ENGENHARIA NA PRÁTICA:
IMPORTÂNCIA TEÓRICA E TECNOLÓGICA

FRANCIELE BRAGA MACHADO TULLIO
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CAPÍTULO 6

BIOSORPTION OF OXYTETRACYCLINE FROM WATER USING MORINGA OLEÍFERA SHELLS

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ABSTRACT: Pharmaceuticals as emerging contaminants have become a new threat to human life. Over the years, the amount of antibiotics and anti-inflammatory drugs has increased in rivers, lakes, oceans, and even in drinking water streams. The wastewater treatment plants (WWTPs) lack the necessary technology to remove a concentration within the range ng/l-mg/l and therefore, the need to develop effective, low cost and environmental friendly methods arise. Biosorption is a separation process, used in the area of Chemical Engineering, that follows the same fundaments of adsorption except for the use of biodegradable materials as adsorbent (biosorbent). This work focuses on studying the main optimal process conditions and the adsorption capacity of Moringa *oleífera* (MO) shells to remove Oxytetracycline (OTC). MO is recognized due to its anti-microbial, nutritional and coagulant properties; meanwhile, OTC is one of the most used antibiotics within the veterinary area.
KEYWORDS: biosorption, Moringa *oleífera,* Oxytetracycline, pharmaceuticals, emerging contaminants.

RESUMEN: Los fármacos, en su papel de contaminantes emergentes, se han convertido en una nueva amenaza para la salud de los seres vivos. Durante las últimas décadas, la presencia de antibióticos y anti-inflamatorios dentro de ríos, lagos, océanos e inclusive en corrientes de agua potable, ha ido creciendo. Las plantas de tratamiento de aguas residuales (ETARs) aún no cuentan con la tecnología adecuada para remover concentraciones dentro del rango de ng/l-mg/l y por ello, surge la necesidad de desarrollar nuevas métodos que sean efectivos, de bajo costo y además, amigables con el ambiente. 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 "biosorbentes". Es de gran interés en el presente trabajo, estudiar las condiciones óptimas del proceso y la capacidad de adsorción que presentan las cáscaras de la planta Moringa oleífera (MO) ante la remoción del antibiótico Oxitetraciclina (OTC). Moringa *oleífera* es reconocida mundialmente debido a sus propiedades anti-microbiales, nutricionales y coagulantes, mientras que OTC es uno de los fármacos más utilizados na área de medicina veterinaria.
PALABRAS CLAVES: biosorción, Moringa *oleífera*, Oxitetraciclina, fármacos, contaminantes emergentes.

1 I INTRODUCTION

Emerging contaminants are pollutants which were not known as a threat to the environment. It involves daily use products or compounds which toxicity has been dismissed until now (Galvín, 2016). Some examples are drugs of abuse, heavy metals, pharmaceuticals, chloroalkanes, polar pesticides, brominated flame retardants, detergents and metabolites of degradation products (Perales, 2016).

1.1 Pharmaceuticals as water surface contaminants

Pharmaceuticals are synthetic or natural chemical compounds used for diagnosis, treatment or prevention in human and animal diseases (Houtman, 2010). They 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 (Perales, 2016).They can get into the environment by different means; they can be found in human and animal's feces and urine. Others are effluents discharged from hospitals and pharmaceutical industries. In every city, all waste ends up in awastewater treatment plant (WWTP). However, WWTPs do not have the necessary technology to minimize the emerging contaminants concentration, so the resulting sludge contains high levels of the drugs, thus making the WWTP the main focus of pollution (Corona, 2013).

1.2 Oxytetracycline (OTC)

Oxytetracycline (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 1*)* (Díaz, 2018). 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. Table 1 summarizes its principal physicochemical characteristics (Díaz, 2018).

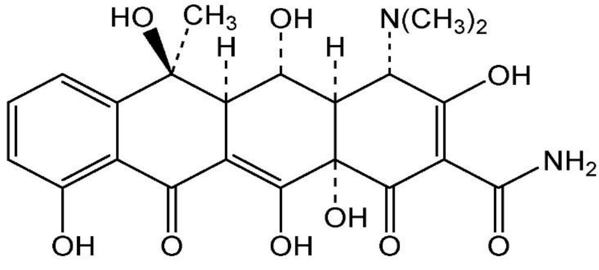

Figure 1Chemical structure of Oxytetracycline (Oliveira, 2013).

Physicochemical properties of Oxytetracycline	
1Molecular 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

Table 1Physicochemical properties of Oxytetracycline (Díaz, 2018).

1.3 Environmental effect of Oxytetracycline on water

OTC has been found in soil, hospital residues, WWTPs, water surfaces (rivers and lakes) and even in drinking water around the world (Díaz, 2018). 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, in the UK it was found values higher than 0,34 μg/l from water surfaces and 0,5 μg/l from water streams (Borghi and Palma, 2014). 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 (Fei et al., 2018).In Asia, it was found a maximum value of 484 μg/l into the river Xiao (Reiss et al., 2019).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 (Reiss et al., 2019).

Oxytetracycline has been declared as a toxic residue for aquatic organisms, humans and animal's health (European Medicines Agency, 1996) (Fraccaroli et al., 2015), high amount of this antibiotic could have negative consequences on the gastrointestinal tract, skin, central nervous system and it also stores up in calcium organs such as bones and teeth (Fraccaroli et al., 2015).

Different methods to remove OTC from water have been developed so far, such as hybrid carbon membrane which reached almost 99% of removal (Li et al., 2017), magnetic ion-exchange resin (Liu et al., 2015), reverse osmosis membrane with a removal percentage higher than 90% (Li and Wang, 2009), and adsorption by activated charcoal, also showing a strong adsorption capacity (Tsatsakis, 2000).

1.4 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 (Estrella, 2017), main 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 (Rivas, 2006). It is important to consider that the process leads to high efficiency, a decrease in the use of chemical products and biological sludge, no nutrients' addition and the possibility to recover both, the contaminant and the biosorbent. However, the adsorbent can be saturated quickly and the process is susceptible to variables such as temperature, pH and presence of other ions. 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. Within the first group, materials such as algae, bacteria, fungi and yeasts can be found, while the second one consists of biopolymers, agro-industrial residues, and plants (Rivas, 2006) (Tovar and Ortiz, 2014).

1.5 MORINGA oleífera Lam

Moringa *oleífera (MO)*, 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 (Perez, 2010).For more than thousands of years, practically all parts of the plant have been used: leaves, stems, pods and fruits. So far it is known, MO is highly nutritive, rich in vitamins, carbohydrates, dietary fiber, fats, proteins, minerals and amino acids (Figure 2) thus it is considered a powerful resource against children malnutrition (Martin, 2013).

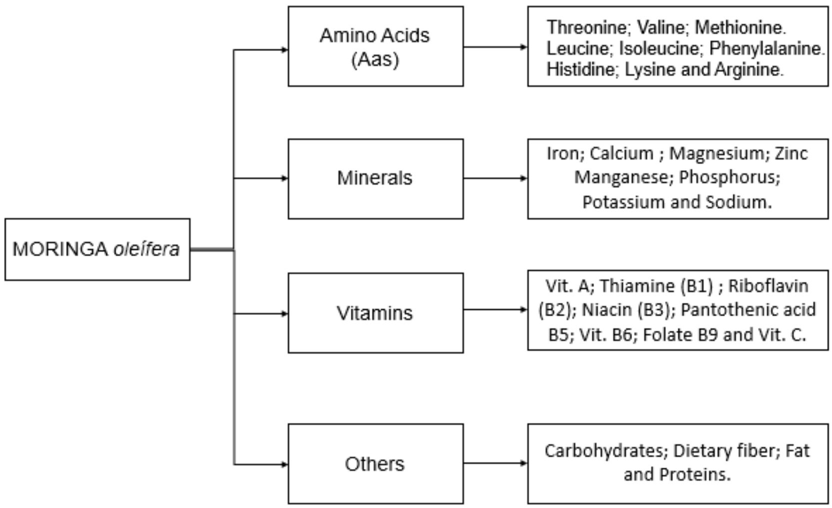

Figure 2 Chemical composition of Moringa oleífera (Abbas, 2018).

Its coagulant and bactericidal properties have enabled its use in wastewater treatment area. It is employedto decrease the turbidity of the water, the presence of bacteria and achieve a high percentage of removal of suspended solids (Martin, 2013). Now it is being studied as possible adsorbent to reduce presence of pharmaceutical and heavy metal in water. The use of MO represents an economical and environmentally friendly option.

2 I MATERIALS AND METHODS

2.1 Chemical solution and biosorbent preparation

Oxytetracycline hydrochloride (>95% crystalline), solutions of NaOH (1M, 0,1M) and HNO_3 (1M, 0,1M) have been employed in this work.For all the experiences, it was prepared 1 mg/l OTC solution.

The *Moringaoleífera* (MO) shells were taken from Luanda, Angola, Africa. They were dried in an oven at 30ºC for one day and pulverized into powder through IKA A11 basic analytical mill. 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. All the experiences were done with the granulometry 0,106 < μm < 0,205.

2.2 Determination of fundamental adsorption process conditions

2.2.1 Effect of initial antibiotic concentration

The Oxytetracycline concentration range was 0,2-1 mg/l while other parameters were kept constant (V=50 ml of solution, at pH 3, adsorbent dosage of 2 g/l, stirring at 150 rpm and temperature at 25°C).

2.2.2 Effect of the temperature

The temperature range used was 20 - 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 pH 3 and stirring speed of 150 rpm).

2.2.3 Effect of pH

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).

3 I RESULTS AND DISCUSSION

3.1 Effect of initial adsorbate concentration

The initial concentration of the adsorbate can determine the limits of the adsorption process. The removal percentage increased with the adsorbate concentration, but the difference was almost insignificantly, which suggests OTC initial concentration does not have enough influence in the adsorbent capacity (Figure 3).

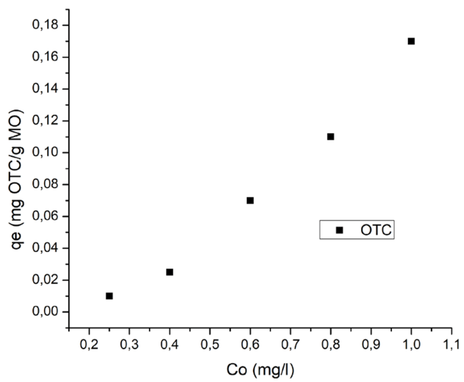

Figure 3 Effect of OTC initial concentration in biosorption process.

3.2 Effect of the temperature

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

3.3 Effect of pH

Evaluate the pH solution, is an important condition in the biosorption process. 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.

The Figure 4 shows how the adsorption capacity of MO increased with the pH. The lowest removal percentage was obtained at pH 3 (31%) and the highest at pH 10 (50.3%).

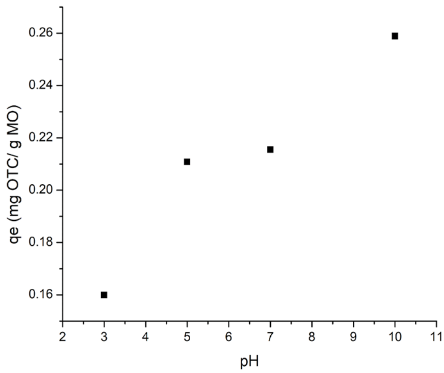

Figure 4 Effect of pH into the OTC adsorption process.

Although adsorption capacity increased with the pH, it did not reach a high value. 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 inpH. Theoretically, it has three pKa values and four ionization states (H_3OTC^+, H_2OTC^+, H_2OTC, and OTC^{-2}) (Díaz, 2018). 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) (Díaz, 2018) (Oliveira, 2013). Give this fact and considering MO surface charges (Araujo et al., 2018) it is likely to assumethe low removal percentage obtained at acid region was caused by electrostatic repulsion and although, the percentage increased at alkaline area, the negative charges of each surface did not allow to obtain an acceptable result.

4 | CONCLUSION

The removal percentage of MO shells increased with the OTC initial concentration. However it was not possible to determine Moringa adsorption capacity between the studied range of concentration (0 - 1 mg OTC/l).The process could be done at an average temperature of 25°C.So far, the results have showed strong pH dependence and low removal rates indicating MO shells are not the most adequate biosorbent to deal with this antibiotic. Despite this, further tests are recommended for better understanding of the biosorption process and the Moringa *oleífera* potential in the field of wastewater treatment

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