OCCURRENCE AND PHOTO-DEGRADATION OF 9 PHARMACEUTICAL RESIDUES IN EFFLUENTS OF WASTEWATER TREATMENT PLANTS (WWTPs)

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TÓM TẮT

NGHIÊN CỨU TỒN DƯ VÀ PHÂN HỦY QUANG HÓA CỦA 9 HOẠT CHẤT DƯỢC PHẨM TRONG NƯỚC ĐẦU RA CỦA NHÀ MÁY XỬ LÝ NƯỚC THẢI

Ngày nay, các dư lượng dược phẩm trong môi trường được biết đến như những chất có thể gây nguy hại cho hệ sinh thái nước và con người. Phân tích, đánh giá tồn dư của 9 dược phẩm (diclofenac, ibuprofen, ketoprofen, naproxen, carbamazepin, atenolol, metoprolol, propanolol và sotalol) đã được nghiên cứu đánh giá trên nước đầu ra 4 nhà máy xử lý nước thải sinh hoạt tại vùng Tây-Nam, Pháp. 32 mẫu nước thải đã được lấy phân tích đánh giá trong 2 năm 2011-2012. Mẫu sau thu thập sẽ được làm giàu bằng hệ chiết pha rắn (SPE) sau đó đem phân tích bằng hệ thống sắc ký lỏng ghép nối 2 lần khối phổ. Tần suất xuất hiện của các chất này trong mẫu là rất cao (>90%) với dải nồng độ từ vài trăm ng/L tới vài µg/L. Nồng độ cao nhất được tìm thấy ở atenolol và sotalol (lên tới 8µg/L and 10µg/L tương ứng). Cũng trong nghiên cứu này, các quá trình phân hủy quang hóa dưới ánh sáng mặt trời cũng được thực hiện. Sự phân hủy của diclofenac, ketoprofen diễn ra nhanh, trong khi ibuprofen, carbamazepin, atenolol, metoprolol có vẻ như bền vững dưới tác động của ánh sáng mặt trời. Thời gian bán hủy của một số chất đo được trong cả 2 môi trường nước (nước đề ion - UPW và nước sông - RW): diclofenac (35 và 36 phút), naproxen (207 và 175 phút), sotalol (142 phút trong nước sông) và propanolol (1124 và 236 phút) tương ứng. Mặt khác, sự phân hủy quang hóa của naproxen, propanolol và sotalol lại bị ảnh hưởng mạnh bởi các chất hữu cơ có mặt trong môi trường nền.

Từ khóa: Dư lượng dược phẩm, LCMSMS, phân hủy quang hóa, nước thải, ánh sáng mặt trời

1. INTRODUCTION

Nowadays, a great number of Pharmaceuticals and Personal Care Products (PPCPs) are used for both human and veterinary health in medical [1]. Presence of pharmaceutical residues in the environment has attracted many scientists over the last decade. The pharmaceuticals, after therapeutic treatment (human or veterinary) were excreted as the parent compounds or as the metabolites in urine and feces before being transferred directly via WWTPs in case of human therapeutics [1-4] or via the ground [5-6] in case of veterinary therapeutic or via the water in case of aquaculture [6].

The effluents of WWTPs are considered as a principal source of pharmaceuticals residues in the aquatic system. Principally, the goal of WWTPs is to remove the classical pollutants such as organic matters, greases, solids (soils and sand) and nutrients, not focus for eliminating the pharmaceutical pollutants. However, recently researches of pharmaceutical residues of influent and effluent showed a high effective removal of these pollutants in Sweden [7], in USA [8], in Korea [3-4] and in Spain [9]. For instance, Nonsteroidal Anti-Inflamatory Drugs (NSAIDs) experienced for highest removal up to 100% for paracetamol [9-10], 99% for ibuprofen [11]. In contrast, WWTPs cannot eliminate all pharmaceuticals residues. Carbamazepin is poor removed in WWTPs from 1-30% [2, 12-13], these poor removals were also found for β-blockers [10, 14] or for some sulfonamides [3, 9]. Moreover, recent researches in effluents of WWTPs show the presence of many pharmaceuticals in the range of some ng/L up to some µg/L. These results have attracted much attention because the pharmaceutical residues have been increasing in evaluating the environment risk [6, 15, 16].

Besides, after discharging into aquatic system, the treated water also has been emitted by solar light. To better understand the elimination of pharmaceutical residues under the solar light, laboratory studies were performed [12]. These researches showed that the photo-degradation of pharmaceuticals residues was influenced by the change of pH values [17], presence of natural photo-sensitizers such as humic acid, nitrate ion [18-19]. The presence of NOM/DOM (natural organic matter/dissolve organic matter) also plays an important role in photochemical processes in surface water. They can act as inner filter, as initiator or as inhibitor of reactive species [20-21].

In this research, we focused on monitoring the concentration of nine pharmaceutical residues which are frequently detected in surface water, in 4 effluents of WWTPs in France from 2011 to 2012. Moreover, the photodegradation of these compounds in both ultrapure water and river water under solar light was also performed.

2. MATERIALS AND METHODS

2.1. Sampling sites selection

In this study, effluents of 4 WWTPs in South-West of France were collected. 2 effluents nearly Perigueux (namely TOX1, TOX2) which are locating around the Isle River has constructed for a medium nominal capacity (48300 and 10000 inhabitants

respectively). One WWTPs at Bordeaux has a huge treatment capacity (408300 inhabitants) TOX3 and the last one at Biganos has constructed for medium capacity (135000 inhabitants) (TOX4). Three WWTPs (TOX1, TOX3 and TOX4) are using bio-filter and TOX2 is using extended aeration activated sludge as main parameter to reduce organic matters. Moreover, these WWTPs are also pre-treating by other processes such as physical decantation, phosphorylation or chemical deodorization. Samples are taking by mean 24h with help of an auto-sampler (TOX1, TOX2 and TOX4) or by punctual method (TOX3). All samples are taken at point of effluents before discharging in the environment. For each WWTP, 8 samples were collected in the period from 2011 to 2012. The principal parameters of treatment processes were described in table 1.

All samples were kept in glass bottles (20L) pre-baked at 450°C in 6h or in plastic bottles (10L) pre-rinsed several times with ultrapure water in the laboratory and rinsed with sample water on site. The samples were kept to cold (4°C) using glaciers and ice-breaker and brought back to the laboratory in 24h.

In laboratory, samples were filtered with glass microfiber filters (GF/F Whatman®, $\phi \leq 0.7\mu m$) by vacuum filtration unit to eliminate the suspended matters. The pre-filter (GF/A Whatman®, $\phi \geq 1.6\mu m$) likely used if the samples greatly have charged the suspended matters. All glass microfiber filters have been also baked at 450°C in 6h to eliminate all organic contaminants. The filtered samples were stored in 4°C, then extracted and analyzed in next 48h or stocked in deep freezer at -20°C in order to analyze later.

Table 1: Principal parameters in 4 collected WWTPs.

WWTPs	NC/ML (EI) $x10^3$	AI/RI m^3/day $x10^3$	Treatment process	SP tMS/year	Sampling
TOX1	48.3/47.9	8.5/14	Secondary treatment Physico-chemistry primaries treatment Dephosphorisation Biofilter	1204	Mean 24h
TOX2	10/6	0.92/3.2	Secondary treatment Extended aeration activated sludge	80	Mean 24h
TOX3	408.3/380.3	65.2/100	Secondary treatment Pretreatment Physical decantation Biofilter	2704	Punctual
TOX4	135/77.9	21/15.8	Secondary treatment Physical decantation Biofilter Chemical deodorization	1522	Mean 24h

Source: http://assainissement.developpement-durable.gouv.fr/

NC/ML: Nominal capacity/maximal load AI/RI: Average input/reference input
SP: Sludge products tMS: tone of solid mass
EI: Equilibrium inhabitant

2.2. Chemicals and reagents

All standard compounds which are analytical purity has been purchased from Sigma-Aldrich. LGC standard and Cluzeau Info Labo (France).

All the reagents and extraction solvents were acetonitrile (ACN, Baker, ultra gradient HPLC grade (Atlantic labo, Bruges, France)), methanol (MeOH, Merck Lichrosolv, gradient grade for LC (VWR, Strasbourg, France)), ultrapure water (milliQ, Millipore, Saint Quentin en Yvelines, France) synthesized in the laboratory and natural mineral water (NMW, Vittel, Nestle (France Boissons, Lormont, France)), the reagents were purchased acetic acid glacial (CH_3COOH) from Scharlau. HPLC grade (Atlantic labo), formic acid (HCOOH, analyzed 98% purity (Atlantic labo)), hydrochloric acid (HCl, analyzed reagent, 36.5-38% (Atlantic labo)) from Baker, sodium hydroxide (NaOH, normapur 97% purity (VWR)) from VWR BDH. OASIS **MCX** (**M**ixed-mode **C**atione e**X**change 60 mg 3 cc) from Waters (Saint Quentin en Yvelines. France). The filters were 0.7 µm glass fibre filter (GF/F, Whatmann and 1.6 µm glass fibre filter (GF/A. Whatman - Fisher Bioblock Scientific). They were baked at 450°C for 6h before using.

2.3. Sample preparation and analyses

2.3.1. Solid phase extraction (SPE)

200mL filtered samples were adjusted pH2 by using HCl solution (1/3; V/V) then adding internal standard (mixed internal standard: diclofenac D4, ketoprofen D3, ibuprofen D3, naproxen D3, carbamazepin D10. atenolol D7 and propranolol D7 used to determine metoprolol. propranolol and sotalol). The MCX cartridges (60mg, 3cc OASIS®) were preconditioned by 3 ml ethyl acetate then rinsing with 3 ml water at pH2. Sample were loaded with rates of 12-18 ml/min, then put under vacuum 45 mins to eliminate water trace. The analytes were eluted with 3 ml ethyl acetate, then 3 ml mixture of ethyl acetate/acetone (1/1 V/V), then finally mixture of methanol/1,2-dichloroethylene in 5% ammonium solution. The extracted solution were evaporated under nitrogen stream to dry, then transfered to injected vial by helping of 300µL acetonitrile and stored at -20°C for futher analysing.

Extracted samples were injected into RRLC (Rapid Resolution of Liquid Chromatography) combined with a MSMS detector 6410A (Agilent. USA). C18 reverse phase columns were used to separate these compounds. Mass spectrometer detections were operated in ElectroSpray Ionisation (ESI) with positive or negative mode. The detail of transitions and acquisition mode were in table 2.

Table 2: Transitions and acquisition mode.

Parameters				
Compounds	**ESI**	**Frag. (V)**	**E. C. (eV)**	**TQ**
				TC
atenolol	+	130	28	267.2 → 56.0
			22	267.2 → 144.9
atenolol d7	+	130	30	274.2 → 144.9
carbamazepin	+	130	20	237.1 → 194.0
			20	237.1 → 192.0
carbamazepin d10	+	119	16	247.1 → 204.1
metoprolol	+	140	18	268.2 → 74.0
			22	268.2 → 56.0
propranolol	+	120	16	260.2 → 56.0
			32	260.2 → 116.0
propranolol d7	+	110	36	267.2 → 55.9
sotalol	+	110	10	255.0 → 212.9
			30	255.0 → 133.0
sotalol d7	+	103	4	280.2 → 262.1
diclofenac	-	90	6	294.1 → 249.9
			18	294.1 → 214.0
diclofenac d4	-	90	6	298.1 → 253.9
ibuprofen	-	80	1	205.2 → 160.9
ibuprofen d3	-	70	1	208.2 → 163.9
ketoprofen	-	60	1	253.2 → 209.0
ketoprofen d3	-	60	1	256.2 → 212.0
naproxen	-	70	1	229.1 → 169.9
			10	229.1 → 184.9
naproxen d3	-	60	12	232.1 → 172.9

ESI: ElectroSpray Ionisation; Frag: Fragment; E.C. Energy of Collision; TQ: Transition of quantification; TC: Transition of Confirmation

2.3.2. Photo-degradation experiment

To perform this part, a mixture of 9 compounds are prepared in concentration around 20 µg/L. This concentration are chosen to inject directly in LCMSMS without reconcentration step. Thus, it can avoid the errors from SPE step. These 9 compounds were prepared in both type of water (ultrapure and river water which present of natural organic matters and metal ions). The samples were kept in different quartz vials and put in SUNTEST instrument where emitted a simulated solar light. The samples were taken in different times 5, 10, 20, 40 mins and up to 7 hours. The collected samples were analysed by LCMSMS with protocol described in 2.3.1.

3. RESULTS AND DISCUSSION

3.1 Detection frequencies and concentration levels of target compounds in effluents

The Figure 1 shows the total accumulation of 9 studied compounds in 4 WWTPs for the period 2011 – 2012. Generally, the total accumulation concentration has detected at high value from 5000 – 10000 ng/L. The TOX2 has measured at lower concentration

than three others. It can be explained as following: this WWTPs were constructed to treat for only ten thousand inhabitants. Moreover, this WWTPs which treated by activated sludge, the wastewater were treated more long time than TOX1, TOX3, TOX4 which are treated by bio-filter. That could cause more efficient removal of these pharmaceutical compounds.

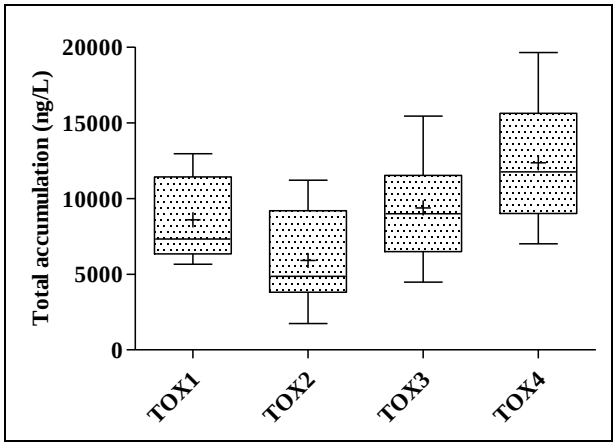

Figure 1: Total accumulation of 9 compounds.

The Table 3 shows that concentration of diclofenac and ketoprofen in effluents are higher than ibuprofen and naproxen in NSAID groups, even these concentration in influents are often detected at lower range [2, 4]. Because of ibuprofen and naproxen have been reported as higher removal efficiency than diclofenac and ketoprofen in NSAID groups [2, 11]. In addition. β-blockers were mesured at high concentration up to 8048 ng/L and 10029 ng/L for atenolol and sotalol respectively. Metoprolol and propanolol were detected in 31/32 samples at lower concentration. These compounds also have poor removal efficiency in WWTPs [9, 14]. The litterature shows that β-blockers could be removed by different processes in WWTPs such as nitrification, oxidation, activated sludge and bio-filter. In case of carbamazepin. this compound is known as an conservative compound which is most stable against treatment process. Its removal efficiency in WWTPs is not significant 1- 30% [2-3, 12].

Table 3: Total accumulation of 9 pharmaceutical compounds in 4 effluents of WWTPs.

Compounds	Frequencies (%)	Min (ng/L)	Max (ng/L)	Mean (ng/L)
diclofenac	100	392	1392	710
ibuprofen	100	47	5182	695
ketoprofen	100	120	4751	1181
naproxen	100	74	2635	864
carbamazepin	100	230	2260	884
atenolol	97	39	8048	1786
metoprolol	97	26	781	151
propranolol	97	58	653	300
sotalol	100	62	10029	2562

3.2. Photo-degradation of pharmaceutical drugs in water by solar light

3.2.1. Analgesics

Figure 2 shows degradation rate of 4 NSAID during 7 hours under simulated solar light. Ketoprofen is disappeared after 40 minutes of emitting and diclofenac is degraded totally after 4 hours in both type of water. In contrast, ibuprofen seems to be stable against solar light while naproxen is also degraded with lower rate than diclofenac and ketoprofen. The previous research for kinetic of degradation showed that diclofenac and ketoprofen have very high rate constant of degradation and the quantum yield under solar [22-23]. The presence of dissolved oxygene might accelerate the degradation of naproxen and ibuprofen [22-23] but not disturb on diclofenac. However, the photodegradation depended on presence of NO_3^- and humic acid [24-25]. This experiment was performed in condition of low absorption and the degradation rate is calculated by equation:

$$ln\frac{[C_t]}{[C_0]} = -k_{app}t \quad (1)$$

Where: C_t, C_o: concentration of each compound at initial time and time t

k_{app}: constant of degradation rate (min^{-1}).

By tracing the semi-logarithmic curve for the disappearance of molecules as a function of time, their kinetics were obtained by first order and their half-life time were calculated by the equation:

$$t_{1/2} = \frac{\ln(2)}{k_{app}} \quad (2)$$

For these 4 compounds, the half-life time of ketoprofen and ibuprofen could not be calculated. The half-life times of diclofenac in ultrapure water and in river water are the same (35 and 36 minutes respectively). Besides, the presence of NOM in river water has disturbed slightly on degraded rate of naproxen. It half-life time decreased from 207 minutes in UPW to 175 minutes in RW.

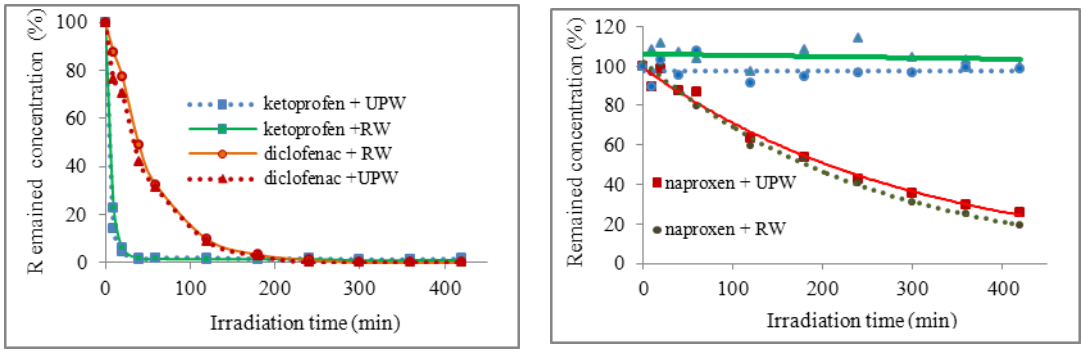

Figure 2: Photodegradation of 4 NSAID in both types of water.

3.2.2. β-blockers

In this group, the concentration of atenolol and metoprolol did not change after 7 hours of emitting in both UPW and RW. In addition, propranolol concentration decreased slightly in UPW (23%) and its degraded rate increased in RW (68%). Sotalol was stable in UPW but it was degraded rapidly in RW (up to 89%). The previous researches showed that atenolol and metoprolol have long half-life time under solar light (70 – 730 hours and 28 – 990 hours respectively) [26]. Their varied half-life time was caused by different irradiation conditions and depended on presence of NOM, pH or NO_3^-. The different degraded rate of propranolol and sotalol in UPW and in RW showed that presence of NOM and NO_3^- disturbed strongly on their photodegradation. This evidence was already reported [18, 24, 26].

By tracing the semi-logarithmic curve for the disappearance of molecules as a function of time, their kinetics were obtained by first order and their half-life time were calculated by the equation (2). The half-life time for sotalol is 142 minutes in RW and for propranolol are 1124 minutes in UPW and 236 minutes in RW. The half-life time of propranolol was also reported at the same range (60-960 minutes) in previous researches [24, 26].

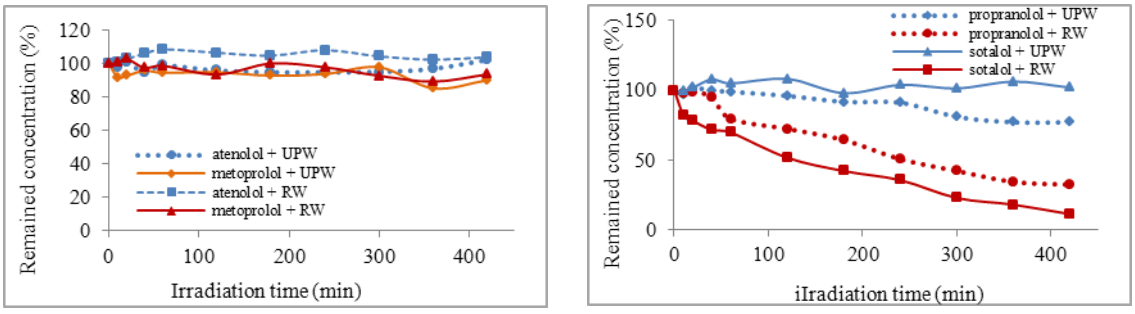

Figure 3: Photodegradation of 4 β-blockers in both types of water.

3.2.3. Carbamazepin

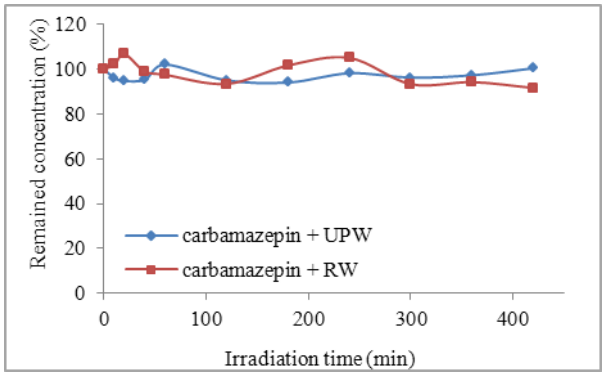

Figure 4: Photodegradation of carbamazepin in both types of water.

Figure 4 showed that carbamazepin concentration did not changed during 7h of irradiation. The research of Andreozzi, 2002 showed that carbamazepin absorbs only irradation which has wavelength less than 325 nm and its concentration decreased only

20% after 60 hours of irradiation under solar UV light. Moreover, the photodegradation of carbamazepin has been accelerated in presence of ion NO^{3-}, O_2 but reduced in presence of humic acid [24, 27, 28].

4. CONCLUSIONS

The occurrence of 9 pharmaceutical residues in 4 WWTPs effluents in South-West of France has been reported for period from March 2011 to September 2012. The analyses were performed by using LC-MSMS system combined with the protocol developed in the laboratory. Almost compounds has been detected in large range of concentration. The highest concentration was found up to 10 µg/L.

The phenomenon of photo-degradation under simulated solar light was also studied in both ultrapure water and river water. Ketoprofen and diclofenac degraded very easily and did not depended on NOM/DOM which is presented in river water, while ibuprofen, atenolol, metoprolol and carbamazepin seem to be stable against solar light. Sotalol and propranolol are strongly affected by experimental matrix. In this research, the half-life time of some compounds are also reported such as diclofenac, naproxen, sotalol and propranolol.

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