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REVIEW ON THE ELIMINATION OF PHARMACEUTICAL SUBSTANCES WITH AOP AND GAC TECHNOLOGIES IN WATERS

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Abstract: The main objective of this review highlights the presence of pharmaceutical compounds in water and pollution problems that can pose a potential threat to human health and have a negative impact on the environment and aquatic life. Contamination by pharmaceutical products constitutes a toxicity problem. It is necessary to find the best available technologies to eliminate these pharmaceutical substances. All available technologies alone cannot completely eliminate pharmaceutical products from water unless combined with other processes which can give an attractive elimination rate. The different treatment processes for the disposal of pharmaceuticals have also been summarized in this review. Among the treatments studied: conventional treatments, advanced oxidation processes, adsorption processes (such as activated carbons, biochars, nano adsorbents, carbon nanotubes and graphene, clays, zeolites, etc.)

Keywords: Ozone process, Toxicity, Pharmaceutical substances, Granular activated carbon (GAC), Advanced oxidation processes (AOP).

1. Introduction

In recent years, pharmaceuticals have been detected in wastewater and surface and groundwater [1]. These pharmaceutical substances are recognized as contaminants of concern that have received increasing attention as chemicals that are found in the environment with very low concentrations (ng/l, µg/l) [2] [3] which can affect the quality of drinking water as well as environmental impacts on ecosystems and especially harmful effects on human health [4]. The presence of pharmaceutical compounds in ecosystems (Table 1) causes aquatic toxicities as well as harmful effects on the environment such as the evolution of resistant bacteria [5] which attacks human health with acute or chronic toxicity.

Table 1

Pharmaceutical substances detected in wastewater.

Pharmaceutical substances	**Molecule formula**	**Concentration (ng/l)**	**Source**
Clofibricacid	$C_{10}H_{11}ClO_3$	0.009	**[6]**
Atenolol	$C_{14}H_{22}N_2O_3$	57	**[7]**
Gemfibrozil	$C_{15}H_{22}O_3$	0.6	**[8]**
Ciprofloxacin	$C_{17}H_{18}FN_3O_3$	0.313	**[9]**
Sulfamethizol	$C_9H_{10}N_4O_2S_2$	11.35	**[10]**
Tetracyclin	$C_{22}H_{24}N_2O_8$	4.88	**[11]**
Amoxicillin	$C_{16}H_{19}N_3O_5S$	7.45	**[12]**
diclofenac	$C_{14}H_{11}C_{12}NO_2$	5.81 6.15	**[13]** **[14]**
Triclosan	$C_{12}H_7Cl_3O_2$	0.5	**[15]**

Several researchers have used treatment processes to remove these pharmaceutical pollutants but not all processes are effective in removing these pharmaceutical substances such as biological methods which are used to treat industrial wastewater and are not ineffective in removing pharmaceuticals, for example. carbamazepine (CBZ) and diclofenac (DCF) [16,17]. Certain treatments can reduce these pollutants. Among the alternative treatments that are capable of degrading or eliminating pharmaceutical substances through the production of hydroxyl radicals (such as HO•) advanced oxidation processes (AOP) [18].

This process gives good results for the degradation of pharmaceutical pollutants with the combination of biological treatments in aqueous matrices. Compounds generated during the preliminary chemical oxidation process can be biologically mineralized [19,20].

Presence of pharmaceutical products in wastewater and their ecotoxicological danger

The presence of pharmaceuticals at water surface levels has been detected in many countries and recognized as an ecological contaminant [21]. The ecosystem is threatened by a new form of pollution linked to human activity: an enormous quantity of drugs released each year into the ecosystem [22] with different concentrations, pharmaceutical substances could be slightly degraded in the ecosystem. water that could present human and/or animal health risks [23] for example endocrine disruption, reproductive problems, microbial resistance and ecotoxicities even at lower concentrations [24].

The excretion of pharmaceuticals is transformed into glucuronide or sulfate by urine or bile and hydrophilic derivatives, as a metabolite or as a mixture of metabolites [25]. The ecotoxicological impacts of these pharmaceutical products on life are unknown [26].

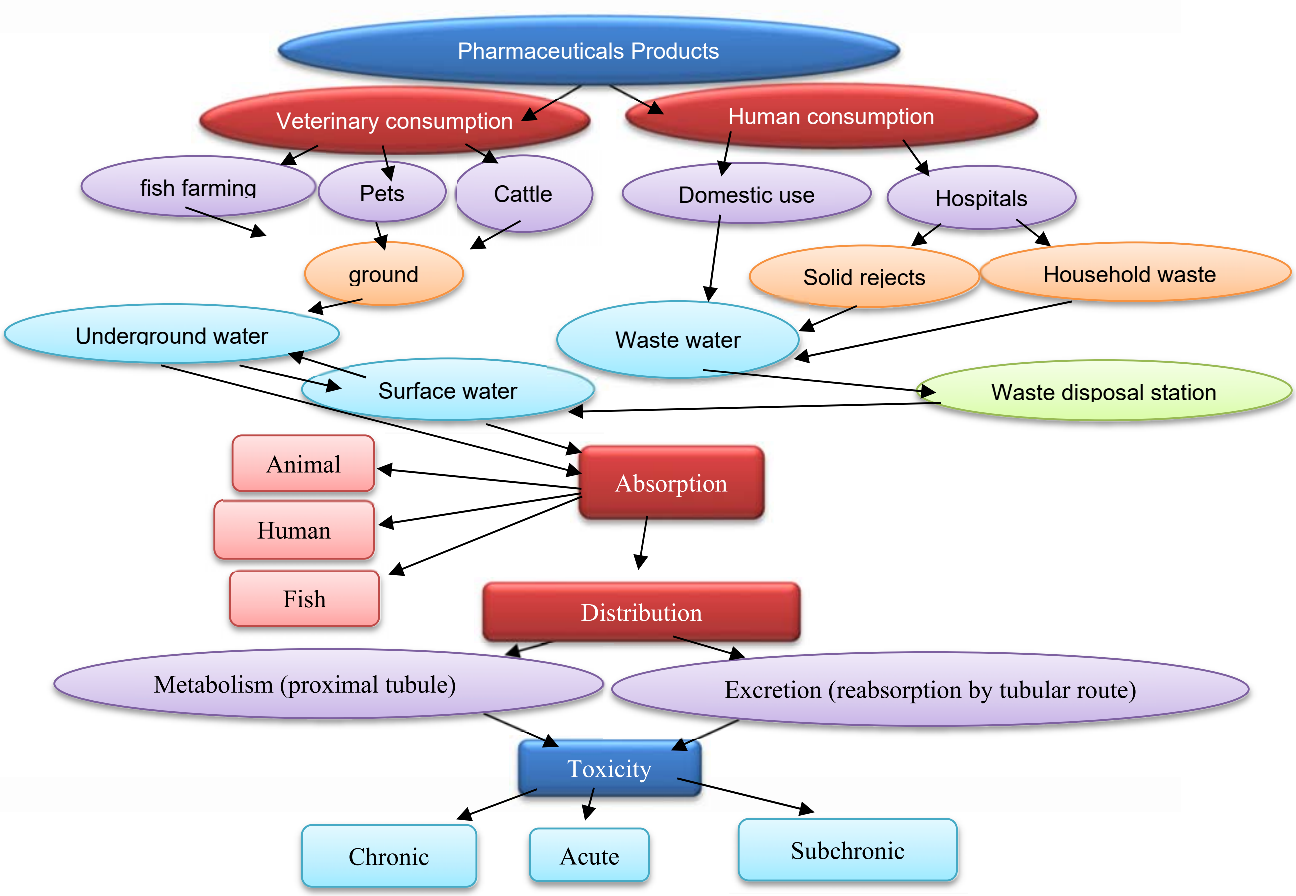

Fig. 1 - Diagram explains the different stages of the effect of pharmaceutical products on human health.

2. Technologies for pharmaceutical wastewater treatment

In recent years, pharmaceutical substances have caused significant damage to the physicochemical quality of water [27]. Several technologies have been investigated to remove pharmaceutical contaminants found in surface water and wastewater but are difficult to remove due to resistance to degradation even at low concentrations [28]. the process which reduces the concentrations of pharmaceutical substances with an interesting elimination rate is the advanced oxidation process or the coupling with the adsorption process by activated carbon, the advantage of the adsorption process does not produce any risk of toxicity with an effective elimination percentage and with a cheaper cost [29].

2.1. Elimination technologies with AOP

As noted above, polluted water can generally be treated effectively by biological treatment plants, using adsorbents or chemical treatments (chlorination, ozonation or permanganate and oxidation). However, these procedures are sometimes unable to degrade pollutants to the levels required by law or essential for further use of the effluent. AOP (advanced oxidation processes) are very effective in the oxidation of many inorganic compounds. These processes are all based on the generation of free radicals ($HO^{\cdot}$, O^{-2}, HO^{-2}), in particular the hydroxyl radical ($HO^{\cdot}$). highly reactive species that can successfully attack most molecules, with high reaction rate constants of 106 to 109 M/s. These radicals can generate many pollutants which makes AOPs very versatile **[30,31]**. Their potential for removal Pharmaceutical pollutants from water are discussed below.

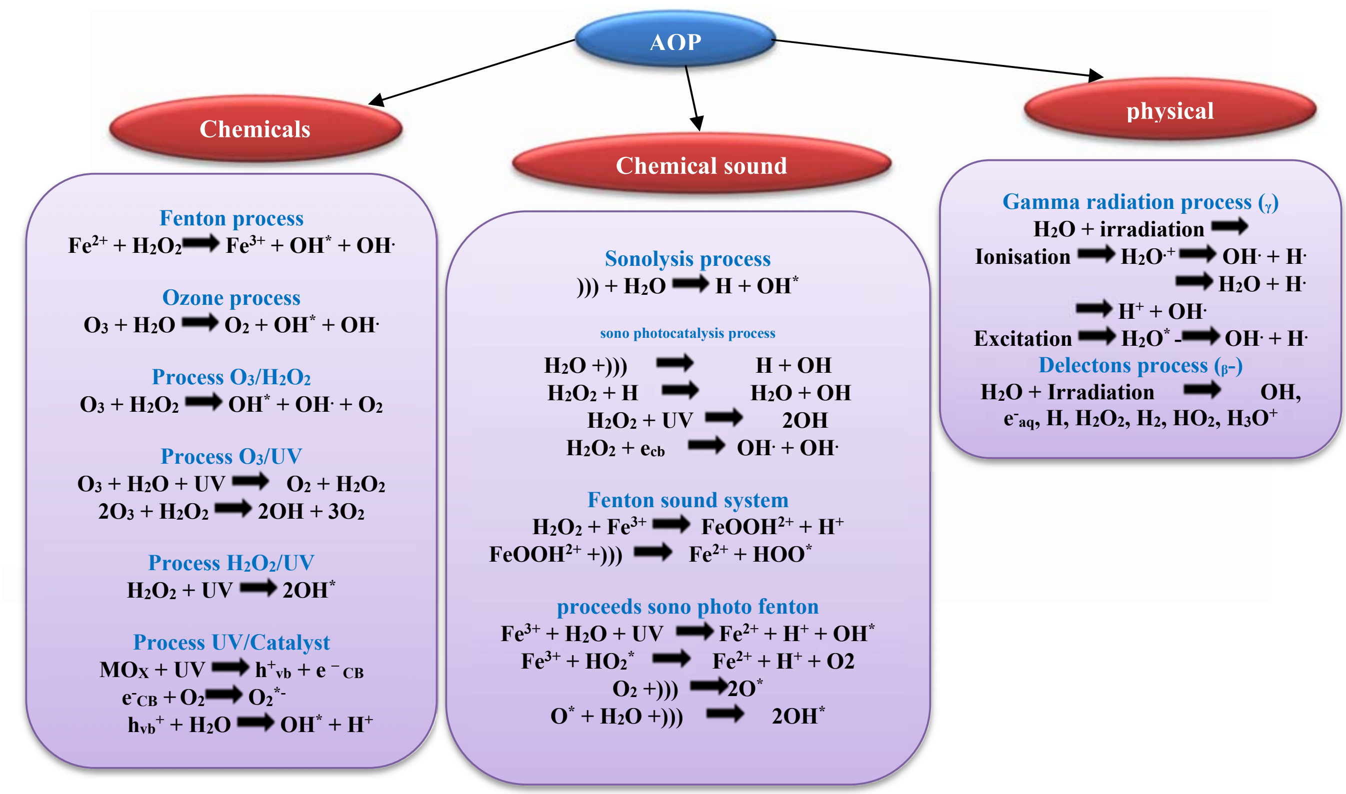

Fig. 2 - AOP (advanced oxidation processes).

2.1.1. Elimination with ozone process

Advanced oxidation processes are methods capable of degrading several types of pharmaceutical pollutants from an aqueous medium with the exception of a few pharmaceutical substances which resist biodegradation due to their complicated chemical structures which sometimes require greater numbers of hydroxyl radicals for gradients.

Among these AOP methods we are talking about the ozone process which produces many hydroxyl radicals to degrade organic pollutants present in the aqueous medium, it degrades many pharmaceutical substances with interesting elimination percentages as shown in Table 2, the percentages elimination that are weak have amide bonds that are resistant to ozone [32]

Table 2

Comparison of AOP degradation efficiencies in leachates and antidotal effluents

Medicaments	Initial concentration mg/l	Process used	Contact time (min)	Final concentration	Source
Trimegestron	0.1mg/l	O_3	1	0mg/l	**[33]**
Carbamazepin	65 ng/l	O_3/H_2O_2	5	2 ng/l	**[34]**
Fluoxetin	54 ng/l	O_3/H_2O_2	5	15 ng/l	**[34]**
Fluoxetin	54 ng/l	O_3/H_2O_2	10	3 ng/l	**[34]**
Ofloxacin	565	O_3/H_2O_2	5	33 ng/l	**[34]**
Enrofloxacin	-	$O_3/UV/H_2O_2$	20	88%	**[35]**
Enrofloxacin	-	O_3/UV	30	75%	**[35]**
Enrofloxacin	-	$O_3/UV/H_2O_2$/FENTON	15	100%	**[35]**
Diclofénac	0.016 mg/l	O_3	-	100%	**[36]**
Kétoprofèn	346 microg/l	O_3	-	70%	**[37]**
Ciprofloxacin	572 ng/l	O_3	-	98%	**[37]**

In this case it is necessary to use a combination of ozone process with other process to produce many hydroxyl radicals, such as cokgor which uses the coupling of hydrogen peroxide with ozone which gives an efficient degradation of penicillin [38].

In the following figure the authors use several processes with the combination of O_3 by the systems O_3/UV, O_3/H_2O_2, O_3/H_2O_2/UV, O_3/TiO_2 and O_3/TiO_2/UV, which gives a total elimination of Amoxicillin at 3min in all the processes displayed except ozone alone gives total elimination up to 5min. The objective of this research is the aid of ozone for the productions of hydroxyl radicals OH to improve the oxidation rates for the attack and elimination of pharmaceutical products.

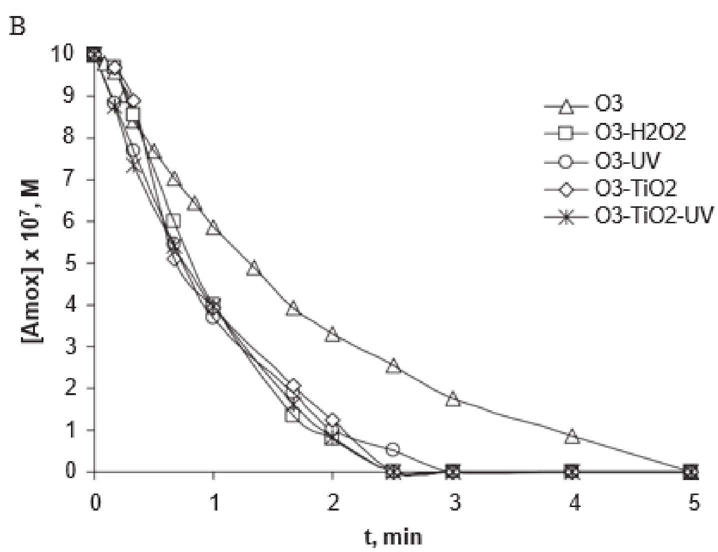

Fig. 3. - Comparison of the combination of ozone process with other advanced oxidation process is evolution of the concentration with the reaction time for amoxicillin [39].

The curves that are displayed in Figure 4 of the four pharmaceutical pollutants in wastewater represent 6 effluents for each effluent 6 different O_3 dose (mg/l) as follows:

- Effluent 1 (10.2mg/l, 6.9mg/l, 5mg/l, 2.6mg/l, 1.3mg/l, 0.6mg/l)
- Effluent 2 (11.7 mg/l, 7.1 mg/l, 5.4 mg/l, 2.4 mg/l, 1.2 mg/l, 0.6mg/l)
- Effluent 3 (8 mg/l, 5.3 mg/l, 3.5 mg/l, 2 mg/l, 1.1 mg/l, 0.5mg/l)
- Effluent 4 (7.8 mg/l, 5.5 mg/l, 3.6 mg/l, 2.1 mg/l, 1.1 mg/l, 0.6mg/l)
- Effluent 5 (8.9 mg/l, 6.1 mg/l, 4.4 mg/l, 2.3 mg/l, 1.1 mg/l, 0.5mg/l)
- Effluent 6 (7.7 mg/l, 6.2 mg/l, 4.5 mg/l, 2.4 mg/l, 1.2 mg/l, 0.6mg/l)

This figure demonstrates that the highest doses of ozone degraded the substances and each active ingredient their maximum dose. Once the ozone dose has been exceeded, elimination rates decrease, meaning an exponential decay for pharmaceutical substances.

Our opinion for the shift in percentages for the degradation of active pharmaceutical (AP) is the structural form which reacts with ozone and directly consumes low concentrations or other form with different matrices which require higher doses.

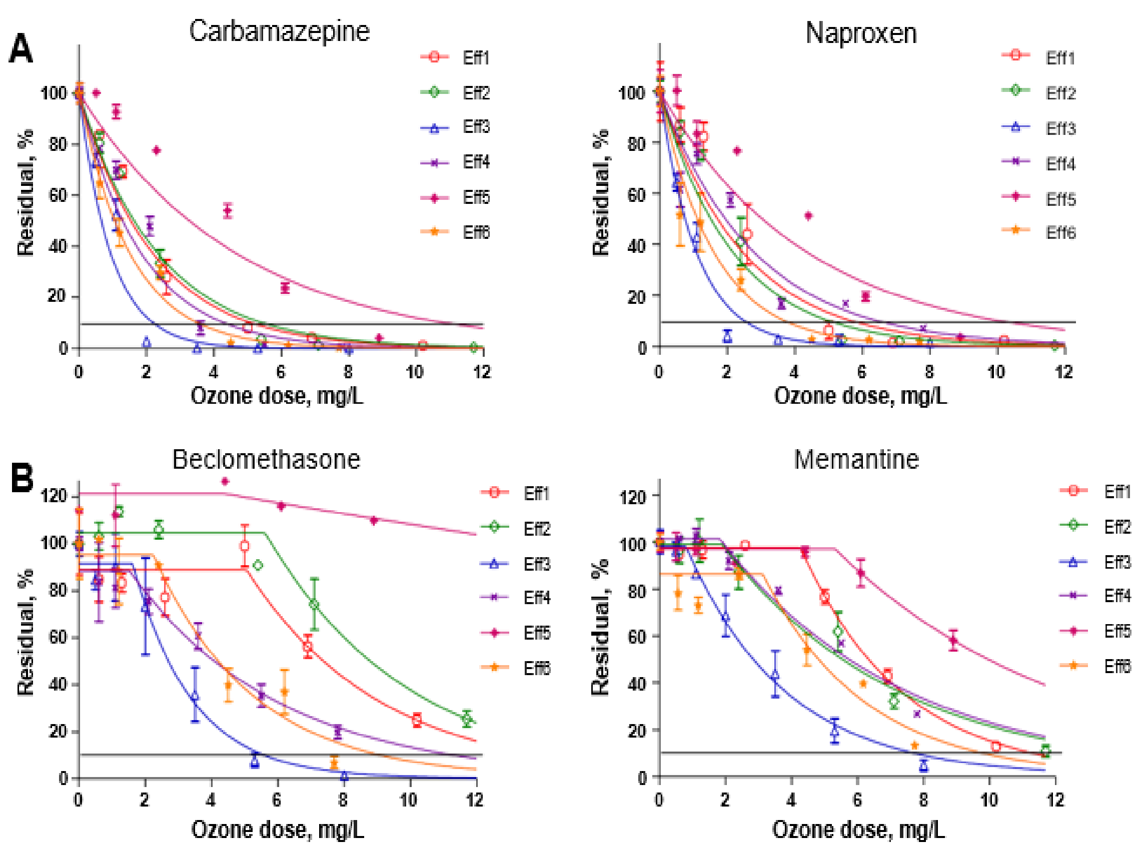

Fig. 4 - Concentration profiles for selected APIs in different WWTP effluents, which follow a first-order decay with the delivered O_3 dose (DO_3) (A) or exhibit an apparent lag phase (B). The intersection of the black horizontal line with the remaining API concentration of 10% (y-axis) indicates the corresponding DDO_3. The T-bar represents the standard deviation with n = 3 [40].

2.1.2. Elimination by the activated carbon adsorption process

Activated carbon contains several forms that can be used to remove pharmaceutical contaminants, such as powdered activated carbon (PAC), granular activated carbon (GAC). Both their removal efficiency due to the pore surface area **[41]** and the pore volume for the adsorption of pharmaceutical substances, as presented in Figure 4 of an activated carbon prepared with a specific surface area of pac1 1750 m^2/g and pac2 2950 m^2/g, for the pore volume (pac1 10.60 cm^3/g, pac2 20.75 cm^3/g).

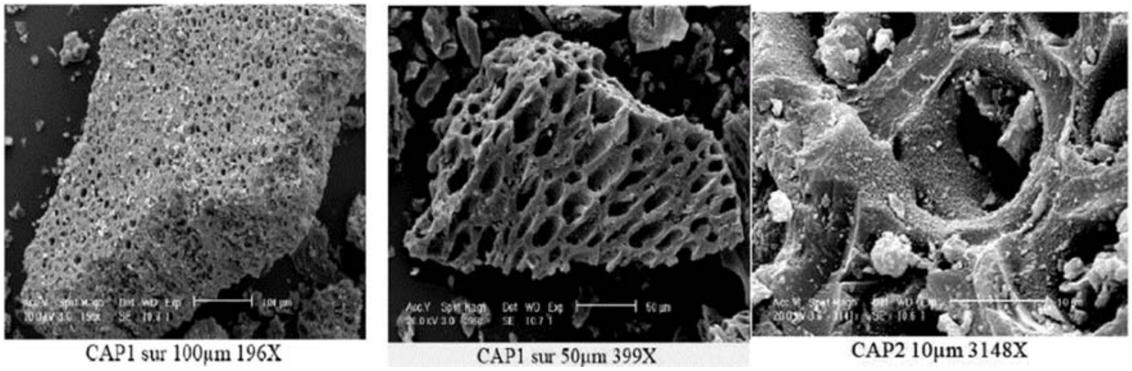

Fig. 5 - Prepared activated carbon CAP1 and CAP2**[42].**

Adsorption has been the subject of extensive studies for the elimination of different pollutants [43] as the study of Kazemi discovered an effective elimination of mercury ions with the adsorption process by powdered activated carbon until 98% [44].

The following figure presents the maximum and minimum removal results for 66 pharmaceutical products by the activated carbon adsorption process which gives variation in adsorption of these pharmaceutical pollutants to each other, due to each product pharmaceutical their chemical structure which is responsible for the variation in adsorption rate by the actif carbon (AC) (see Table 3).

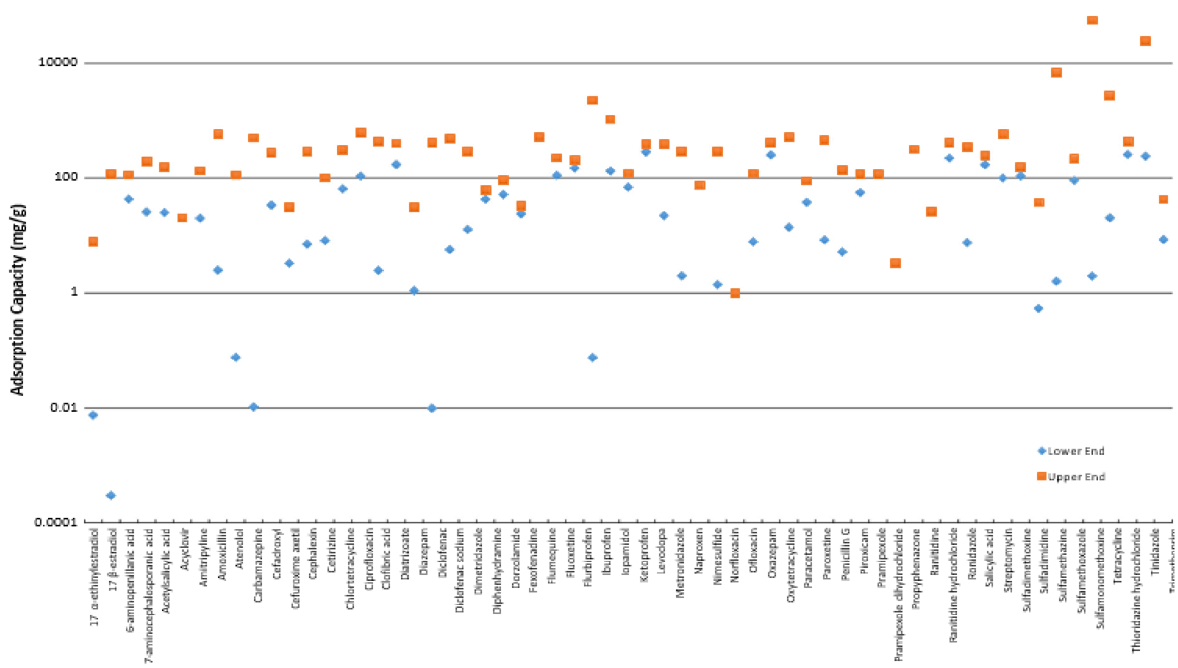

Fig. 6 - Maximum and minimum adsorption capacity of different types of activated carbons for the elimination of 66 pharmaceutical products (by mass of pharmaceutical products per mass of AC used) [45].

Table 3

Elimination of pharmaceutical products by granulated activated carbon.

Drugs	Initial concentration	Method used	Removal percentage (%)	Source
Diclofenac	1008 ng/l	GAC	72	**[46]**
sulfamethoxazole	145 ng/l	GAC	59	**[46]**
17b-estradiol	2 mg/l	GAC	20–97	**[47]**
Amoxicillin	100-500 mg/l	GAC	96.5	**[48]**
Diclofenac sodium	10-30	GAC	76-93.6	**[49]**
Azithromycin	20	GAC	55	**[50]**

The contact time with the AC and the concentration also plays a role on the adsorption rate as presented in Figure 6 on the elimination of keprofen, when the concentration is high the adsorption will be increased.

Such as Cyclamen persicume tubers (423.3 to 606.78 m^2/g), peach pits (1053 m^2/g), date pits (1044m^2/g), coconut shells (850.64m^2/g) or Ziziphus spina-christi seeds (914.23 m^2/g) [51].

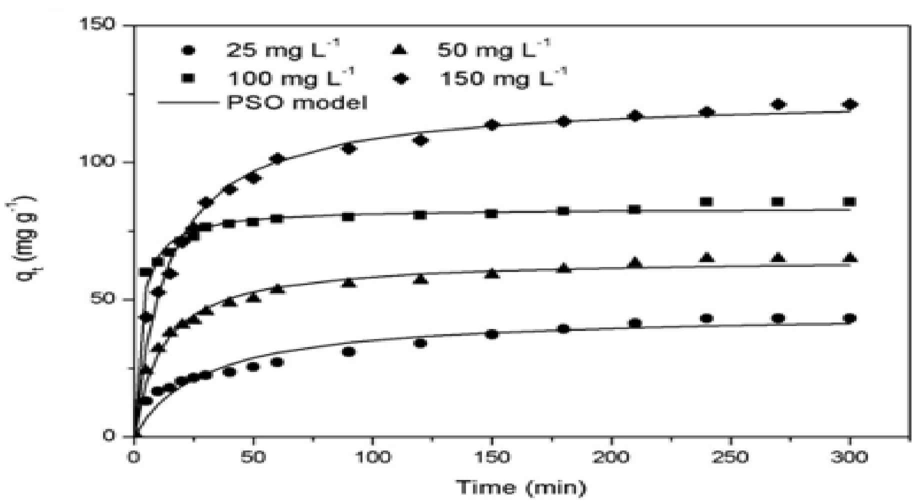

Fig.7 - Adsorption kinetic curves of ibuprofen on AC (298 K, pH 2, adsorbent dosage of 0.5 g/L)**[52].**

The authors of this work studied four different processes on the surface of activated carbon (amine functional groups (AC-NH2 and AC-APTES), thiol functional groups (AC-MPTMS), a covalent organic polymer (AC -COP) tested on six pharmaceuticals as pollutants in water (carbamazepine (CBZ), lorazepam (LOR), sulfamethoxazole (SMX), piroxicam (PIR), paroxetine (PAR), and venlafaxine (VEN) in different matrices (ultrapure water, and effluents

wastewater treatment plant (STEP)). The AC-NH2 process gives high absorption for PAR and VEN, and for the AC-MPTMS process gives a very high elimination rate concerning SMX but like AC alone On the other hand, the AC-APTES and AC-COP processes give poor results. The operation of these processes with activated carbon does not give a good improvement than activated carbon alone for the degradation of. pharmaceutical substances.

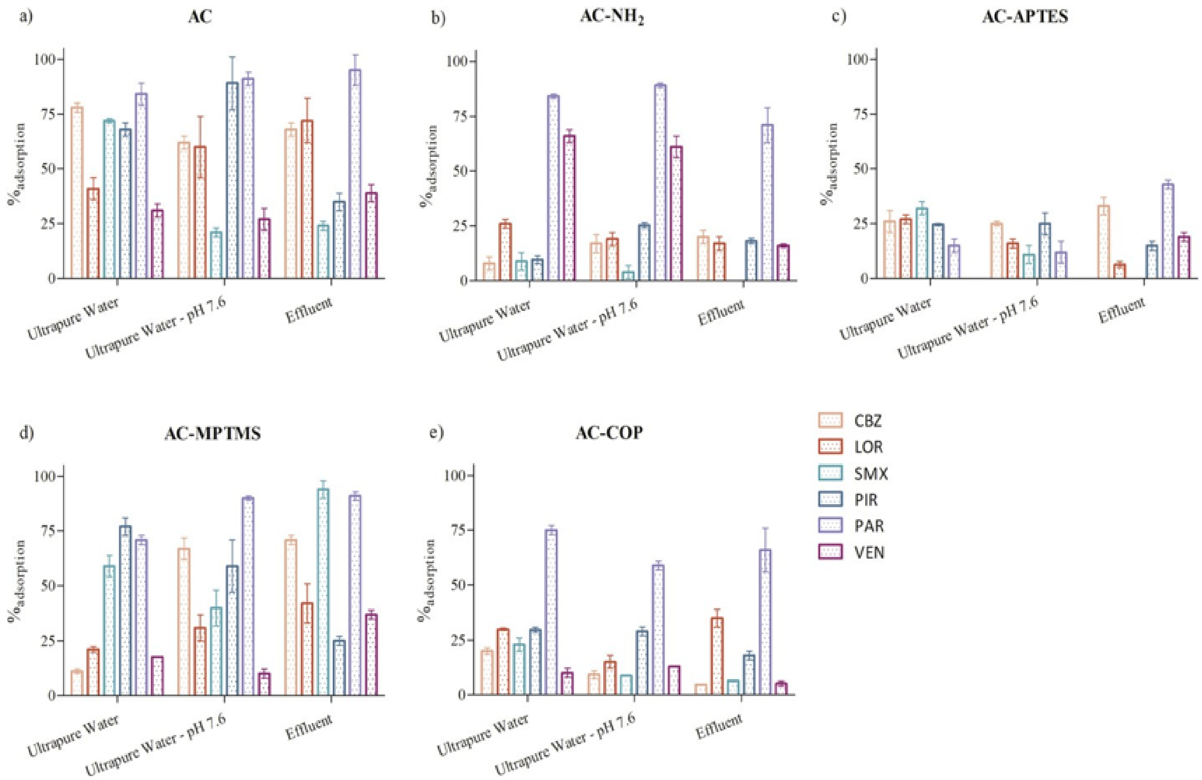

Fig. 8 - Adsorption of the six pharmaceutical products studied (CBZ, LOR, SMX, PIR, PAR and VEN) in different matrices (ultrapure water, ultrapure water at pH 7.6 and WWTP effluent) on AC and functionalized AC. Error bars correspond to standard deviations (n = 3) **[53]**.

The authors also made a combination with TiO_2 at different mass ratios (-9%, -16.6%, -33.3%) (see Figure 9) and noted a decrease in the elimination rate with the increase in the ratio. of mass which gives a maximum elimination rate at 700 °C on all the processes used with a very high elimination rate in activated carbon alone and AC/TiO_2 -9% with percentages 98% and 90% respectively. These values highlight that the activated carbon process does not work with TiO_2, due to the reduction in removal rates due to the physical changes (total surface area and pores decrease in volume (see following figure).

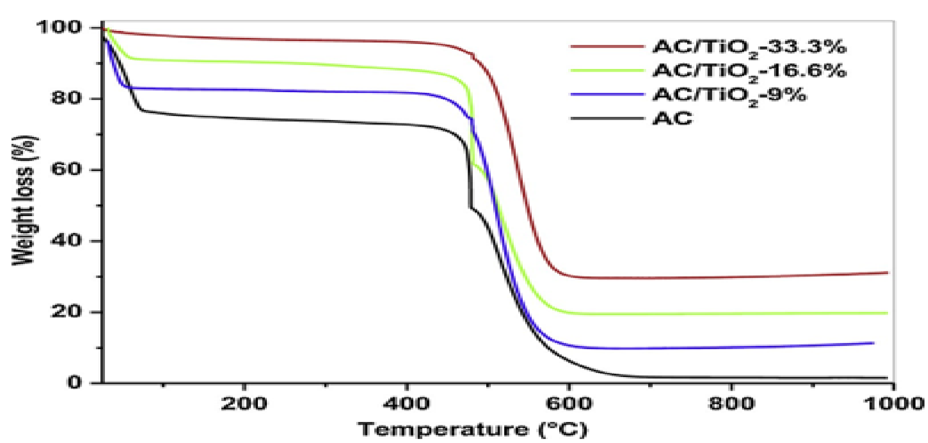

Fig. 9 - TGA profile of AC and AC/TiO_2 composites.

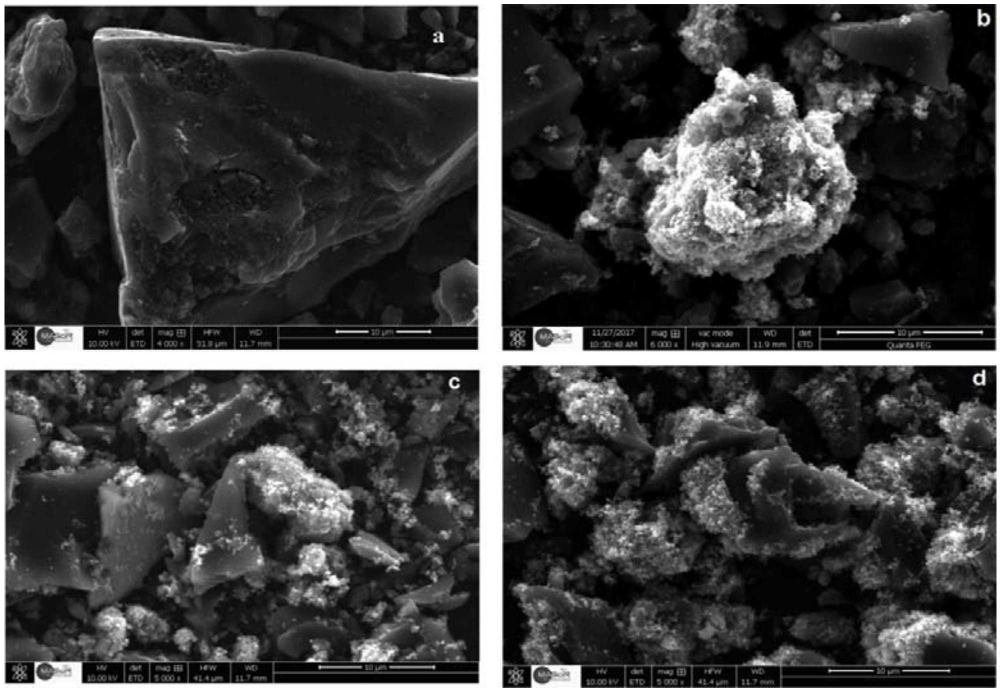

Fig.10 - SEM image of AC (a), AC/TiO2: 9% (b), 16.6% (c) and 33% (d)[54].

3. Conclusion

In this review on the elimination of pharmaceutical products found on the surface of water, we have carried out some research with different studies established by several authors on the elimination of pharmaceutical waste to avoid toxicological effects on human or animal health .

After several studies, it was found that advanced oxidation processes can degrade many pharmaceutical pollutants present in water, but the percentage of degradation changed depends on the initial concentration (fig7) and the chemical structure of the pharmaceutical substance (see Figure 4).

Let us conclude in this advanced oxidation process that the percentage of degradation increases with the number of POA couplings used (example: the O_3 process no better than O_3/UV and no better than O_3/UV/TiO_2 (see figure 3)), and we also see the difference in the elimination percentages of Enrofloxacin (table2) with the processes O_3/UV/H_2O_2 ,O_3/UV, O_3/UV/H_2O_2/FENTON gives 88%, 75% and 100% respectively.

But the process most used in the majority of research is the ozone process because it produces a lot of hydroxyl radicals and is capable of attacking the chemical structure of pharmaceutical products and degrading them.

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