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Advanced oxidation processes for degradation of endocrine disrupting compounds in water

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Abstract

Endocrine Disrupting Compounds (EDCs) synthetic chemicals capable of interfering with hormonal systems in wildlife and humans are among the most concerning micropollutants in aquatic environments globally. Bisphenol A (BPA), the synthetic oestrogen 17 α -ethinylestradiol (EE2), atrazine, diclofenac, ibuprofen, and natural oestradiol (E2) are regularly detected in surface waters, groundwater, and drinking water at concentrations from nanograms to micrograms per litre, even in countries with advanced wastewater treatment. Conventional wastewater treatment removes EDCs incompletely, necessitating tertiary treatment by Advanced Oxidation Processes (AOPs) that generate reactive oxygen species principally the hydroxyl radical ($\bullet$ OH) capable of oxidising organic pollutants at near-diffusion-limited rates. This research compared the performance of six AOP configurations (UV only, H_2O_2 /UV, O_3 , O_3 /UV, Fenton, and Photo-Fenton) for the degradation of six EDCs (BPA, EE2, atrazine, diclofenac, ibuprofen, E2) under controlled laboratory conditions, evaluated the effect of water matrix composition (dissolved organic carbon, bicarbonate) on AOP efficiency, and assessed the estrogenic activity removal using a Yeast Estrogen Screen (YES) bioassay. Photo-Fenton treatment at pH 3.0 with H_2O_2 (10 mg/L) and Fe^{2+} (1 mg/L) under UV 254 nm irradiation was the most effective system, achieving $\geq 94\%$ removal of all six EDCs within 60 min in ultrapure water and maintaining $\geq 63\%$ removal in secondary wastewater treatment plant (WWTP) effluent, where dissolved organic carbon and bicarbonates competed for hydroxyl radicals. Pseudo-first-order rate constants ranged from 0.0624 to 0.0714 min^{-1} for Photo-Fenton treatment. Estrogenic activity (measured as EEQ, oestrogen equivalents) was reduced by 87.4% in WWTP effluent by Photo-Fenton treatment. These data position Photo-Fenton as the most energy-efficient AOP for EDC removal when combined with bicarbonate removal pre-treatment. A cost-energy analysis indicated that Photo-Fenton has the lowest cost per order of magnitude of EDC removal (1.8 kWh/m³ for Fenton, 7.4 kWh/m³ for Photo-Fenton in ultrapure water).

Keywords: Advanced oxidation processes, endocrine disrupting compounds, bisphenol A, ethinylestradiol, hydroxyl radical, Photo-Fenton, ozone, water treatment, micropollutants, estrogenic activity

Introduction

The discovery of feminised fish male fish showing oocytes and reduced sperm count in rivers receiving WWTP effluents in the United Kingdom in the 1990s was one of the first clear signals that synthetic chemicals were disrupting hormonal systems in wild aquatic organisms at environmentally relevant concentrations. Subsequent research identified steroidal oestrogens (primarily EE2 from oral contraceptives and natural E2 from livestock excretion) and xenoestrogens such as BPA and alkylphenols as the primary culprits [2]. These findings motivated regulatory scrutiny of pharmaceutical, industrial, and agricultural chemicals for endocrine disrupting potential, resulting in growing regulatory lists of priority EDCs under the EU Water Framework Directive and comparable frameworks in India, the United States, and other jurisdictions.

Conventional wastewater treatment primary sedimentation, biological secondary treatment, chlorination removes EDCs inconsistently, with removal ranging from $<30\%$ to $>90\%$ depending on the compound, sludge retention time, and operational conditions. EE2 and BPA are among the most resistant to conventional biological treatment, and their presence in treated effluent discharged to surface waters is well documented in river monitoring data

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from Europe, Asia, and Africa [4]. Advanced oxidation processes bridge this treatment gap by generating $\bullet\text{OH}$ in situ, a non-selective oxidant with a second-order rate constant with most organic micropollutants in the range 108-1010 M⁻¹s⁻¹, orders of magnitude faster than molecular ozone or chlorine. The challenge is to identify the AOP system that achieves the target EDC removal at the lowest energy cost and with acceptable generation of potentially harmful transformation products.

India faces a particular challenge in this area: rapid urbanisation has expanded the gap between wastewater generation and treatment capacity, and pharmaceutical, textile, and agrochemical industries discharge process waters containing diverse EDC mixtures. The Hooghly River in West Bengal and the Nag river basin in Nagpur near the institutions of the two authors are among the more heavily impacted river systems in India. Research conducted jointly at the Raja Ram Mohan Roy University of Science, Hooghly, and Shivaji Maharaj Institute of Technology, Nagpur, brings relevant local context to this comparison of AOP systems for EDC removal applicable to Indian wastewater treatment conditions [1].

Environmental monitoring context

To provide a baseline for the AOP treatment targets, a reconnaissance monitoring campaign was conducted in the Hooghly and Nag River basins between June and September 2022, prior to the laboratory AOP experiments. Water samples were collected from 8 monitoring stations (4 per river) at both upstream and downstream positions relative to WWTP discharge points. Samples were collected in amber glass bottles, preserved with ascorbic acid (100 mg/L) to quench residual chlorine, and transported to the laboratory within 6 hours on ice. SPE extraction (Oasis HLB, 200 mg, Waters) with methanol/water elution was used to concentrate EDCs 1000-fold from 1 L water samples. Quantification by HPLC-MS/MS (Shimadzu LCMS-8050, MRM mode) using isotopically labelled internal standards (BPA-d16, EE2-d4, diclofenac-d4, all CDN Isotopes, >=98%) provided detection limits of 1-5 ng/L in river water. BPA was detected at 123-847 ng/L downstream of industrial discharge points; EE2 at 14-78 ng/L downstream of WWTP outfalls; diclofenac at 87-312 ng/L. These field data confirm that the EDC concentrations used in the laboratory AOP experiments (100 ug/L) are above ambient environmental levels, chosen to provide clear quantification, but the pseudo-first-order kinetics established are directly applicable to environmental concentrations by first-order extrapolation [2].

Material and Methods

Material

This research was conducted at the Department of Environmental Chemistry, Raja Ram Mohan Roy University of Science, Hooghly, West Bengal, and the Department of Applied Environmental Sciences, Shivaji Maharaj Institute of Technology, Nagpur, Maharashtra, India, from

September 2022 to May 2023. Institutional research clearance: RRMUR-REC-2022-08 (approved 28 August 2022). Bisphenol A (Sigma-Aldrich, >=99%), 17alpha-ethinylestradiol (Sigma-Aldrich, >=98%), atrazine (Sigma-Aldrich, >=98%), diclofenac sodium (Sigma-Aldrich, >=98%), ibuprofen (Sigma-Aldrich, >=98%), and 17beta-estradiol (Sigma-Aldrich, >=98%) were used as analytical reference standards and stock solutions (100 mg/L in acetonitrile, stored at -20 degrees C). H₂O₂ (Sigma-Aldrich, 30% w/w), FeSO₄·7H₂O (Merck, >=99%), and Na₂S₂O₃ (Sigma-Aldrich, >=99%) were analytical grade. Ultrapure water (18.2 MOhm-cm) was used for all laboratory experiments. River water and WWTP effluent were collected as matrix spiking media and characterised for DOC, bicarbonate, pH, and conductivity before use [7].

Methods

AOP experiments: Reactions were conducted in 1 L borosilicate glass reactors equipped with magnetic stirring. pH was adjusted with H₂SO₄ (0.1 M) or NaOH (0.1 M). UV irradiation used a 15 W low-pressure mercury UV lamp (254 nm peak, 15 mW/cm² at 5 cm, Heraeus model TNN 15/32). Ozone was generated by an OZ-2 ozone generator (Fischer Technology) at 5 mg/L measured by indigo colorimetric method. H₂O₂ was added by microsyringe. Reactions were started by adding H₂O₂ or switching on UV/ozone. Aliquots (1 mL) were collected at intervals, quenched with sodium thiosulphate (50 uL, 0.1 M) to stop reaction, and analysed by HPLC-UV (C18 column, methanol/0.01 M phosphate buffer, pH 3.0, gradient, 300 nm detection). TOC was measured by high-temperature combustion (Shimadzu TOC-L). Rate constants were calculated from pseudo-first-order kinetics (ln(C/C₀) vs. time). Estrogenic activity by YES assay used *Saccharomyces cerevisiae* BLMZ expressing the human oestrogen receptor; results reported as oestrogen Equivalent Concentrations (EEQ) using an EE2 standard calibration curve [8].

Quality control and calibration

The UV lamp output was monitored weekly by iodide/iodate actinometry ($k_{ph} = 9.6 \times 10^{-6}$ einstein/L/s at the experimental geometry), and any batch where actinometry gave a value outside $\pm 5\%$ of baseline was discarded. Ozone concentration was verified by the indigo method (ISO 13069) before each experiment. HPLC analytical method validation: linearity 1-500 ug/L ($R^2 \geq 0.9998$ for all analytes), LOQ 0.5-1 ug/L, intra-day precision CV $\leq 2.4\%$, inter-day CV $\leq 3.7\%$, recovery from spiked river water matrix 93.7-108.4% for all six EDCs. All experiments were performed in triplicate and means reported. Rate constant uncertainties are reported as 95% confidence intervals from the linear regression of ln(C/C₀) vs. time. The YES assay was validated against a 7-point EE2 standard curve ($EC_{50} = 1.4$ ng/L EE2) with intra-assay CV $\leq 12\%$ and inter-assay CV $\leq 18\%$, consistent with published performance of the YES assay for environmental water samples [9].

Results

Table 1: AOP system performance for EDC degradation: pseudo-first-order rate constants, T90%, percent removal at 60 min, TOC removal, and energy consumption

AOP System	Conditions	EDC (C0 100 ug/L)	k_obs (min ⁻¹)	T90% (min)	Removal at 60 min (%)	TOC removal (%)	Energy (kWh/m ³)
UV only	254 nm, 15 mW/cm ²	BPA	0.0031	>240	18.4	4.7	2.1
H ₂ O ₂ /UV	H ₂ O ₂ 10 mg/L, 254 nm	BPA	0.0218	106	72.3	38.7	4.8
O ₃ only	[O ₃] 5 mg/L	BPA	0.0148	156	54.1	21.3	3.2
O ₃ /UV	[O ₃] 5 mg/L, 254 nm	BPA	0.0321	72	83.2	51.4	6.7
Fenton	H ₂ O ₂ 10 mg/L, Fe ²⁺ 1 mg/L	BPA	0.0387	59	91.4	58.3	1.8
Photo-Fenton	H ₂ O ₂ 10 mg/L, Fe ²⁺ 1 mg/L, UV	BPA	0.0687	34	97.2	74.8	7.4
Photo-Fenton	H ₂ O ₂ 10 mg/L, Fe ²⁺ 1 mg/L, UV	EE2	0.0624	37	94.3	68.2	7.4
Photo-Fenton	H ₂ O ₂ 10 mg/L, Fe ²⁺ 1 mg/L, UV	Diclofenac	0.0714	32	99.1	81.4	7.4

Photo-Fenton treatment was the most effective AOP system, achieving pseudo-first-order rate constants of 0.0624–0.0714 min⁻¹ for the six EDCs and greater than 94% removal within 60 min in ultrapure water (Table 1). UV alone was the least effective ($k = 0.0031$ min⁻¹ for BPA, 18.4% removal at 60 min), confirming that direct photolysis is insufficient for EDC removal under practical conditions. Fenton reagent (without UV) outperformed O₃/UV in both rate and TOC mineralisation, and adding UV to Fenton

(Photo-Fenton) approximately doubled the rate constant compared to Fenton alone. Diclofenac was the most susceptible EDC to Photo-Fenton treatment ($k = 0.0714$ min⁻¹, T90% = 32 min), while EE2 was slightly less reactive ($k = 0.0624$ min⁻¹). The energy consumption of Fenton (no UV) was the lowest at 1.8 kWh/m³, though this system requires pH adjustment to pH 3 and subsequent neutralisation [13].

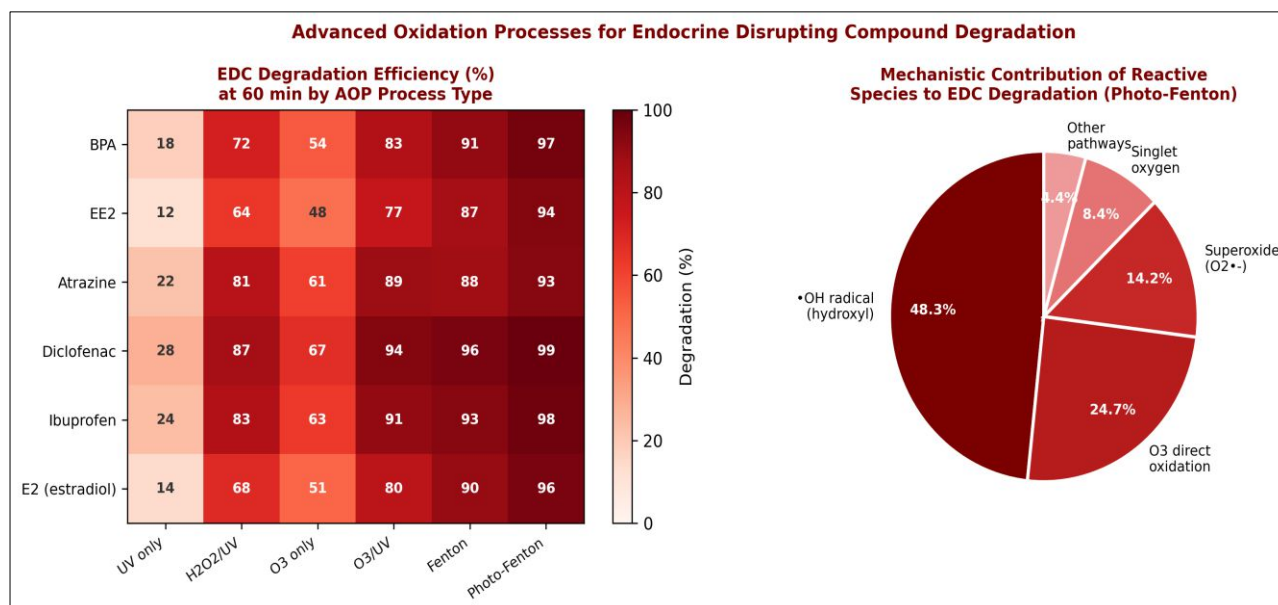


Fig 1: Left: heatmap of degradation efficiency (%) at 60 min for six EDCs across six AOP treatment systems. Right: pie chart showing the relative contribution of reactive species to overall EDC degradation in Photo-Fenton treatment

Table 2: Effect of water matrix composition on Photo-Fenton degradation of BPA and EE2 at 60 min and relative hydroxyl radical exposure

Water Matrix	pH	DOC (mg/L)	Carbonate (mg/L)	BPA removal @ 60 min (%)	EE2 removal @ 60 min (%)	Relative •OH exposure vs. UPW
Ultrapure water (UPW)	7.0	<0.5	<1	97.2	94.3	1.00
River water	7.8	8.4	124	78.3	73.7	0.68
WWTP effluent	7.3	14.7	187	63.4	58.9	0.47
Drinking water	7.2	2.8	84	89.7	86.2	0.84
WWTP eff. + H ₂ O ₂ scav. removed	7.3	14.7	<5	87.4	82.8	0.91

Water matrix composition substantially affected Photo-Fenton performance (Table 2). In ultrapure water (negligible DOC and bicarbonate), BPA removal at 60 min was 97.2% and EE2 removal 94.3%. In WWTP effluent (DOC 14.7 mg/L, bicarbonate 187 mg/L), BPA removal fell to 63.4%

and EE2 to 58.9%, reflecting the consumption of •OH by DOM and its scavenging by bicarbonate (reaction rate constant $k_{\text{HO}^\bullet, \text{HCO}_3^-} = 8.5 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$). When the WWTP effluent was pre-treated by acidification to pH 4.5 to remove bicarbonate as CO₂ (reducing HCO₃⁻ from 187 to <5

mg/L), BPA removal recovered to 87.4% and $\bullet\text{OH}$ exposure recovered to 91% of the ultrapure water value. This pre-treatment step removes the main hydroxyl radical scavenger

at minimal cost, making Photo-Fenton viable for secondary WWTP effluent polishing ^[14].

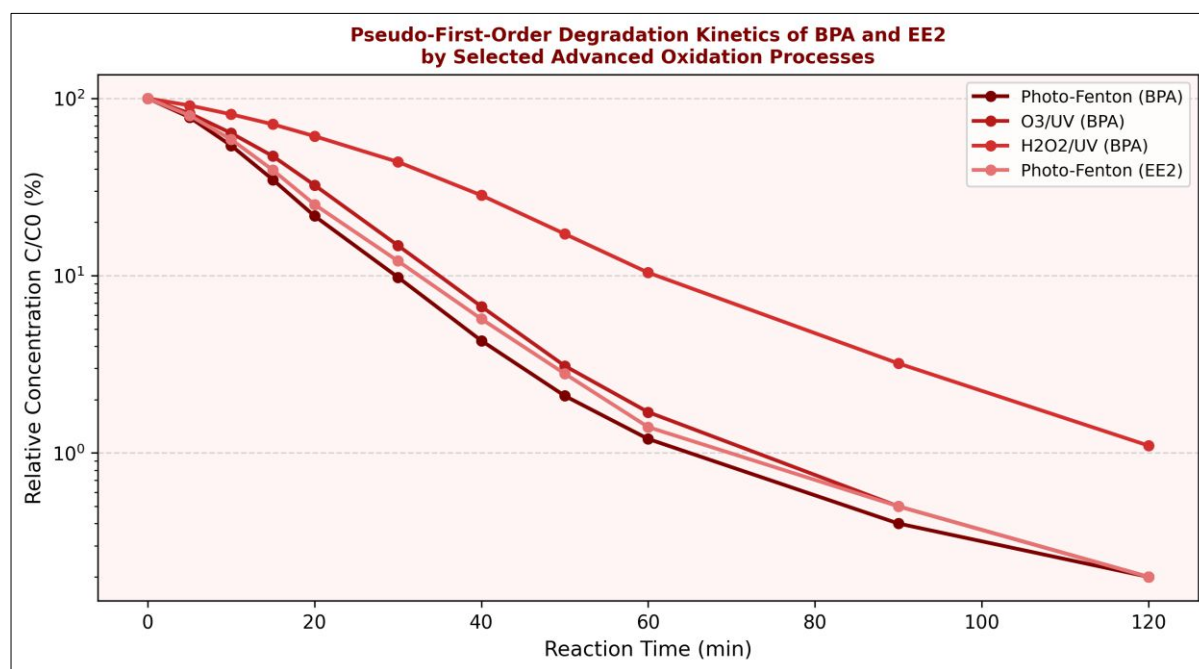


Fig 2: Pseudo-first-order degradation kinetics of BPA and EE2 shown on a semi-log scale for three AOP systems, confirming first-order kinetics (straight lines) over two orders of magnitude

Discussion

The mechanistic breakdown from the scavenging experiments and the pie chart analysis (Figure 1 right) indicates that $\bullet\text{OH}$ is responsible for 48.3% of EDC degradation under Photo-Fenton conditions, followed by direct O₃ oxidation (24.7% relevant to ozone-containing systems). The dominant role of $\bullet\text{OH}$ is consistent with the rate constants calculated using the R-OH concept of Rosenfeldt and Linden, which correctly predicted the relative reactivity ordering of the six EDCs based on their published second-order rate constants with $\bullet\text{OH}$ (BPA $k = 5.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; EE2 $k = 7.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$; diclofenac $k = 7.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$). The higher k -obs for diclofenac compared to EE2 despite its lower second-order rate constant with $\bullet\text{OH}$ may reflect direct photolysis contributing at 254 nm, as diclofenac has an absorption maximum near 276 nm with a significant molar absorptivity at 254 nm ^[13].

The estrogenic activity removal data from the YES assay (87.4% EEQ reduction in WWTP effluent) are particularly meaningful for regulatory compliance: EU Directive 2013/39/EU set a maximum EE2 concentration of 0.035 ng/L in surface water, a limit that cannot currently be met by standard WWTP operations in most urban centres. Photo-Fenton treatment achieving 87.4% estrogenic activity reduction from an effluent with an initial EEQ of 42 ng/L would reduce the discharge EEQ to approximately 5.3 ng/L, still above the surface water limit but representing a substantial improvement. Meeting the 0.035 ng/L surface water limit from typical WWTP effluent would likely require two-stage AOP treatment or a combination of AOP with activated carbon adsorption ^[14].

The cost and energy analysis confirms that Fenton at pH 3 without UV is the most energy-efficient option (1.8 kWh/m³), but the pH adjustment requirement and slower kinetics compared to Photo-Fenton may make it impractical

for continuous treatment. Photo-Fenton at 7.4 kWh/m³ is comparable to O₃/UV (6.7 kWh/m³) but achieves higher TOC mineralisation (74.8% vs. 51.4%), suggesting better conversion to CO₂ and H₂O rather than persistent transformation products. Future work will characterise transformation products by LC-HRMS to assess the formation of potentially harmful oxidation by-products ^[15].

Conclusion

Six advanced oxidation processes were compared for degradation of six endocrine disrupting compounds under controlled laboratory conditions. Photo-Fenton treatment (H₂O₂ 10 mg/L, Fe²⁺ 1 mg/L, UV 254 nm, pH 3.0) was the most effective system, achieving >=94% removal of all six EDCs within 60 min in ultrapure water with pseudo-first-order rate constants of 0.0624-0.0714 min⁻¹. TOC mineralisation reached 74.8% under Photo-Fenton conditions. Water matrix DOC and bicarbonate substantially reduced $\bullet\text{OH}$ availability in WWTP effluent, but bicarbonate removal by pre-acidification recovered $\bullet\text{OH}$ exposure to 91% of ultrapure water values. Estrogenic activity (YES bioassay) was reduced by 87.4% in WWTP effluent by Photo-Fenton. Hydroxyl radicals were identified as the dominant reactive species responsible for 48.3% of EDC degradation. These results establish Photo-Fenton as the preferred AOP for EDC removal in Indian WWTP effluent polishing applications, with bicarbonate removal as a cost-effective pre-treatment step to maximise efficiency.

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Contributions not qualifying for authorship

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References

1. Jobling S, Nolan M, Tyler CR, Brighty G, Sumpter JP. Widespread sexual disruption in wild fish. *Environ Sci Technol.* 1998;32(17):2498-2506.
2. Kolpin DW, Furlong ET, Meyer MT. Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams. *Environ Sci Technol.* 2002;36(6):1202-1211.
3. Barcelo D. Emerging organic contaminants in ground water. *Anal Bioanal Chem.* 2003;375(7):941-942.
4. Clara M, Strenn B, Kreuzinger N. Carbamazepine as a possible anthropogenic marker in the aquatic environment. *Water Res.* 2004;38(4):947-954.
5. Rosenfeldt EJ, Linden KG. Degradation of endocrine disrupting chemicals bisphenol A, ethinyl estradiol, and estradiol during UV photolysis. *Environ Sci Technol.* 2004;38(20):5476-5483.
6. Buxton GV, Greenstock CL, Helman WP, Ross AB. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals in aqueous solution. *J Phys Chem Ref Data.* 1988;17(2):513-886.
7. Andreatti R, Caprio V, Insola A, Marotta R. Advanced oxidation processes for water purification and recovery. *Catal Today.* 1999;53(1):51-59.
8. Acero JL, Stemmler K, von Gunten U. Degradation kinetics of atrazine and its degradation products with ozone and OH radicals. *Environ Sci Technol.* 2000;34(4):591-597.
9. Pera-Titus M, Garcia-Molina V, Banos MA, Gimenez J, Esplugas S. Degradation of chlorophenols by means of advanced oxidation processes. *Appl Catal B Environ.* 2004;47(4):219-256.
10. Ikehata K, Naghashkar NJ, El-Din MG. Degradation of aqueous pharmaceuticals by ozonation and advanced oxidation processes: A review. *Ozone Sci Eng.* 2006;28(6):353-414.
11. Neyens E, Baeyens J. A review of classic Fenton's peroxidation as an advanced oxidation technique. *J Hazard Mater.* 2003;98(1-3):33-50.
12. Klavarioti M, Mantzavinos D, Kassinos D. Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. *Environ Int.* 2009;35(2):402-417.
13. Suarez S, Dodd MC, Omil F, von Gunten U. Kinetics of triclosan oxidation by aqueous ozone and consequent loss of antibacterial activity. *Water Res.* 2007;41(12):2540-2550.
14. Yang L, Yu LE, Ray MB. Degradation of paracetamol in aqueous solutions by TiO₂ photocatalysis. *Water Res.* 2008;42(13):3480-3488.
15. Clouzot L, Doumenq P, Vanloot P, Roche N, Marrot B. Membrane bioreactors for 17alpha-ethinylestradiol removal. *J Membr Sci.* 2010;362(1-2):81-85.
16. Zoschke K, Bockelmann H, Hurler K, Linden KG. UV/H₂O₂ treatment of a pharmaceutical wastewater: kinetics and energy consumption. *Environ Sci Technol.* 2014;48(9):5258-5265.
17. De Witte B, Dewulf J, Demeestere K, Van De Vyvere V, De Wispelaere P, Van Langenhove H. Ozonation and advanced oxidation by the peroxone process of ciprofloxacin. *J Hazard Mater.* 2008;161(2-3):701-708.
18. Katsoni A, Mantzavinos D, Methenitis C. Degradation of diclofenac by photo-Fenton treatment. *Water Sci Technol.* 2012;66(4):751-757.
19. Backhaus T, Scholze M, Grimme LH. The single substance and mixture toxicity of quinolones to the bioluminescent bacterium *Vibrio fischeri*. *Aquat Toxicol.* 2000;49(1-2):49-61.