DETECTION AND FATE OF PHARMACEUTICAL COMPOUNDS AND PERSONAL CARE PRODUCTS IN THE ENVIROMENT

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European Union
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SHORT DECRIPTION OF THE PRESENT STUDY

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SHORT DESCRIPTION OF THE PRESENT STUDY

Used:

- novel,
- powerful and
- «green» analytical protocols

for rapid and accurate measurement of trace amount of insect repellents and parabens in various aqueous matrices.

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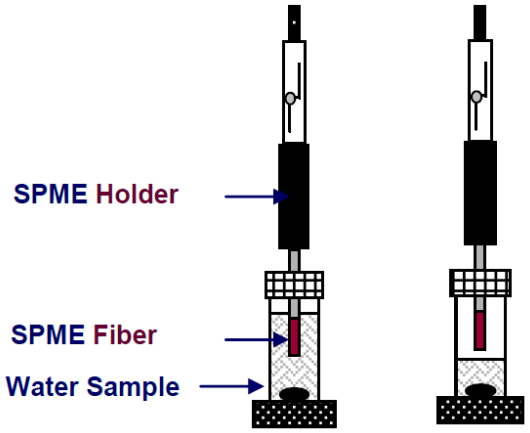
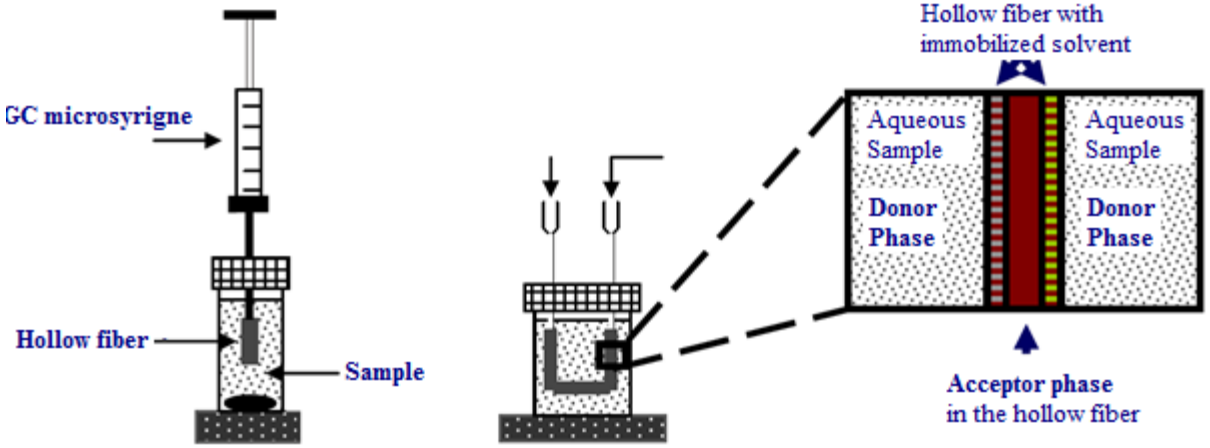
Pre-concentration Techniques

Solid phase microextraction:



Liquid phase microextraction:



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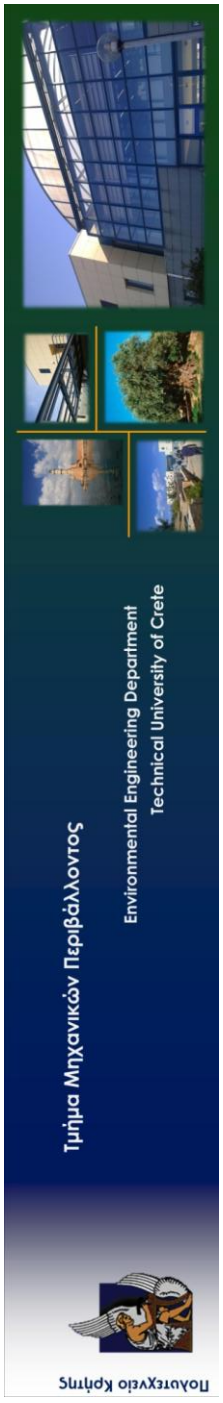
Analytical Techniques

Liquid chromatography:

Gas chromatography:



SHORT DESCRIPTION OF THE PRESENT STUDY

Study of the photolytic fate of these compounds in various aqueous environmental matrices in order to:

- determine the rates of decomposition,
- the effect of environmental matrix in the process of photolysis.

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DETAILED DECRIPTION OF THE PRESENT STUDY

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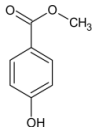
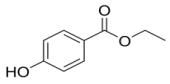
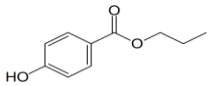
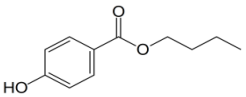
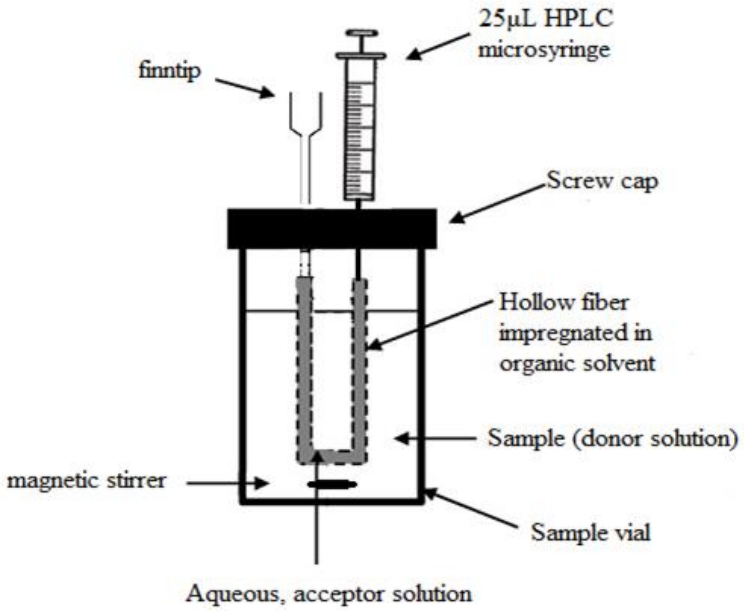
Application of three phase hollow fiber liquid phase microextraction for the extraction of four parabens in water samples

Compound	Molecular Weight	Chemical structure	pk_a	LogKow
Methylparaben	152.2		8.47	1.91
Ethylparaben	166.2		8.50	2.34
Propylparaben	180.2		8.47	2.94
Butylparaben	194.2		8.47	3.50

- esters of p-hydroxybenzoic acid
- widespread use as preservatives in many types of products
- used singly or in combination
- estrogenic activity
- emerging pollutants
- their determination is becoming increasingly important since they are continuously released into the environment.

K. Tsourounaki and E. Psillakis, ''Application of three phase hollow fiber liquid-phase microextraction for the extraction of four parabens in water samples'', **7th International Conference on Instrumental Methods of Analysis Modern Trends and Applications "IMA 2011"** 18-22 September 2011, Chania, Crete, Greece

Hollow fiber LPME procedure:



Time	%B (5mM NH_4OAc)	%A (MeOH)
0	70	30
22	35	65
25	70	30

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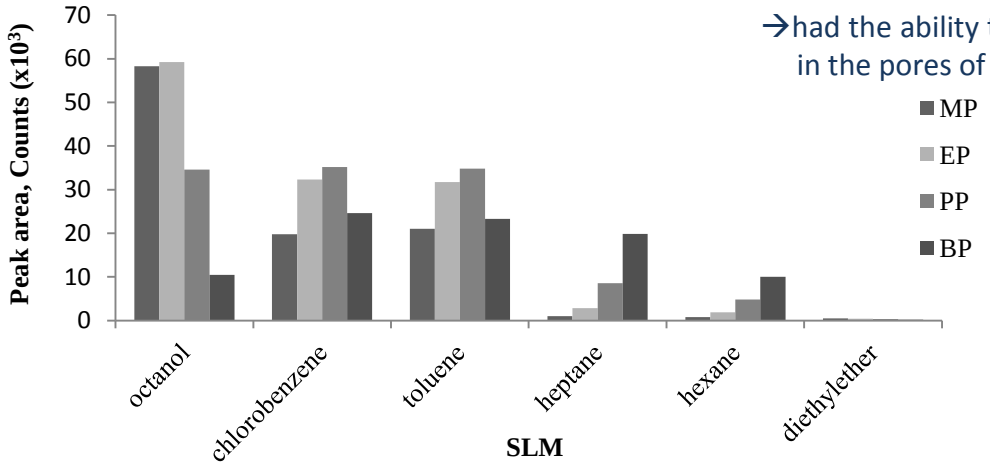
RESULTS

Application of three phase hollow fiber liquid phase microextraction for the extraction of four parabens in water samples

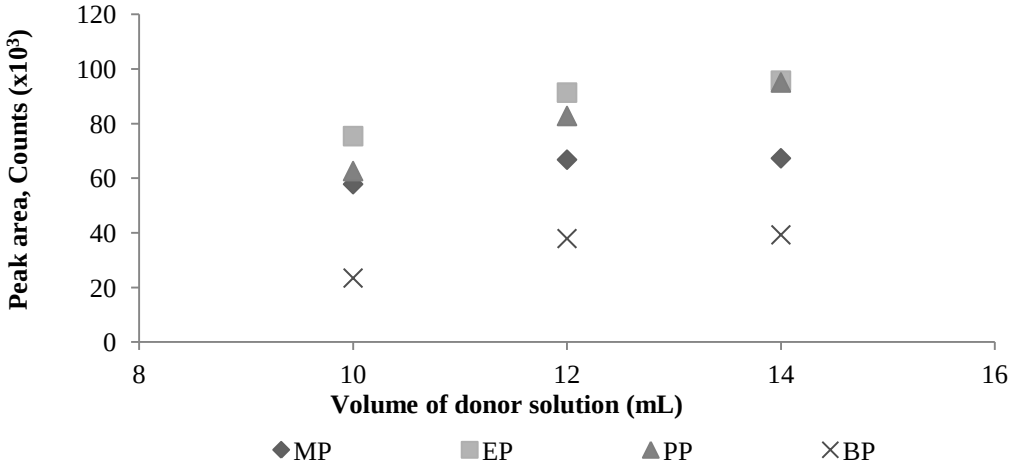
Optimization

➢ **Supported liquid membrane:** six water-immiscible solvents : when the solvent used as organic phase was less polar, parabens with long side chain presented higher recoveries

1-octanol →highest response of the instrument
→showed low solvent loss during extract
→had the ability to be easily immobilised in the pores of the hollow-fibre



➢ **Sample volume:** the amount of analytes transferred to the acceptor solution increases with increasing sample volume →**14 m**L was the best volume between 10, 12 and 14mL



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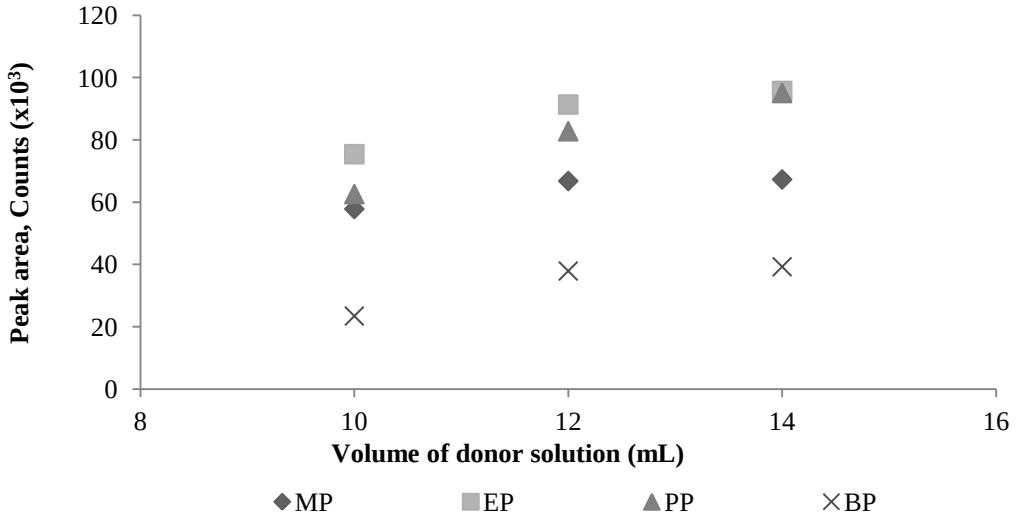
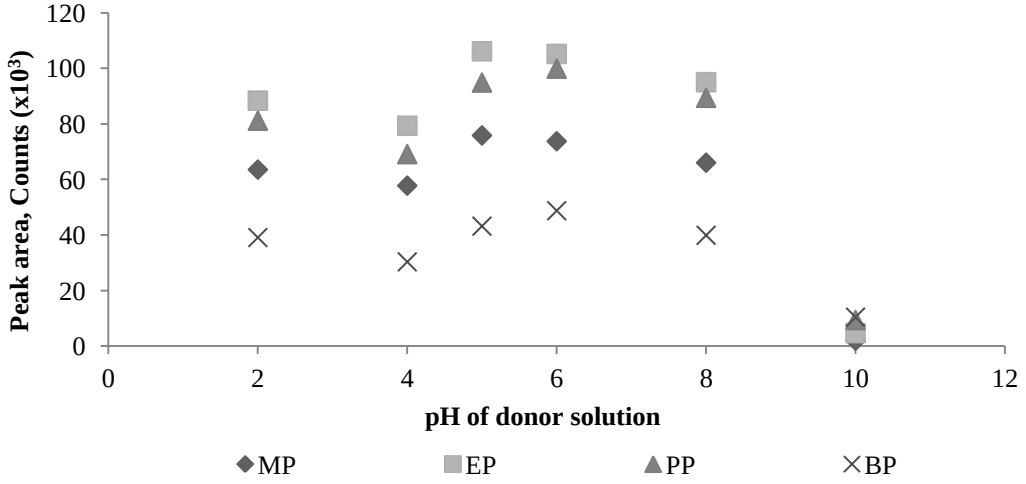
Optimization

➢**Acceptor volume**: the analytical signal virtually decreases with increasing acceptor volume → **18μL** corresponding to **5.5cm** hollow fiber was applied to subsequent experiments due to the lower final concentration, that achieved.



➢ **pH of sample**: **at** pH 2 to 4 hydrolysis → extraction efficiencies very low → could not be extracted into the organic phase at pH 8 deprotonation → made them remain much more into the aqueous phase



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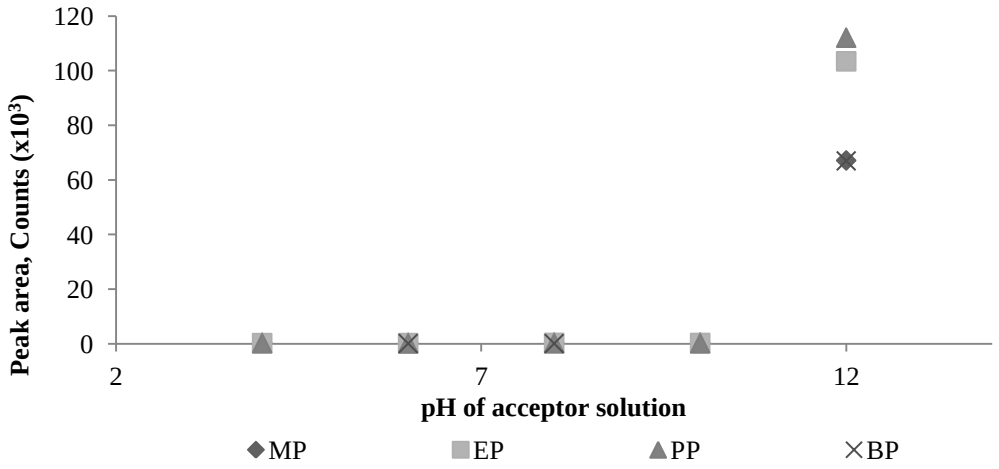
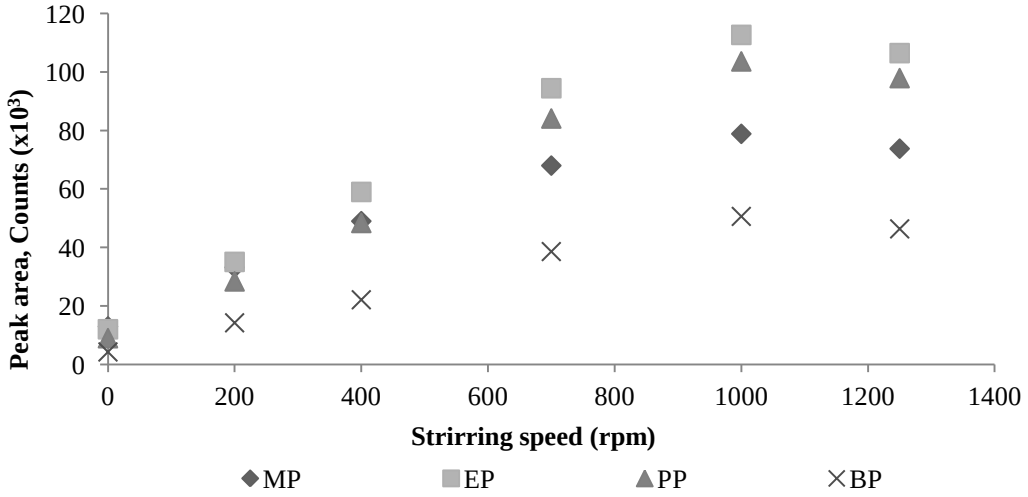
Optimization

pH of acceptor solution: all parabens were extracted only at **pH 12,** when the pH of donor solution was 6. pH 12 guaranteed the deprotonated form and prevented analytes from back-diffusion to the SLM.



➢**Stirring rate:** the optimal extraction was attained at **1000 rpm.** At higher speed air bubbles were generated that could adhere on the hollow fiber surface and promote solvent evaporation.



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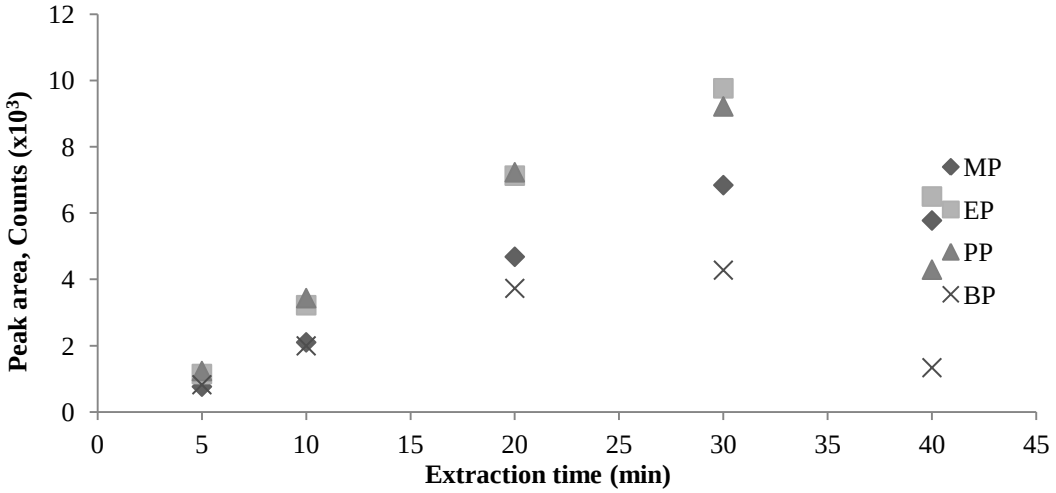
Optimization

➢**Extraction time:** the amount extracted increased dramatically with increasing exposure time from 0 to 30 min. After 30 min, the curves decreased due to the evaporation of the organic solute. Thus, the extraction time for all subsequent experiments was standardized at 30 min



Validation of the method

Compound	Conc. range (μg L⁻¹)	r²	LODs (μg L⁻¹)	Repeatability (% RSD)[a]	Repeatability (% RSD)[b]	Relative recoveries Tap[c]
MP	0.5-1000	1.0000	0.506	2.6	3.5	79.9 (4.4)
EP	0.5-1000	0.9993	0.445	1.6	4.5	87.5 (3.7)
PP	0.5-1000	0.9955	0.316	3.7	6.8	92.0 (4.2)
BP	0.5-500	0.9981	0.541	7.0	8.9	92.0 (5.3)

[a] Spiking level 10 μg L⁻¹; n = 5.
[b] Spiking level 100 μg L⁻¹; n= 5
[c] tap Spiking level 1 μg L⁻¹; % RSD values given in parentheses; n = 5.

K. Tsourounaki and E. Psillakis, ''Application of three phase hollow fiber liquid-phase microextraction for the extraction of four parabens in water samples'', **7th International Conference on Instrumental Methods of Analysis Modern Trends and Applications "IMA 2011"** 18-22 September 2011, Chania, Crete, Greece

Matrix effect:

The proposed method was applied to the analysis of spiked (at 100ppb) water samples (including tap water, lake and river water, samples from the inflow and outflow of urban wastewater treatment plant).
The results demonstrated a **strong matrix effect**, affecting significantly the effectiveness of the method and giving very low recoveries.

Therefore, pretreatment with addition of **8mg/100ml $Na_2S_2O_3$** was tested in tap water to ensure the removal of available free chlorine, that react with parabens creating chlorinated by-products.

Recoveries of the parabens were within the range of 79.9–92.0% for the tap water.

The applicability of the developed method was demonstrated for three different water samples originating from baby bathwater. For the MP, the concentrations were high and ranged from 3.5 to 9.1 μg L^{-1}, while the other parabens recorded infection levels below the LODs.

K. Tsourounaki and E. Psillakis, ''Application of three phase hollow fiber liquid-phase microextraction for the extraction of four parabens in water samples'', **7th International Conference on Instrumental Methods of Analysis Modern Trends and Applications "IMA 2011"** 18-22 September 2011, Chania, Crete, Greece

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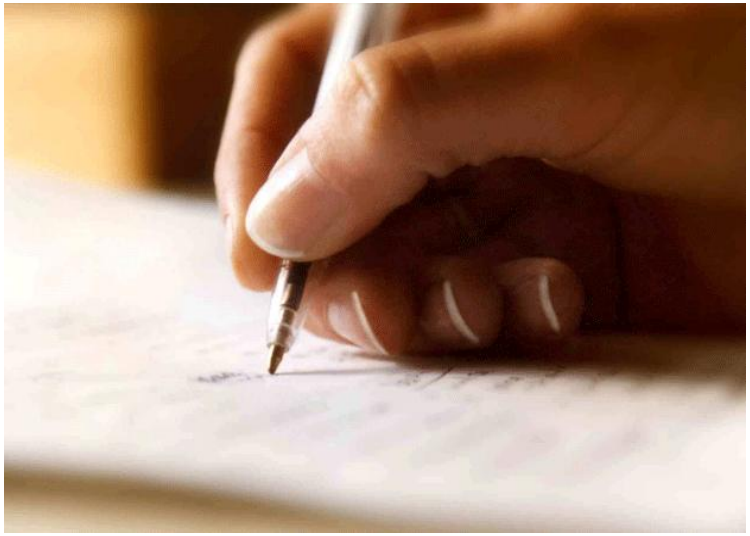
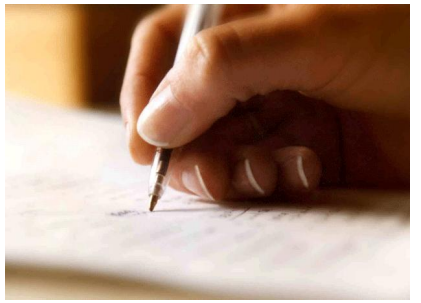
CONCLUSIONS



Application of three phase hollow fiber liquid phase microextraction for the extraction of four parabens in water samples

CONCLUSIONS



- ✓ **HF-LPME →**
- simple method
- low detection limits,
- good accuracy,
- low cost,
- low solvent consumption → which makes the process environmentally friendly.

K. Tsourounaki and E. Psillakis, ''Application of three phase hollow fiber liquid-phase microextraction for the extraction of four parabens in water samples'', **7th International Conference on Instrumental Methods of Analysis Modern Trends and Applications "IMA 2011"** 18-22 September 2011, Chania, Crete, Greece

The occurrence of personal care products (PCPs) in the aquatic environment

PCPs →**an emerging worldwide issue**, because :

- persistent,
- long-term chronic exposure of aquatic organisms to concentrations of PCPs

❑negatively impact the health of the ecosystem and humans
❑interactive effects of PPCPs (cumulative stress and synergic toxicity effects)
❑endocrine-disrupting compounds (EDCs)

Parabens and their halogenated byproducts are present in the aquatic environment at low (ng/L) concentration levels

Sometimes by products are more harmful from the initial substance due to the upcoming bioaccumulation and toxicity

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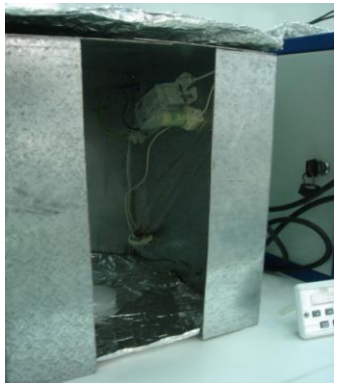
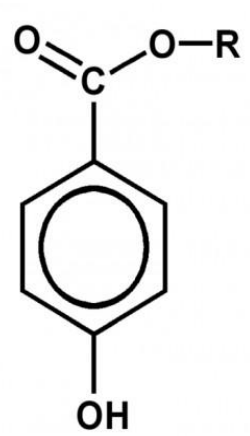
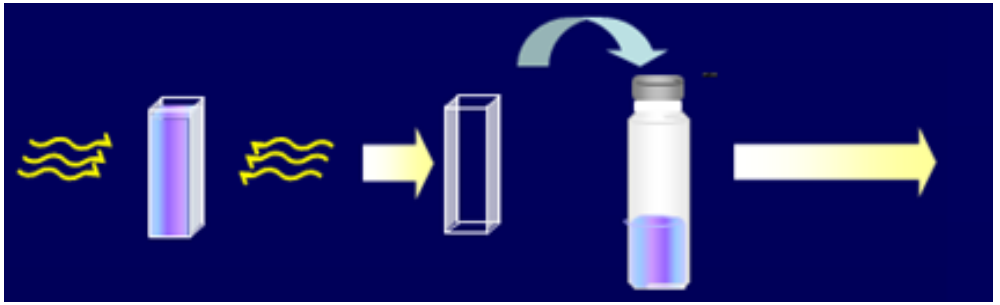
Photodegradation of four parabens in various environmental solutions at 254 nm



UV IRRADIATION:

- Two 8 W low pressure Hg lamps, 254 nm
- Irradiation Time: 0-360 min





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K. Tsourounaki, G. Aroniada, E. Psillakis, ''Photodegradation of methylparaben in various environmental aqueous solutions by 254 nm irradiation'', 3rd **International Conference on Industrial and Hazardous Waste Management "CRETE 2012"** 12-14 September 2012, Chania, Crete, Greece

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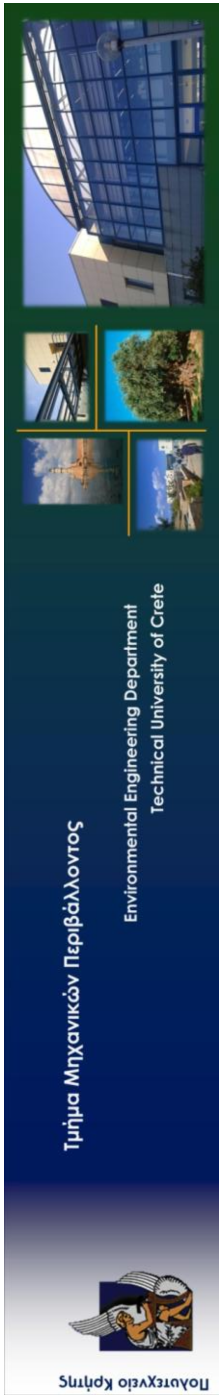
RESULTS

Photodegradation of four parabens in various environmental solutions at 254 nm

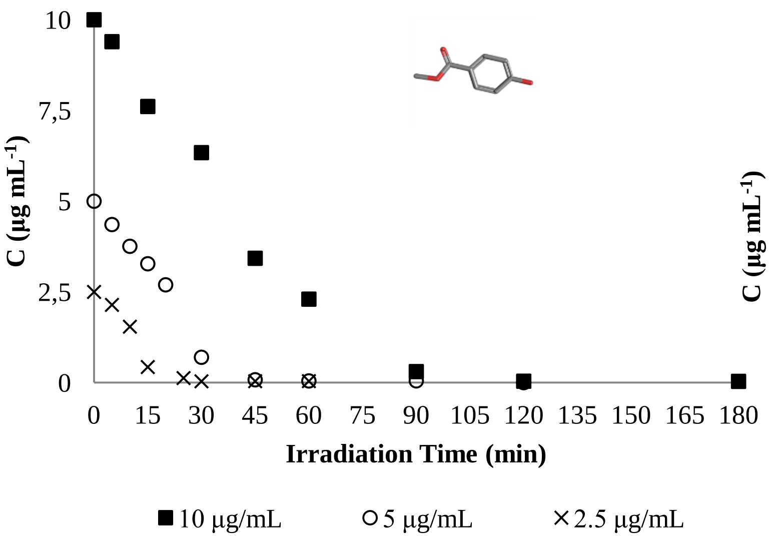


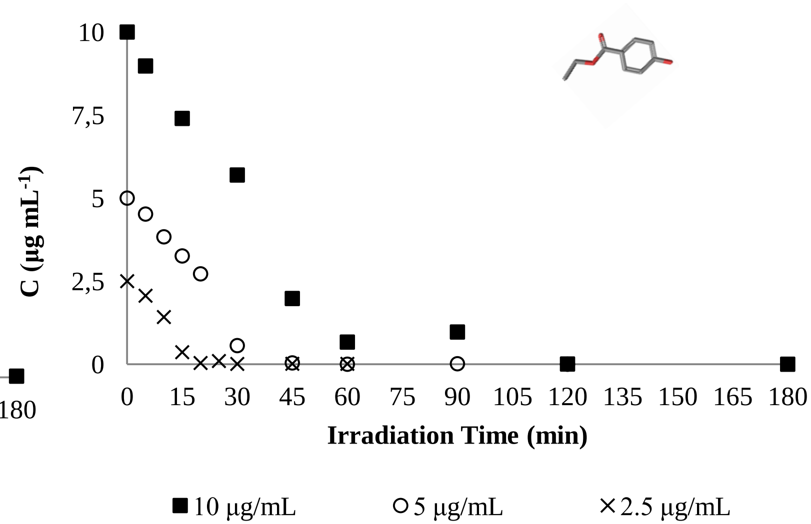
Effect of initial concentration

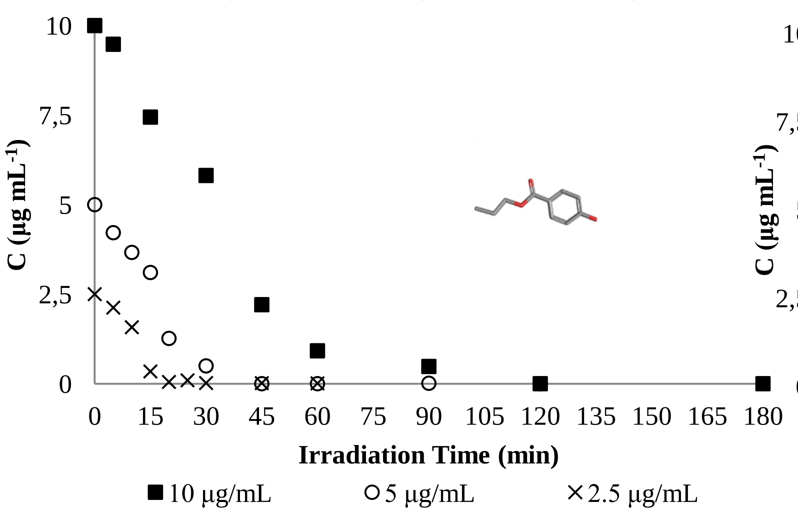
decrease in degradation efficiency at high concentrations

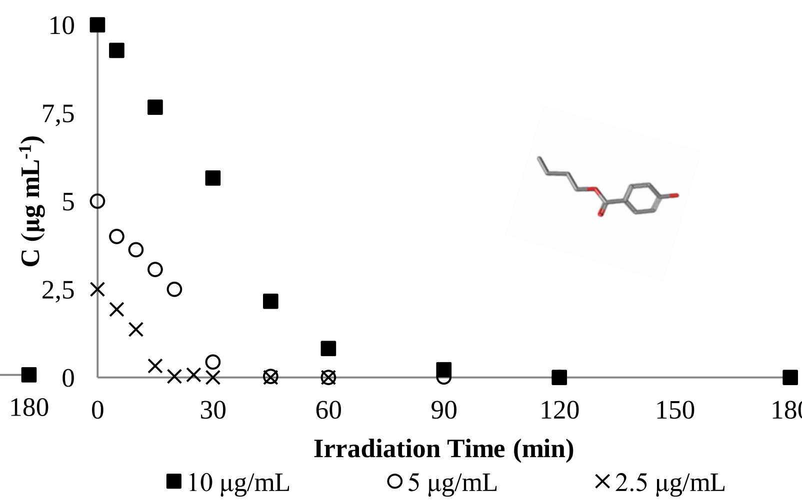
more light energy is available to be absorbed by parabens molecules in lower concentrations

pseudo first-order kinetic model









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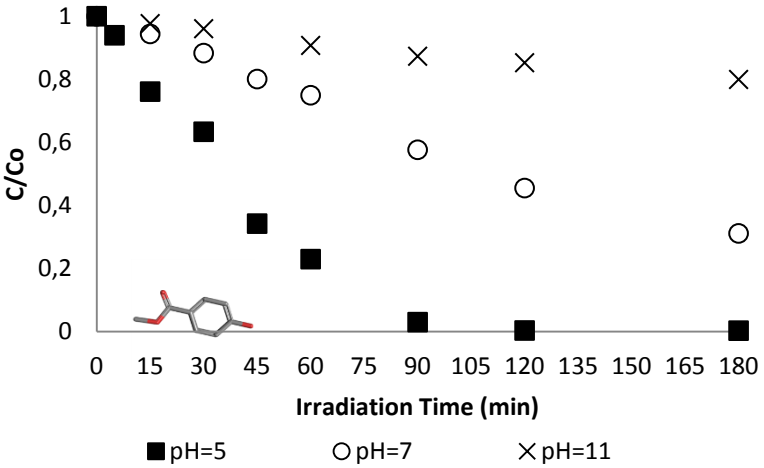
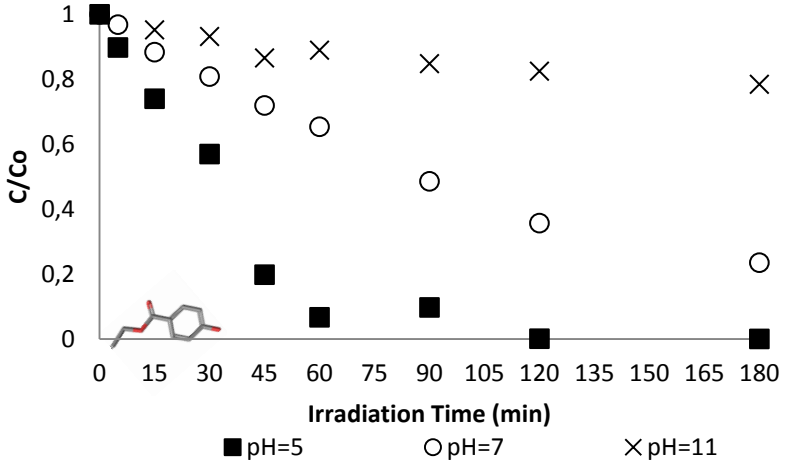
pH effect

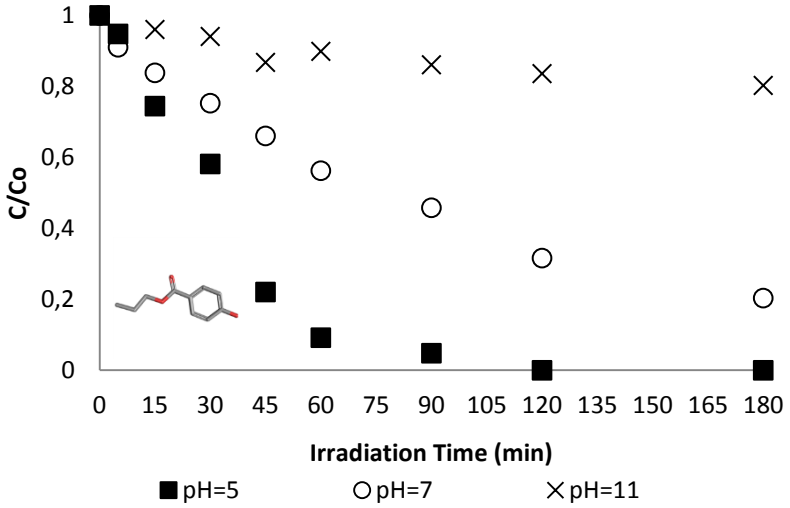


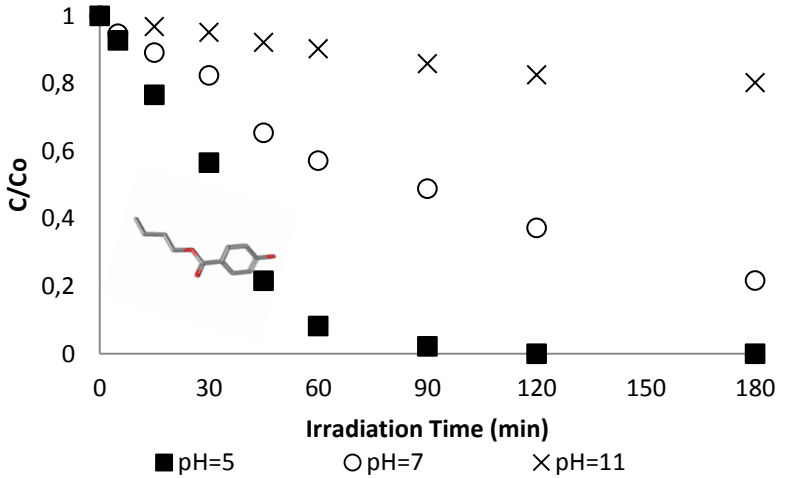


a decrease in degradation rate with increasing pH, confirming that the molecular form is more photoreactive than the anionic form

at pH 5 a complete removal (losses >90%) of all parabens can be achieved by an irradiation period of 90 min

the deprotonation did not facilitate their direct photodegradation by UVC irradiation.





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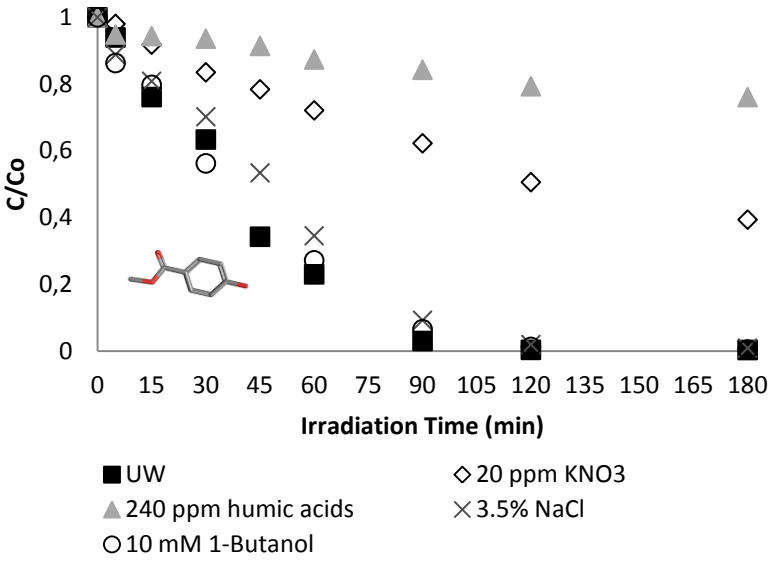
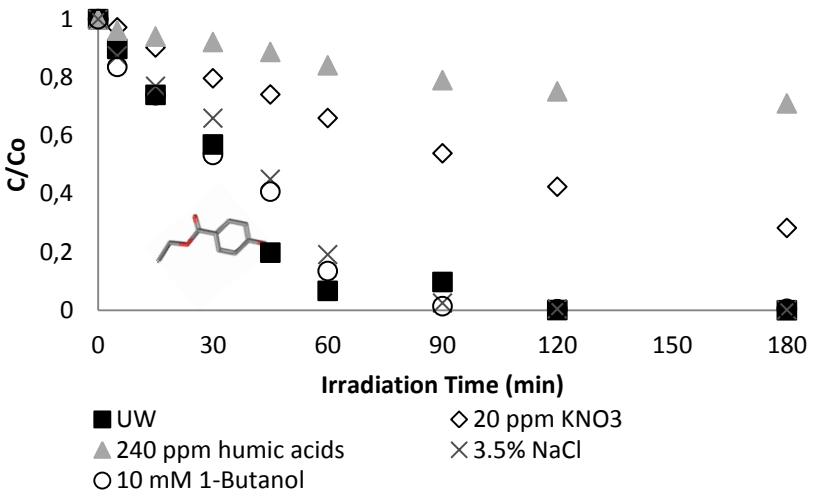
Effect of radical scavenger, HA, nitrate ions, salinity

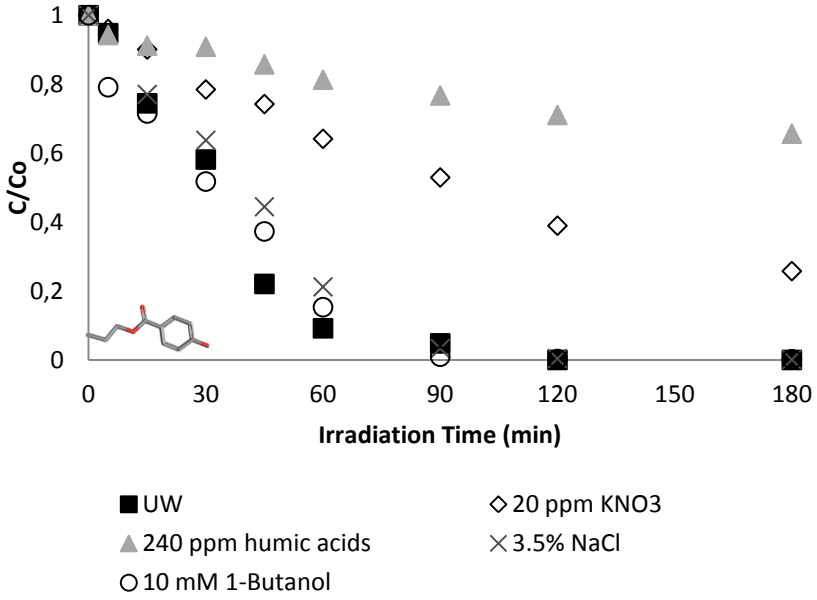
NO_3^- act as optical filters → inhibition



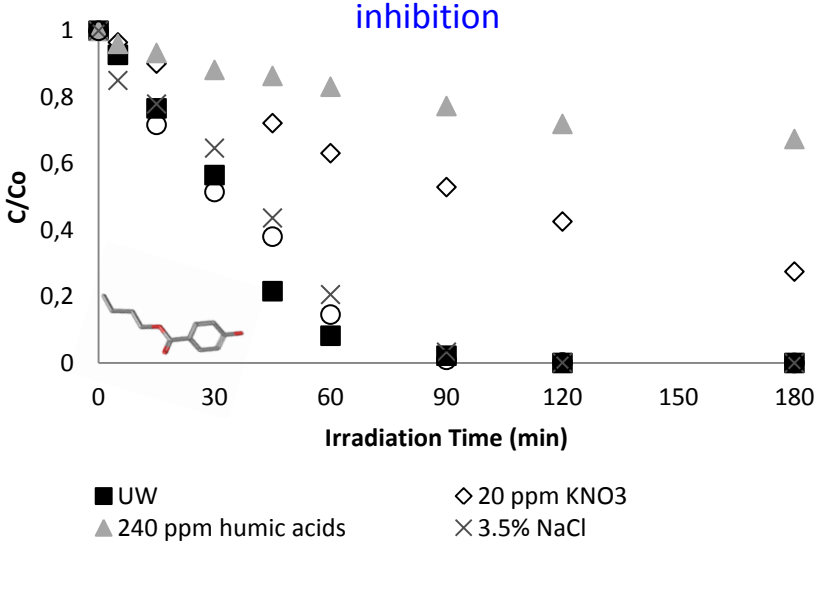
NaCl had a minor effect



1-butanol as radical scavenger had no effect



HA act as inlet filters and radical quenchers → inhibition



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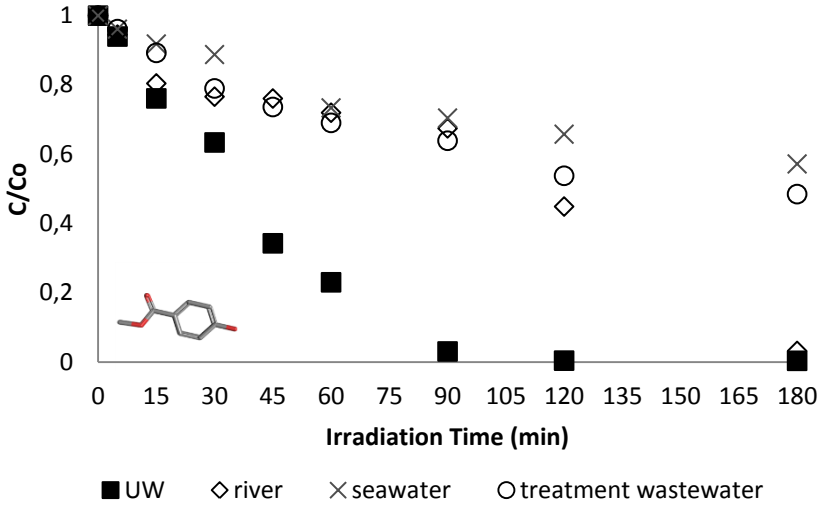
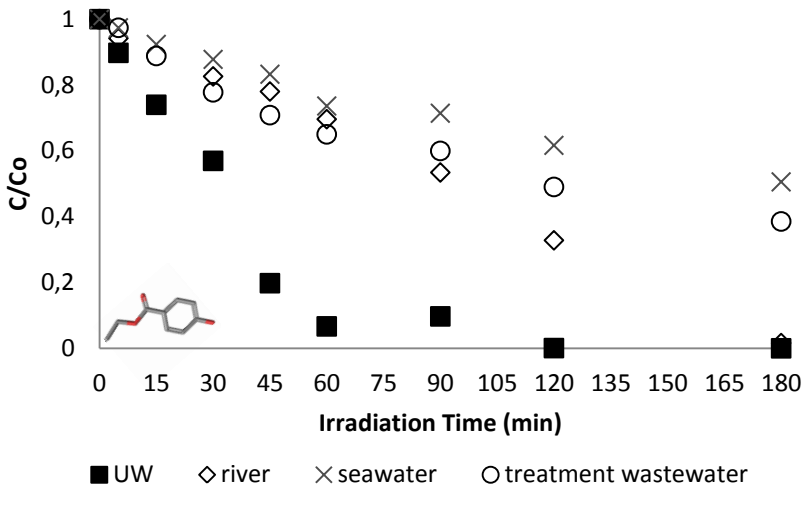
Effect of Matrix





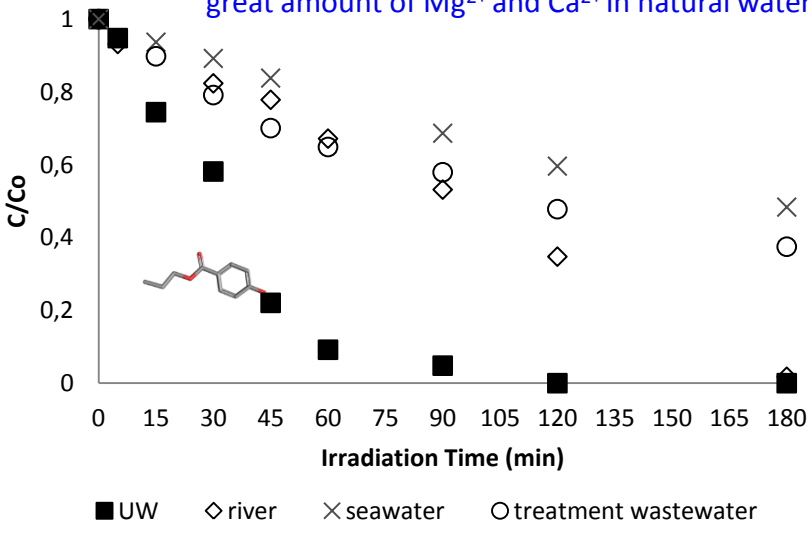
matrix effect →due to the dissolved species acting inhibitory in the reaction of photolysis

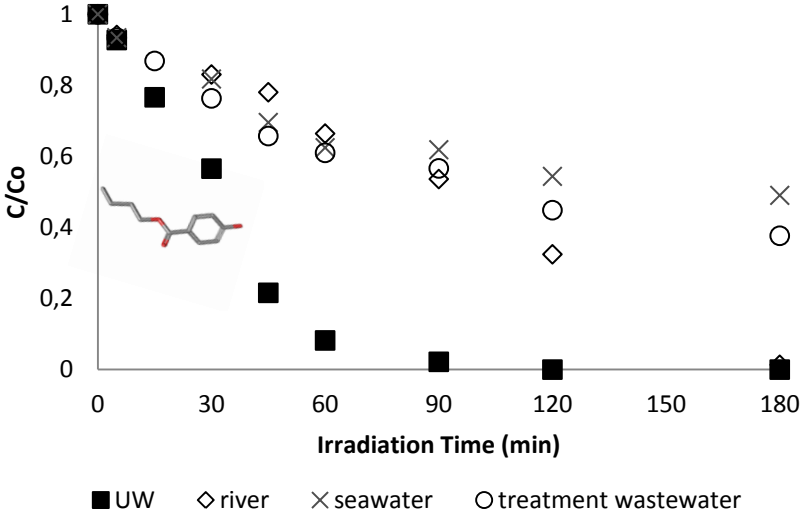
HA at times interact with micropollutants by quenching and scavenging effects

Halide ions can act as scavengers of free radicals and block the electron transfer reaction of organic substances

NO_3^- cause light screening effects

great amount of Mg^{2+} and Ca^{2+} in natural waters can also inhibit the photodegradation of parabens





K. Tsourounaki, G. Aroniada, E. Psillakis, ''Photodegradation of methylparaben in various environmental aqueous solutions by 254 nm irradiation'', 3rd International Conference on Industrial and Hazardous Waste Management "CRETE 2012" 12-14 September 2012, Chania, Crete, Greece

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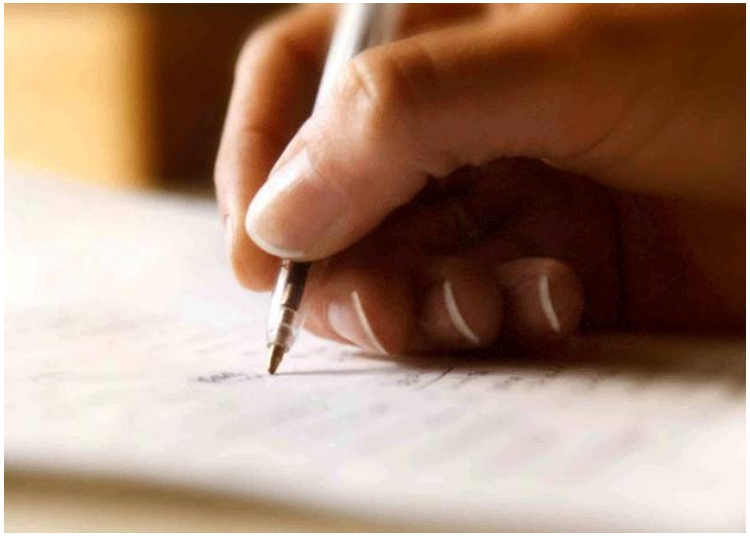
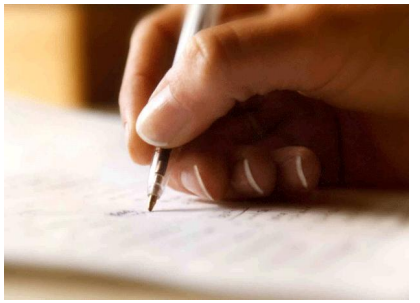
CONCLUSIONS



Photodegradation of four parabens in various environmental solutions at 254 nm

CONCLUSIONS



✓ The photodegradation of parabens →

- Effective (nearly complete removal within 90 minutes of irradiation).
- pseudo-first-order kinetic behavior.
- pH-dependent.
- hydroxyl radicals did not participate in the phototolysis of parabens.
- the presence of humic acids and nitrate ions appeared to act as filters
- the presence of sodium chloride slightly affected photolysis.
- In environmental matrices, the presence of HA, nitrate ions and others constituents acted inhibitory in the aqueous photolysis of parabens.

The photodegradation of parabens employing UV irradiation may emerge as a viable method for the future because of its cost efficiency.

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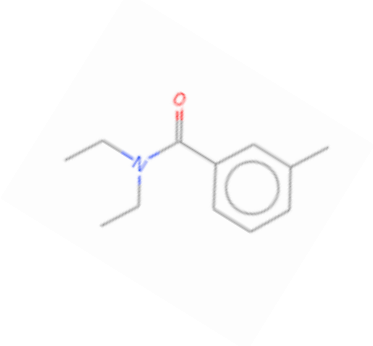
Insect repellents

An insect repellent → produce a vapor layer →has an offensive smell or taste



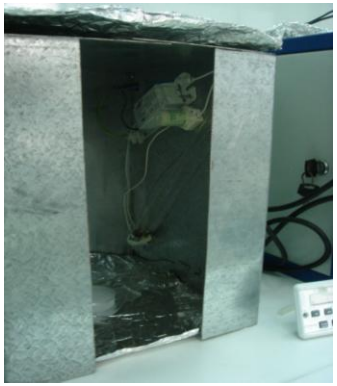
Association with
- some adverse health effects
- Death

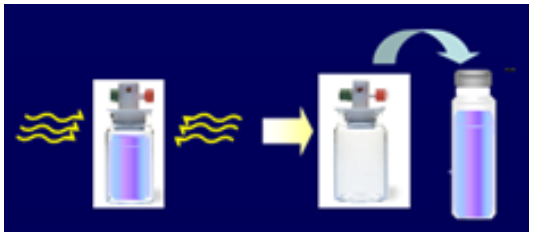
Occurrence
- in wastewater treatment plants
- finished waters from drinking water process

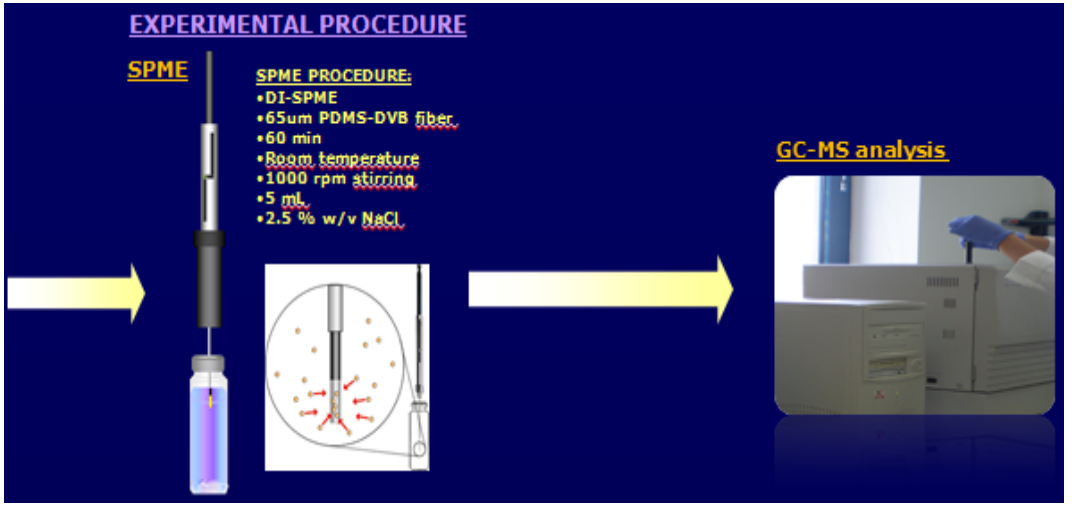
insect repellents must be either removed from water supplies or degraded

K. Tsourounaki and E. Psillakis, "Application of solid phase microextraction for studying the photolysis of di-n-propylisocinchomeronate in water", 8th International Conference on Instrumental Methods of Analysis Modern Trends and Applications "IMA 2013" 15-19 September 2013, Thessaloniki, Greece

Application of solid phase microextraction to the study of the photolysis of insect repellents in various enviromental solutions







Compound	Conc. range (μg L^{-1})	r^2
DEET	1-40	0,9966
Butopyronoxyl	1-40	0.9978
MGK-326	5-40	0.9903

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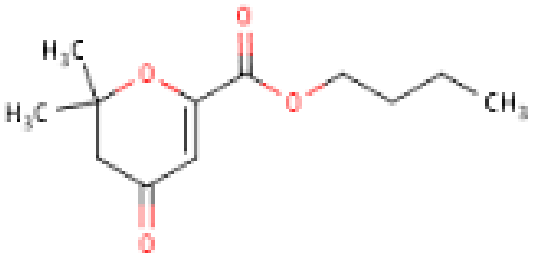
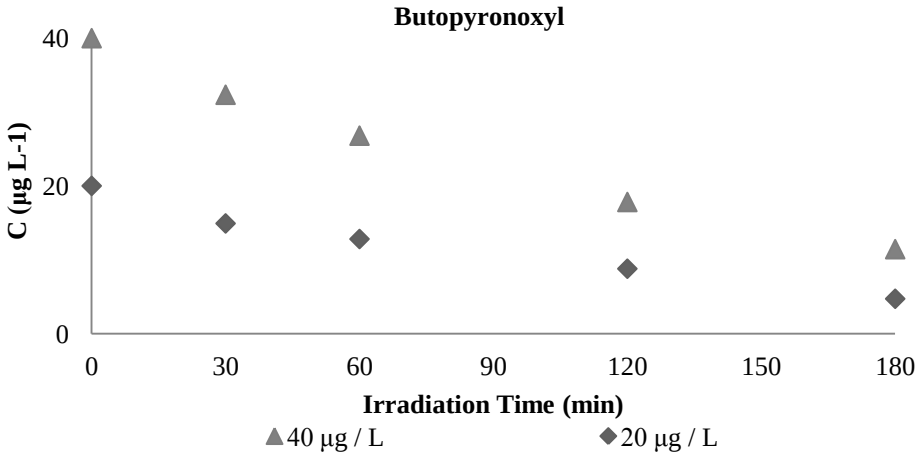
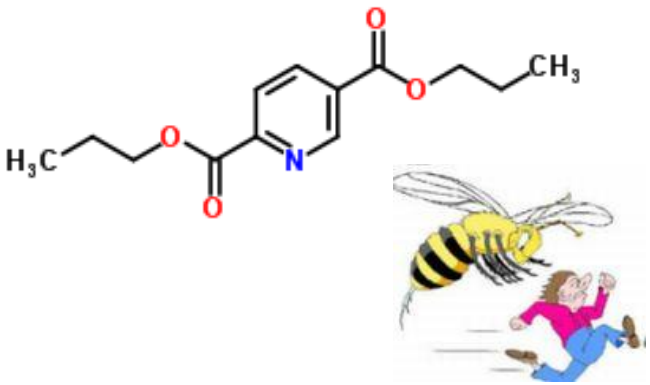
RESULTS

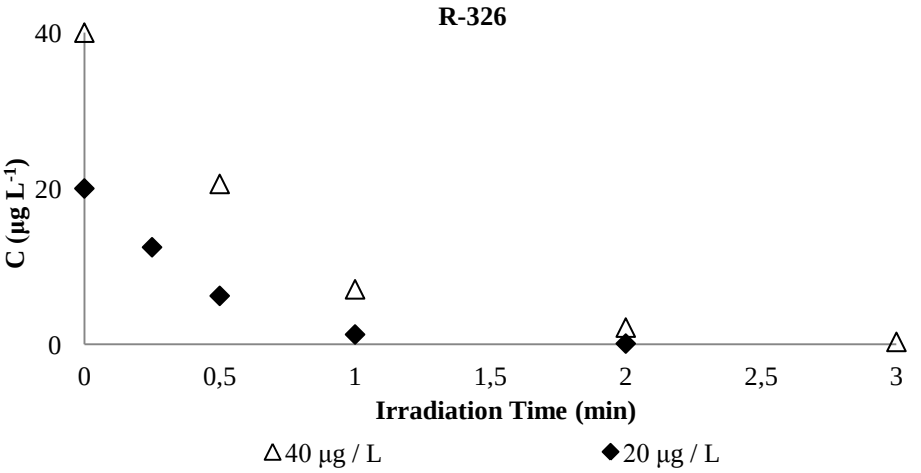
Application of solid phase microextraction to the study of the photolysis of insect repellents in various enviromental solutions

Effect of initial concentration









The results indicated a decrease in degradation efficiency at high concentrations

Small differences in half-lives due to the fixed energy pack, which was used in the experiments in different concentrations.

Pseudo 1st order kinetic

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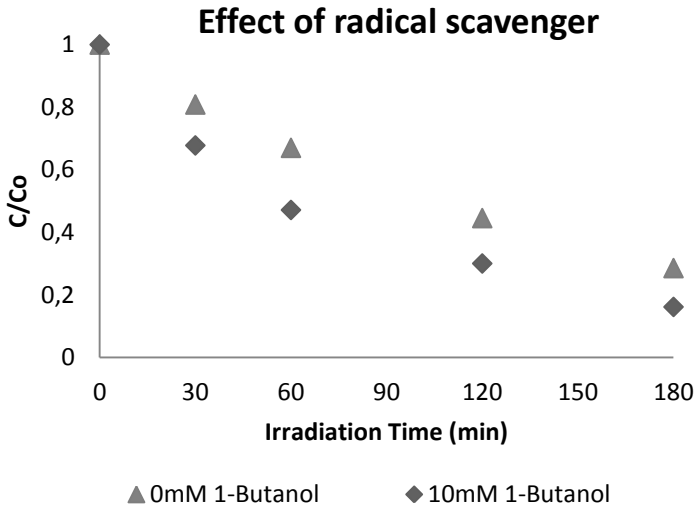
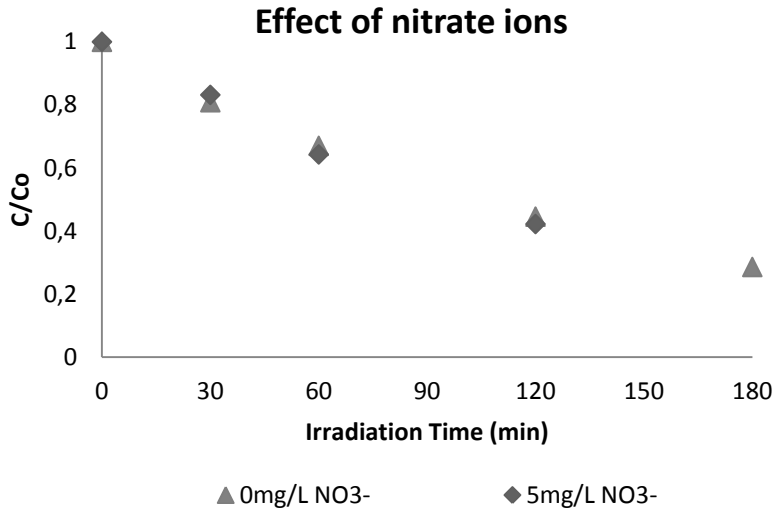
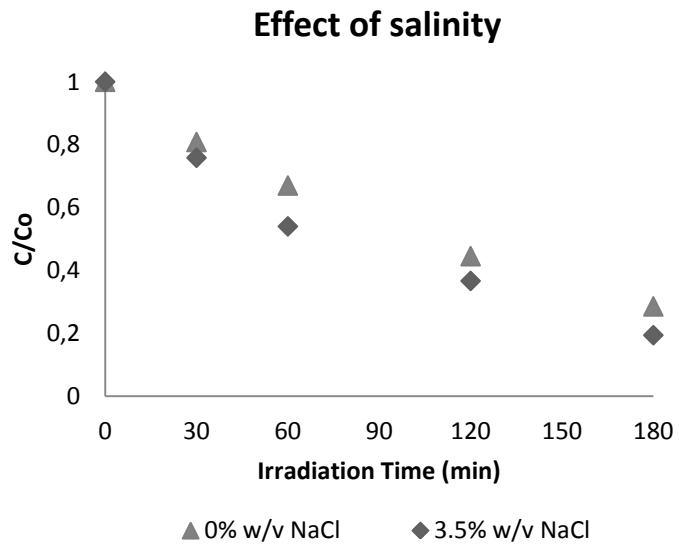
Photodegradation of Butopyronoxyl



increase the photolytic rates



NO_3^- had no effect



increase the photolytic rates due to salting out effect

There was a matrix effect in the determination of butopyronoxyl by applying direct SPME

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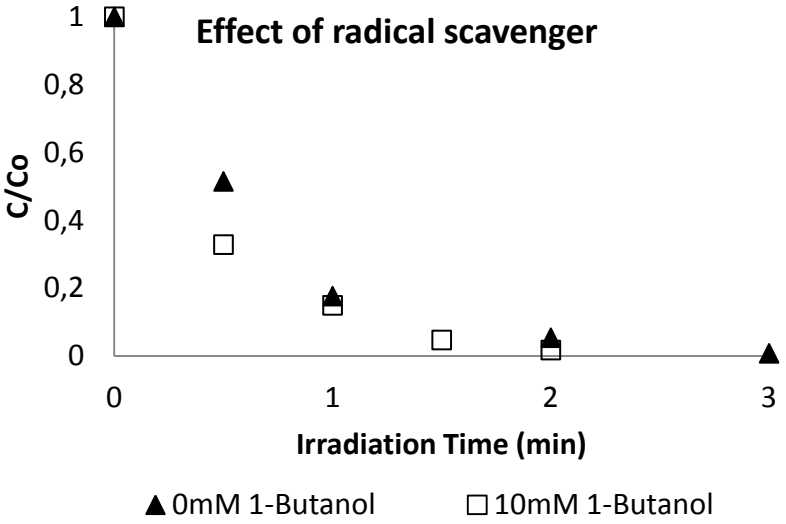
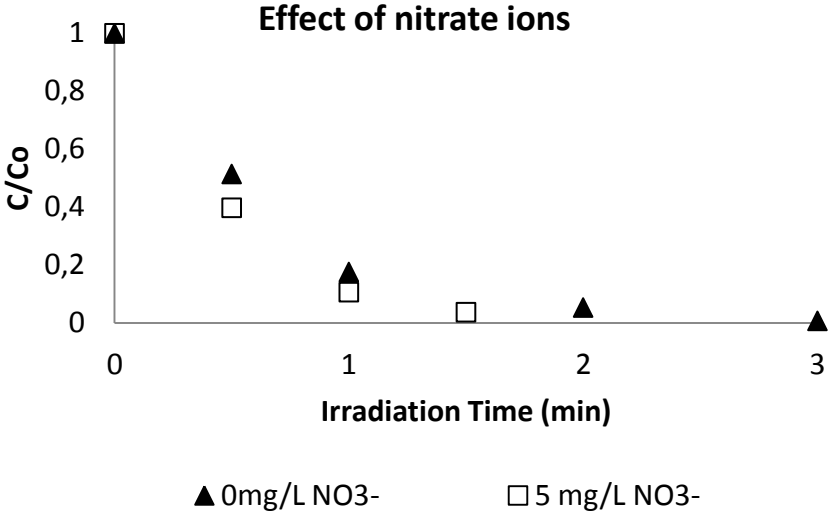
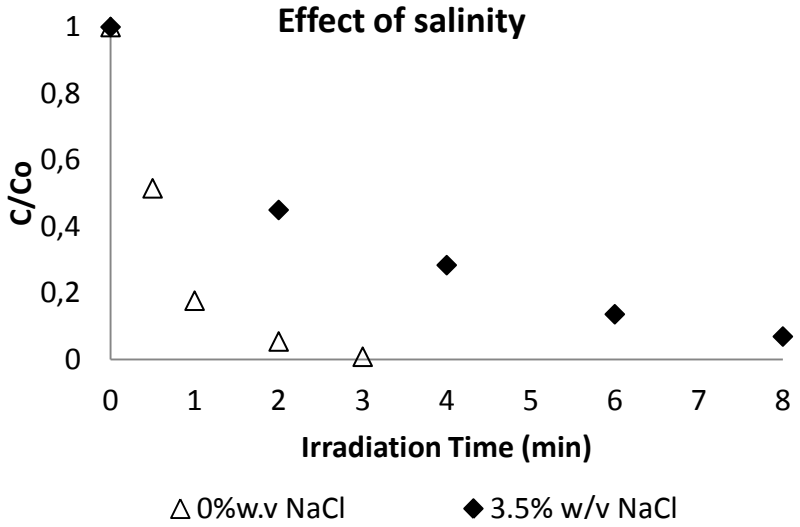
Photodegradation of R-326



1-butanol as radical scavenger had no effect



NO_3^-not significantly affect the photolytic rates



R-326 degraded at faster rates in the absence of sodium chloride

→Cl^- can remove or deactivate the reaction products from the aqueous solution

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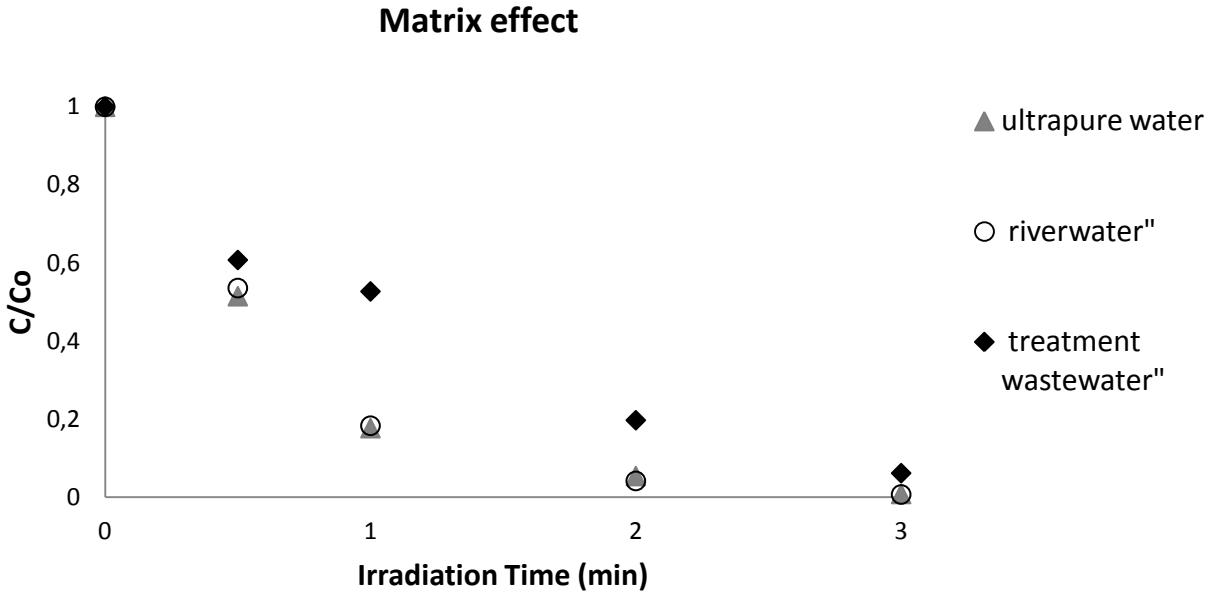
Photodegradation of R-326



photolysis is enhanced in the order UW=river > treatment wastewater

DOM appeared to be a photodegradation inhibitor in the studied conditions

→ This inhibition could be either the radical scavenging or light attenuation

Suspended matter may scatter incident light, greatly reducing penetration of light beneath the surface

The presence of various ions can also significantly affect the phototransformation of pollutants in various water matrices

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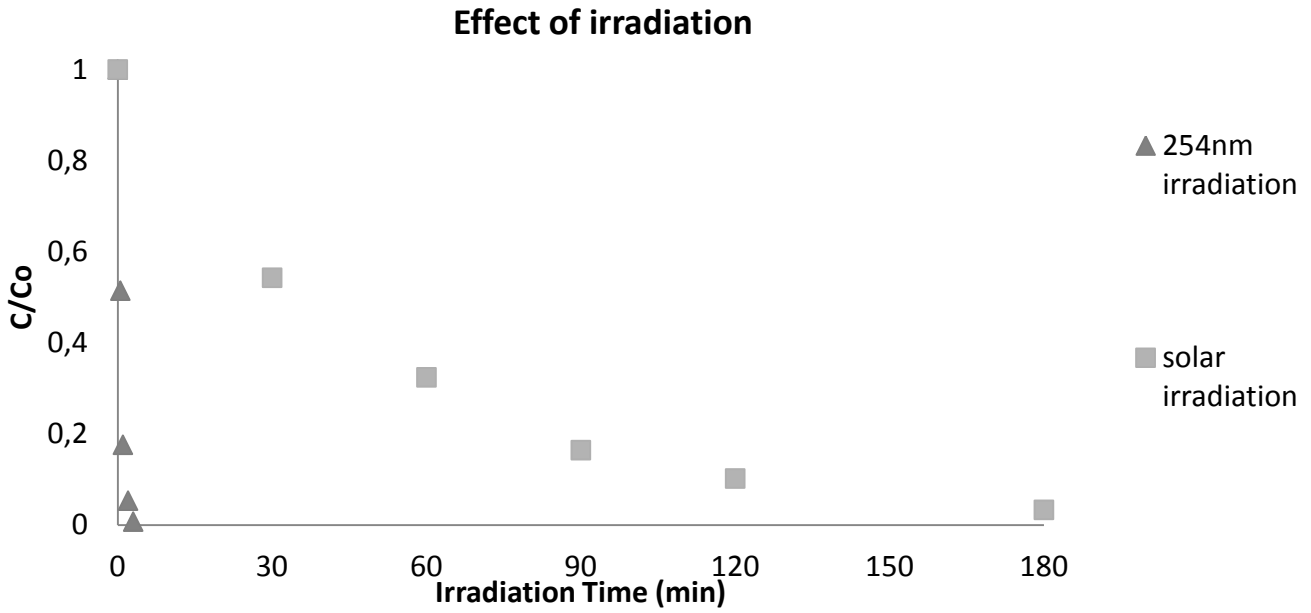

R-326prefer regions of ultraviolet light with absorption maximum at 230 and 273 nm

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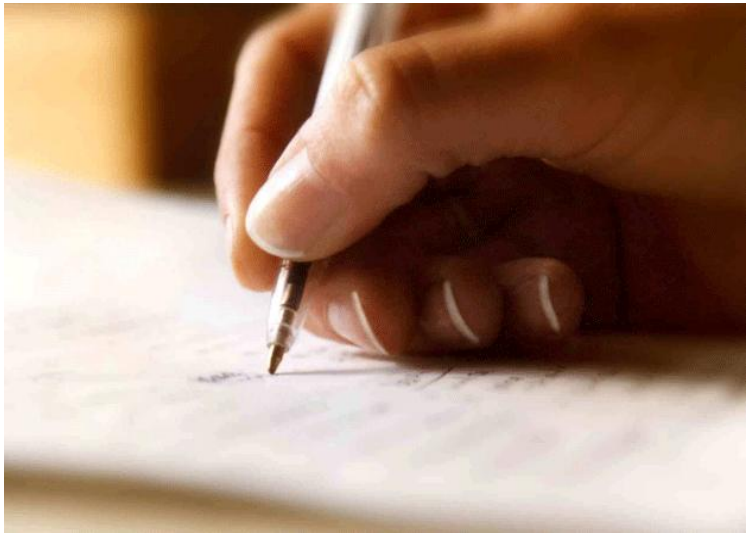
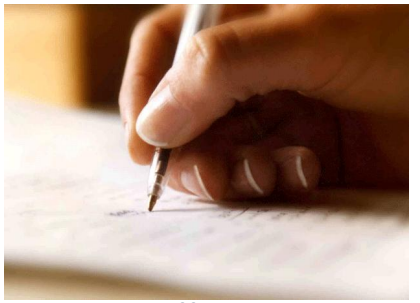


Application of solid phase microextraction to the study of the photolysis of insect repellents in various enviromental solutions

CONCLUSIONS



✓ **Di-SPME →**

- sufficiently sensitive
- linear method
- fast and efficient tool for the determination of insect repellents in wastewater and drinking water samples.

✓ **The photodegradation of insect repellents→**

- quite efficiently (nearly complete removal of R-326 in ultrapure water was achieved within 3 min of irradiation, while the butopyronoxyl took more than 180 min).
- Pseudo first-order kinetic behavior.
- Salinity-dependent
- hydroxyl radicals did not participate in the phototolysis of R-326.
- nitrate ions and 1-butanol not slightly affected photolysis of insect repellents
- The photodegradation of R-326 in ultrapure and river water was faster than in treatment wastewater. The present investigations revealed that the present of DOM, suspended matter and different ions acted inhibitory.

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THANK YOU FOR YOUR ATTENTION