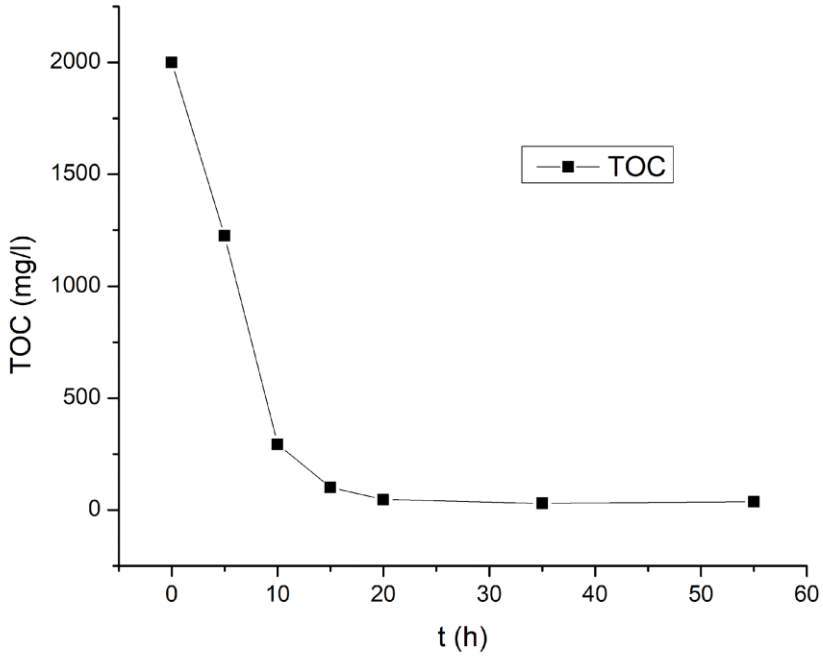


Figure 18 TOC's analysis of Moringa oleífera shells through the washing process.

8.4 Measurement of the samples by UV-Vis Spectrophotometer

The first attempt to measure the samples was in the UV-Vis Spectrophotometer JASCO-530. However, the adsorption results of MO with OTC and also with DCF, showed concentration values outside the expected range, indicating that perhaps the functional groups of the adsorbent absorb at the same wavelength (360 cm^{-1} for OTC and 276 cm^{-1} for DCF).

Another alternative was to assume that the quelation phenomenon has been developed between the drugs and the adsorbent. The quelation is known as the ability of a chemical compound to react with a metallic ion and obtain as a result, another compound with different chemical properties [68].

Taking into account the complex chemical composition of the adsorbent and its high percentage of calcium, it is possible that quelation effects between the OTC and the calcium ions exist [69]. Mainly, due to the fact that the antibiotic chemical structure presents numerous active ligation sites to form metal complexes in solution that may interfere with the absorption and the activities of the molecules. Also, it has been

demonstrated through UV-Vis spectrum data that the tetracyclines present the group of β-diketones as the responsible of ligation between the antibiotic and the metallic ions [69].

In the case of Diclofenac sodium, it has been published some results that show its quelation capacity with Mg(II), Ca(II), Sr(II) and Ba(II) ions and also confirm itself as a bidentate chelating agent, increasing the possibilities that the assumption previously mentioned has occurred [70].

The main reason for choosing the UV-Vis spectrophotometer as the first option to read the samples was because of its simplicity, its speed and it does not require the use of expensive solvents. However, due to the mentioned drawbacks, it was necessary to start reading the samples with the ultra-definition liquid chromatography equipment (HPLC).

8.5 Measurement of the samples by HPLC

8.5.1 Standard Curve of Oxytetracycline solution by HPLC

The standard curve was made and measured in the LSRE laboratory through the preparation of the following OTC concentrations: 0.2, 0.4, 0.6, 0.8 and 1 mg/l. All the dilutions were made with distilled water (Figure 21).

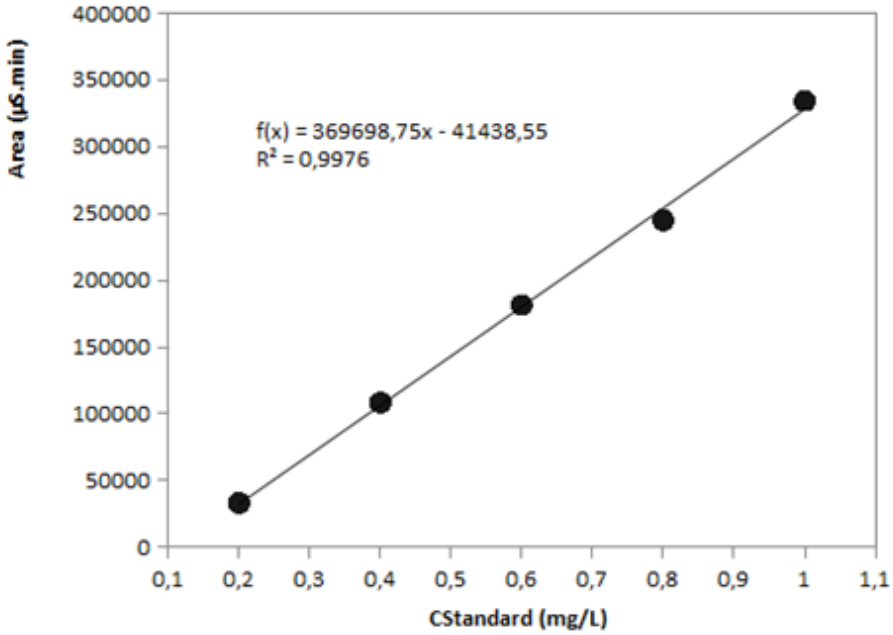


Figure 19 Standard curve of OTC adsorption process measured by HPLC.

8.5.2 Standard Curve of Diclofenac Sodium solution by HPLC

The standard curve was made and measured in the LSRE laboratory through the preparation of the following DCF concentrations: 0.01, 0.05, 0.1, 0.25, 0.5, 0.75, 1, 1.5 and 2 mg/l. All the dilutions were made with distilled water (Figure 22).

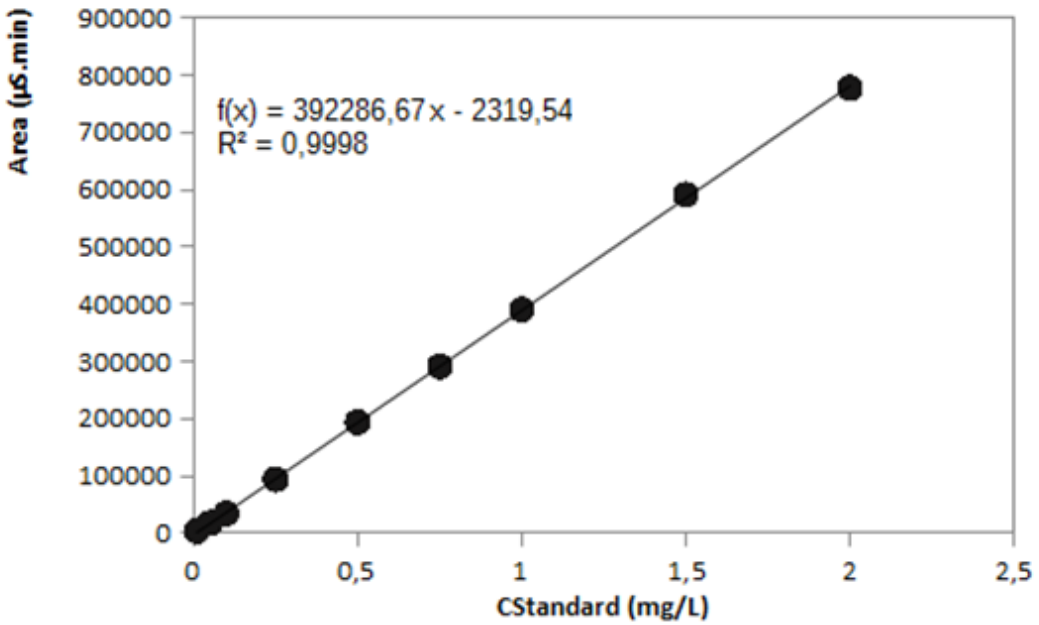


Figure 20 Standard curve of DCF adsorption process measured by HPLC.

8.6 Determination of fundamental adsorption process conditions

8.6.1 Effect of pH

The pH plays an important role in the removal processes of Diclofenac and Oxytetracycline. The adsorption of pharmaceuticals was studied at pH range of 2-10 while keeping other parameters constant.

Oxytetracycline has three pKa values (3.27, 7.32 and 9.11) and its adsorption process presents high pH dependence. The Figure 23 shows how the adsorption capacity of MO increases with the pH. The lowest removal percentage was obtained at pH 3 (31%) and the highest at pH 10 (50.3%). Although, the adsorption capacity increased it did not reach a high value of removal. Maybe, this can be explained through the chemical changes the antibiotic suffered with the variation of pH. OTC is in its cationic form at pH<3.27, as a zwitterion in a pH range of 3.27-7.32 and in its anion form (OTC^- and OTC^{-2}) when the pH>7.32 [19]. Knowing this and taking into account the previously characterization of MO

surface (Figure 19), maybe the low removal percentage obtained at acid region was caused by electrostatic repulsion between both compounds and although, the percentage increase at alkaline area, the negative charges that each surface presents does not allow to obtain an acceptable result. In conclusion, there is not a huge affinity between OTC and MO, the biosorption with Moringa *oleífera* as biosorbent is not the most adequate method to remove the presence of this antibiotic from water.

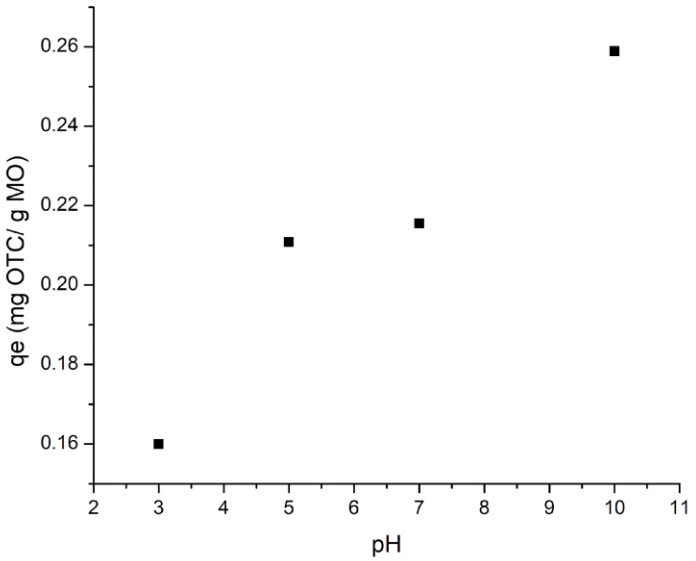


Figure 21 Effect of pH into the OTC adsorption process.

In the case of DCF adsorption, Figure *24* shows how the adsorption capacity of the adsorbent decrease when the pH increase. The lowest removal percentage is obtained at pH 8 (4.8%) and the highest at pH 2 (87.3%). It seems the Moringa *oleífera* has a better affinity with the DCF than with the OTC. This behavior is due to the fact that the DCF surface is charged negatively at low pH values and the MO is charged positively, so the attraction between each surface is high, improving the adsorption process. At alkaline pH, the adsorption capacity is low due both surfaces are charged negatively and a big electrostatic repulsion is developed between them.

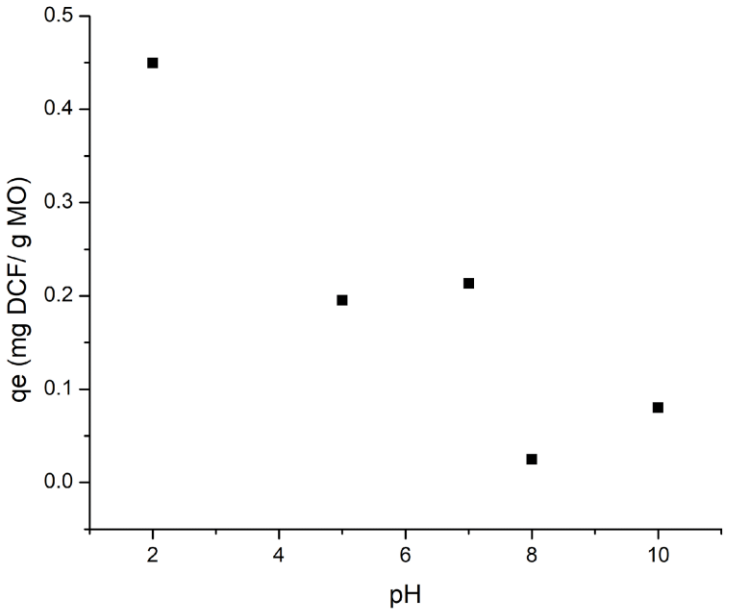


Figure 22 Effect of pH in DCF adsorption process.

After analyzing the results, it is possible to conclude that Moringa *oleífera* is an adequate adsorbent to remove Diclofenac from water (0.4497 mg DCF/ g MO).

8.6.2 Effect of the temperature

In the case of OTC, as the temperature increases, the percentage of removal also increases. The maximum value of removal is obtained at 40°C but the difference in efficiency between the temperatures is so low that it does not justify spend high values of energy. The process could be done at an average temperature of 25°C.

In the case of DCF removal, the efficiency decrease as the temperature increases. This phenomenon is typical from adsorption process, because it is considered an exothermic system. The maximum removal percentage is obtained at 20°C indicating it is the ideal temperature for the adsorption process.

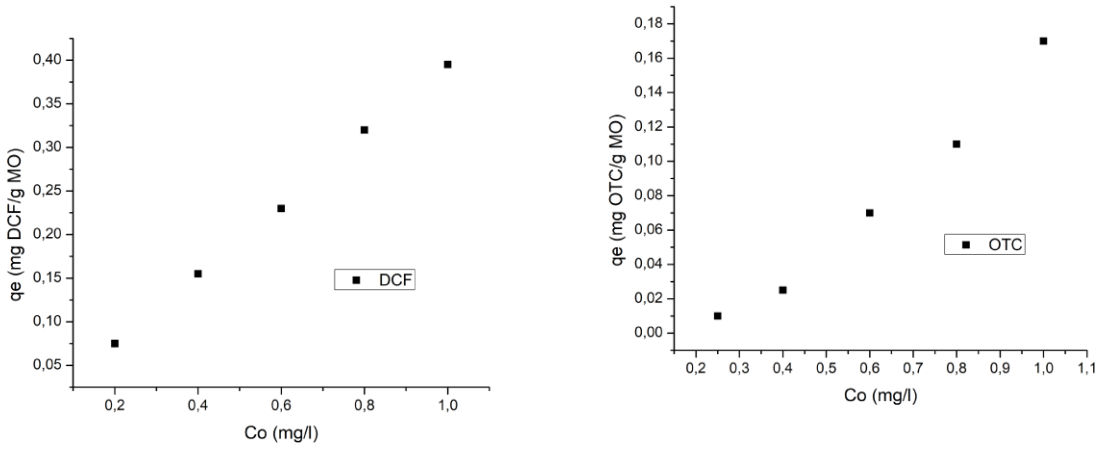
8.6.3 Effect of total organic carbon of the adsorbent

One of the principal reasons to make this experience was the inconvenient with the readings of the samples in the UV-Vis equipment. Through the HPLC measurement it was possible to determine that the amount of carbon in the adsorbent has no influence in its adsorption capacity. After this result, it was not necessary to use washed material for the experiences.

8.6.4 Effect of initial adsorbate concentration

The initial concentration of the adsorbate can determine the limits of the adsorption process. Figure 26 shows that in both cases, the removal percentage increases with the adsorbate concentration. In OTC removal, the increase is almost insignificantly, which suggests the initial concentration of the solute does not have enough influence in the capacity of the adsorbent while in DCF removal, it is possible to see a higher increase may be due to the fact, the interaction between both surfaces increase allowing a better removal of the antibiotic.

Between the range of 0-1mg/l of the adsorbates concentrations, it was not possible to determine the adsorption's limit of the MO. In future work, would be necessary to work with a higher range of concentrations.



(a) (b)

Figure 23 Effect of initial concentration of DCF (a) and OTC adsorption process (b).

8.7 Adsorption equilibrium study

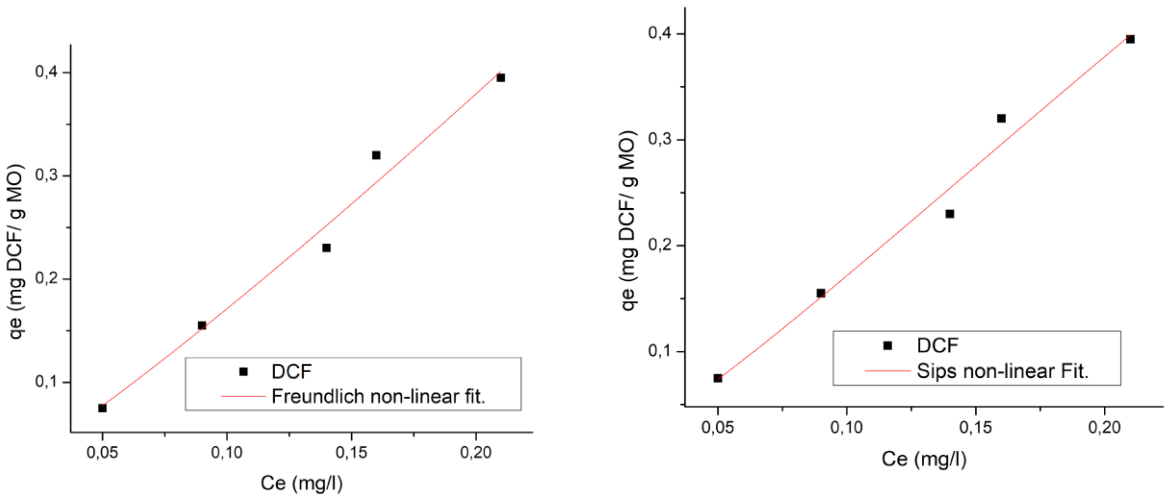
Langmuir, Freundlich, and Sips equations were used to find the most adequate isotherm model for describing the adsorption capacity and the interaction between the adsorbent and adsorbate during the process.

Langmuir's model was not suitable to describe the adsorption processes. The plot for Freundlich and Sips isotherm models are shown in Figure 26 and Figure 27. The isotherm parameters calculated from the plot are in Table 11. The adsorption isotherms were best

fitted by the Freundlich model (R^2>0.96), indicating that the sorption processes took place in heterogeneous surfaces. It was also, obtained a *n* value smaller than 1, which means, in both cases, the adsorption was highly nonlinear. A greater non-linearity indicates more heterogeneity in sorption sites as a result of the interaction between both surfaces [71]. On the other hand, the Kf value shows the affinity between the adsorbate and the adsorbent. The DCF adsorption presents the highest Freundlich's coefficient which means a higher sorption affinity between the DCF and the MO. To evaluate which model presents the best fit, it was also calculated the statistic F-value of every isotherm. Through the F-value, it is possible to confirm or refute the conclusion obtained by R^2. A bigger F-value indicates a greater correlation between the empirical data and the proposed model. Also, if the statistic value of Prob>F shown in the table is greater than the significance level (in this case, 0.05) means the R^2 is not a good parameter to define the best-fitted model. For all the equilibrium isotherm models, it was obtained a Prob>F lower than 0,005. The Freundlich isotherm presents the lowest Prob>F (0.00026 for DCF and 0.0002 for OTC) and the greatest F-value (414,47 for DCF and 488,268 for OTC) indicating that represents the most adequate model to describe both adsorption processes. The same conclusion was obtained by the determination coefficient (R^2).

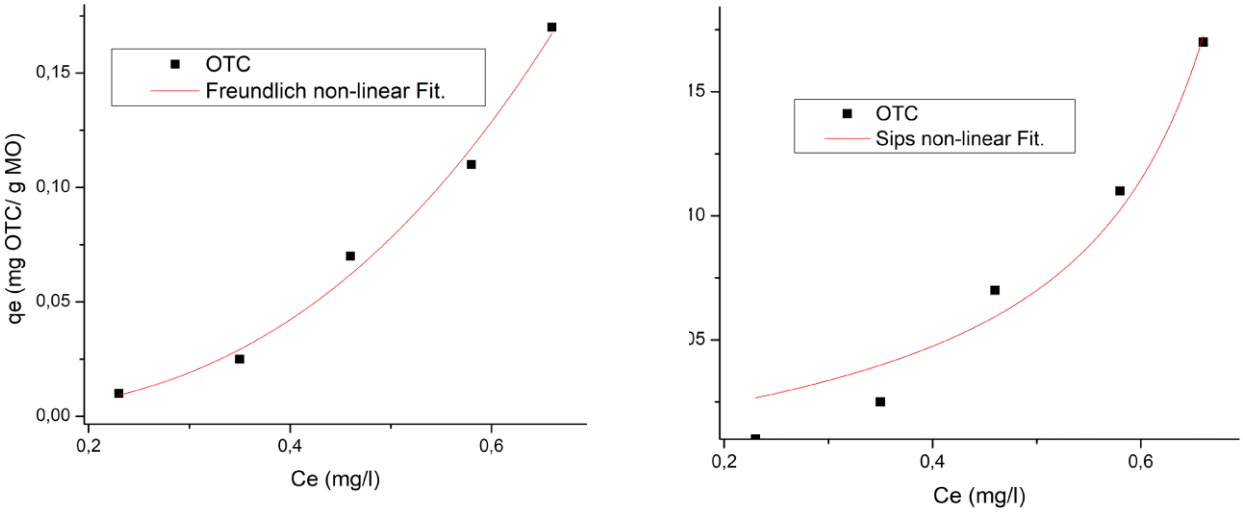
Table 11 Isotherm parameters of Freundlich and Sips models for Diclofenac and Oxytetracycline adsorption.

Parameters	**DCF**	**OTC**
Freundlich Isotherm model		
Kf	2,403	0,524
n	0,872	0,364
R^2	0,975	0,989
F-Value	414,47	488,268
Prob>F	0,00026	0,0002
Sips Isotherm model		
q_{max}(mg/g)	2,48	0,00138
Ks	1,404	-0,99
n	0,784	-0,043
R^2	0,963	0,949
F-Value	188,678	68,14
Prob>F	0,00527	0,0032



(a) (b)

Figure 24 Equilibrium isotherms fitting for DCF adsorption by Moringa *oleífera* shell.

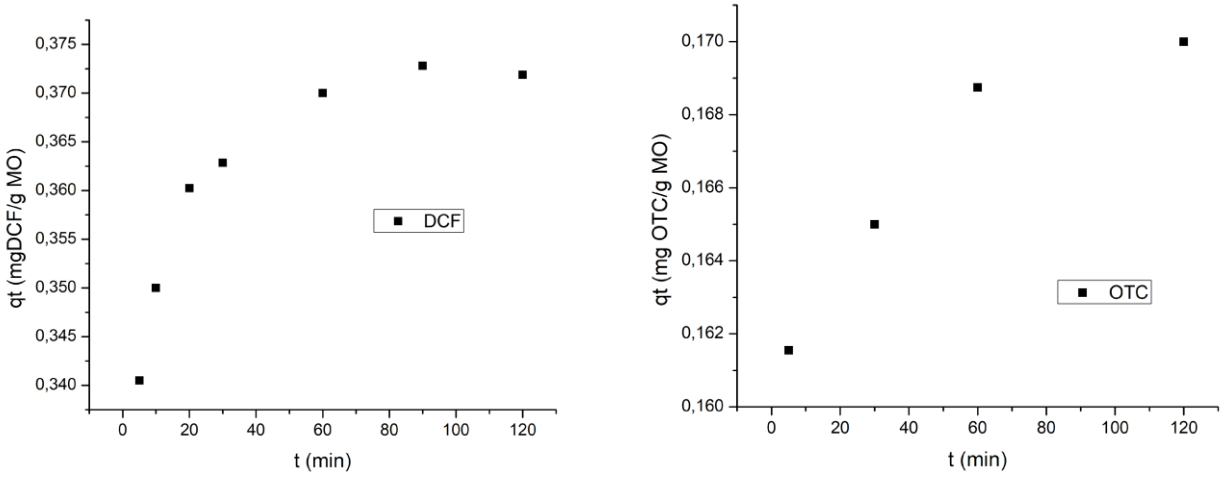


(a) (b)

Figure 25 Equilibrium isotherms fitting for OTC adsorption by Moringa oleífera shell.

8.8 Adsorption Kinetic study

Figure 28 a, describes the kinetics adsorption process of the DCF solution. A removal percentage of almost 75% was reached at approximately 90 min which indicates the Moringa *oleífera* represents an acceptable option to remove the anti-inflammatory from the water. Figure28 b shows the kinetics adsorption process of the OTC solution. A percentage of only 34% was reached after two hours, indicating it does not present a great affinity between the antibiotic and the adsorbent's surface, maybe due to its complex chemical structure or pH dependence. It was not necessary to take numerous samples because, as it can be seen, in two hours the removal percentage only increased almost 3%. Maybe, in order to have better results, would be necessary to increase the time contact between both surfaces or increase the amount of the adsorbent.



(a) (b)

Figure 26 Adsorption capacity of MO through the time for DCF (a) and OTC (b) removal.

To describe the adsorption kinetics, it was used the Pseudo-first-order model, the Pseudo-second-order model and the Intraparticle Diffusion model (Figure 29 and Figure 30).

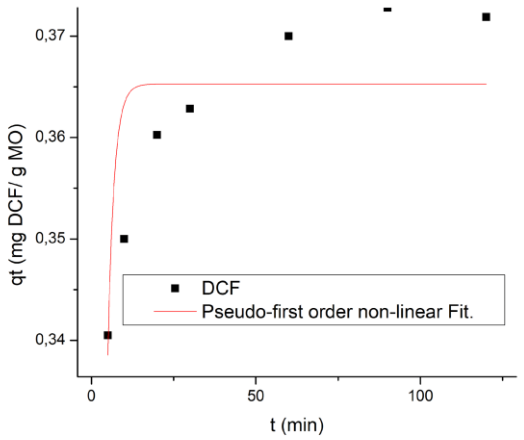
Kinetics parameters such as the rate constants, equilibrium adsorption capacities, related correlation coefficients and F-values are summarized and presented in the Table 12.

Following the same analysis criteria as in the study case of equilibrium isotherms, for DCF adsorption process, the kinetic data were best fitted by the model of Pseudo-second-order, indicating maybe the adsorption process is governed by chemisorption, strong chemical interaction between the DCF and MO surfaces.

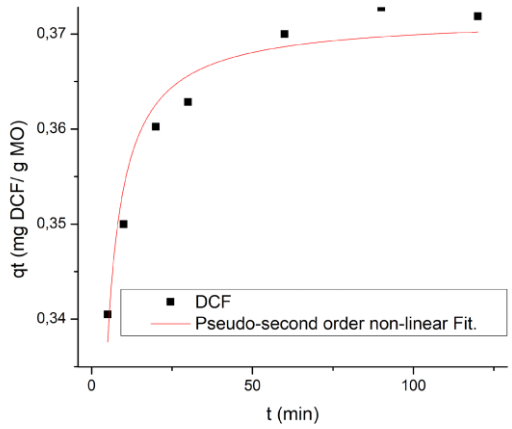
For OTC sorption, the kinetic data were best fitted by the Intraparticle Diffusion model. The fit is similar to a linear curve describing how the process is governed by the diffusion on the surface or sin of the fluid and then by the diffusion between both materials.

Table 12 Kinetic parameters of the pseudo-first and pseudo second order and Intraparticle Diffusion model of Diclofenac and Oxytetracycline adsorption.

Parameters	**DCF**	**OTC**
Pseudo-first-order model		
$K_1(min^{-1})$	0,5231	0,6545
qe(mg/g)	0,3653	0,168
R^2	0,5452	0,5378
F-Value	6823	8173
Prob>F	4,93*10^-9	1,22*10^-4
Pseudo-second-order-model		
$K_2(min^{-1})$	5,31	25,28
qe(mg/g)	0,3718	0,1688
R^2	0,9311	0,6925
F-Value	45070	12288
Prob>F	4,40*10^-11	8,13*10^-5
Intraparticle Diffusion model		
$K_3(mg/g/min^{1/2})$	0,0172	0,0049
R^2	0,8933	0,9506
F-Value	29087	76451
Prob>F	1,3*10^-10	1,3*10^-5



(a)



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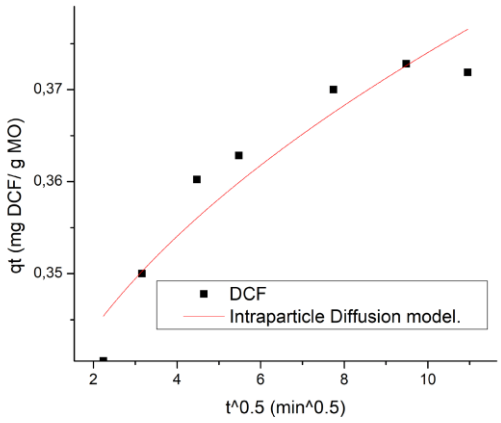
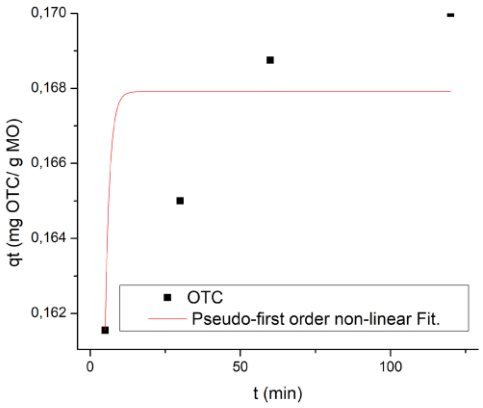
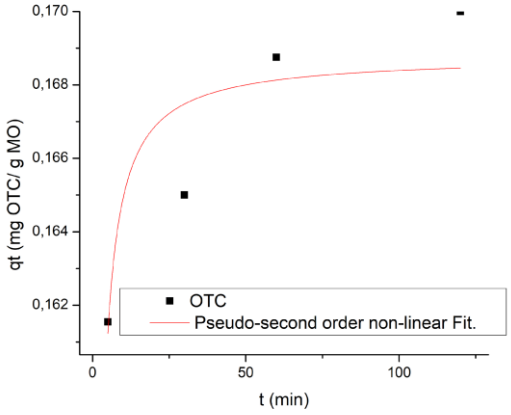


(c)

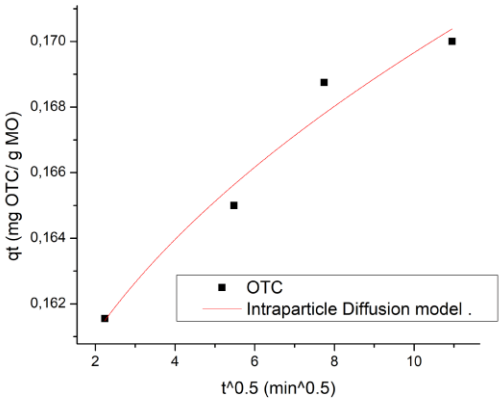
Figure 27 Kinetic for Diclofenac adsorption with Moringa oleífera shells. Pseudo-first-order model (a); Pseudo-second-order model (b); Intraparticle Diffusion model (c).



(a)



(b)



(c)

Figure 28Kinetic for Oxytetracycline adsorption with Moringa oleífera shells. Pseudo-first-order model (a); Pseudo-second-order model (b); Intraparticle Diffusion model (c).

8.9 Adsorption mechanism

Describe the adsorption mechanism is the last step and the most important one. It allows a better understanding of the adsorption process. In the present work, the adsorption kinetics suggested that the DCF removal is governed by chemisorption mechanism and the OTC adsorption by Intraparticle diffusion. The Figure 32 tries to explain the possible adsorption mechanism of DCF removal. As can be seen, the process presents a strong pH dependence. At pH 2, DCF surface is charged negatively and the adsorbent positively, which produces a great electrostatic interaction between the negative ions from DCF (O^- and OH^-) and the positive ions from the MO surface (amines and aromatic compounds) as it was shown in FTIR analysis (Figure 17).

At pH 5, the removal capacity starts to decrease, the MO surface stills positively charged but the DCF begins to have also, positives charges which can produce small electrostatics repulsion between both compounds. The amine group of DCF could interact with the oxygen groups like hydroxyls and carbonyls groups of MO, while the negative Cl ions of DCF could be creating bonds with the aromatics groups (CH) of the adsorbent.

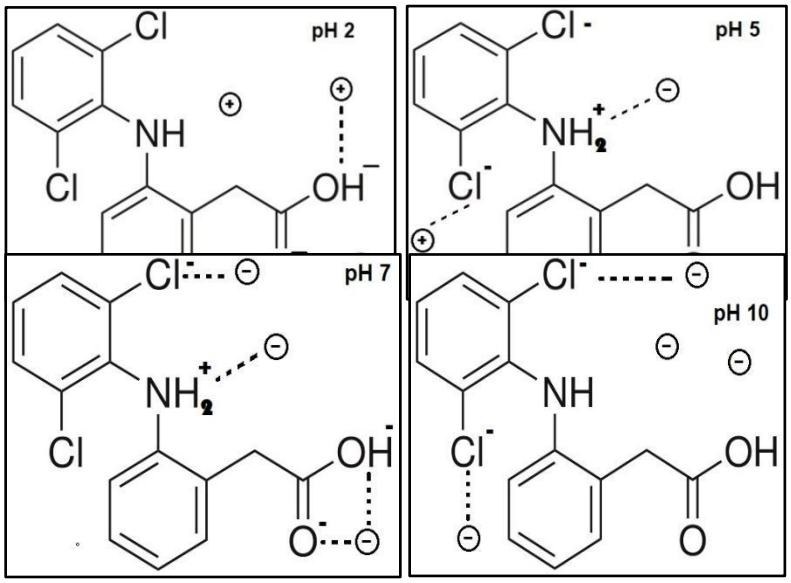


Figure 29 Possible adsorption mechanism for DCF removal using Moringa *oleífera* as adsorbent [64].

At the pH range of 7 and 10, the adsorbent and DCF surfaces are negatively charged causing strong electrostatic repulsion and making the adsorption capacity decrease. Although, there still some interaction between the positive charge of the amine group of DCF and the negative ions from MO, the repulsion between the carbonyl and hydroxyl group of the anti-inflammatory and the functional groups of the adsorbent, is stronger and more relevant.

Establish a possible adsorption mechanism for OTC removal is more difficult than it was for the DCF and it is because, this antibiotic presents a complex chemical structure and numerous properties making it a hard work. According to the results obtained in this study, the MO does not present a high adsorption capacity to remove OTC from water. This behavior could be explained through the strong pH dependence the antibiotic presents. At acid pH the OTC surface is charged positively so a high electrostatic repulsion is produced and the lowest removal percentage is obtained. As the pH grows, the antibiotic's surface starts to become negatively charged which could be the main reason a high adsorption capacity was not obtained. The nature of both surfaces does not allow obtain acceptable results. Even in the optimal conditions, the removal percentage stills low.

CONCLUSIONS

9 CONCLUSIONS

Based on the results, it is possible to conclude that:

- By FTIR analysis, it is known the Moringa *oleífera* presents a complex nature and a huge variety of functional groups, such as hydroxyl (-OH), -CH bonds, carbonyl group (-C=O), -C=C of aromatic compounds, carboxylic acids, amines, amides and phenols compounds. Also, it was possible to conclude that the hydroxyl, carbonyl and aromatic groups are the main responsible of the adsorption process for DCF and OTC.
- The surface charge of the adsorbent is negative for pH>6 and positive when pH<6. The study was made in order to have a clear understanding of the complex interactions between both surfaces (adsorbate and adsorbent).
- The high percentage of carbon contained in the MO was confirmed through a total organic carbon analysis (approximately, 2000 mg/l). After six washing processes, an equilibrium concentration of 40 mg/l was reached.
- The temperature does not have a significant influence on the removal of OTC and DCF. Although, it was concluded the adsorption process could be done at an average
- The amount of carbon (TOC) in the adsorbent has no influence in its adsorption capacity. A similar removal percentage was obtained for both pharmaceuticals.
- The maximum removal percentage was presented at the highest adsorbate concentration. It seems the removal of both pharmaceuticals present a tendency to increase “indefinitely” by increasing the initial concentration of the adsorbate. It would be recommended for a future work, to employ a larger range of concentration just to find out the values of OTC and DCF which saturates MO. Within the studied range, MO presented good adsorption rates.
- The adsorption isotherms were best fitted by the Freundlich model (R^2>0.97), indicating that the sorption processes took place in heterogeneous surfaces.
- Through the kinetic study, for DCF adsorption, a removal percentage of almost 75% was reached at approximately 90 min indicating the Moringa *oleífera* presents an acceptable adsorption capacity. For the OTC removal was obtained a percentage of only 34% after two hours. For a future work, it is recommended to extend the contact time between the adsorbent and the adsorbate (OTC and DCF) to evaluate it has any effect into the adsorption capacity of MO.

- For the DCF adsorption process, the kinetic data was best fitted by the model of Pseudo-second-order (R^2 of 0.9311). For OTC sorption, the kinetics was best fitted by the Intraparticle Diffusion model (R^2 of 0.9506).
- The adsorption process of DCF can be described as a phenomenon governed by chemisorption mechanism, while the OTC adsorption process presents high pH dependence and is governed by intraparticle diffusion forces
- OTC and DCF present high pH dependence. For OTC adsorption, the lowest removal percentage was obtained at pH 3 (31%) and the highest at pH 10 (50.3%) while for DCF adsorption, the lowest was obtained at pH 8 (4.8%) and the highest at pH 2 (87.3%). It seems the Moringa *oleífera* has a better affinity with the DCF than with the OTC. However, after all the experiences, it was possible to confirm that MO presents an acceptable potential adsorption capacity to remove pharmaceuticals. It has become in a promising area of research, which still needs to be explored in order to reach, in a future, the biosorption of pharmaceuticals by the use of Moringa *oleífera* becomes one of the most recommended non-conventional methods of pharmaceuticals removal. This would not only revolutionize the area of environmental and chemical engineering but would also be of great help to continue looking for other methods that can reduce the presence of emerging contaminants into water surfaces.

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