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Analysis of Oxadiazon Herbicide in Natural Water Samples by a Micellar-enhanced Photo-induced Fluorescence

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A micellar-enhanced photo-induced fluorescence (ME-PIF) method was developed to analyze, for the first time, oxadiazole herbicide (namely oxadiazon) in natural water samples. Photo-conversion under UV irradiation of the herbicide into strongly fluorescent photoproducts was performed in aqueous solution and in the presence of two surfactants, cetyltrimethylammonium chloride (CTAC) or Tween 20, at micellar concentrations. The ME-PIF parameters were optimized. The ME-PIF method gave very good results with satisfactory analytical performance for the determination of a selected pesticide with concentration linear dynamic ranges of over one to two orders of magnitude. It yielded good reproducibility (RSD values of between 3.6 and 9.6%) in tap, river and sea water spiked samples, and the limits of detection were in the ng mL^{-1} range.

Keywords Environnent, pesticides, photo-induced fluoresce, micellar-enhanced

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Introduction

Global population growth requires an increase in agricultural production. Because weeds generally slow plant growth, they therefore constitute an obstacle to this production. To effectively improve crop yields, farmers use chemical weed control, where chemicals are applied for weed control in the early stage of cultivation.[1,2] However, any massive use of pesticides imposes the necessity to find easy, quick and simple analytical methods for the control analysis of pesticides in different samples of environmental interest. This trend is also imposed by strict legal rules for control analysis.[3]

Oxadiazon or 5-*tert*-butyl-3-(2,4-dichloro-5-isopropoxyphenyl)-1,2,4-oxadiazol-2(3*H*)-one is an effective herbicide for the control of obnoxious grasses and broad leaf weeds in a wide variety of crops: citrus fruit, vine, cotton, cereals, wines, beans and onions.[4,5] However, herbicide are frequently found at trace levels in the environment, and particularly in surface and ground water.[6] Its persistence is an important matter of concern due to its toxicity and carcinogenicity. Therefore, it is important to develop sensitive analytical methods for determining this pesticide in natural water. We have chosen to use a method based on fluorescence spectroscopy for its sensitivity and moderate price.

The pesticide under study is naturally non-fluorescent, but can be rapidly transformed into strongly fluorescent photoproducts upon UV irradiation. In this work, oxadiazon was studied for the first time by the photo induced fluorescent (PIF) method, already employed for the analysis of other pesticides by classical excitation[7–11] by laser excitation[12–14] or on automatic systems.[15,16]

Micellar medium can also be used to increase the sensitivity of the method, since it creates an apolar media that increases the solubility in water and the fluorescent quantum yield. A study carried out on oxadiazon demonstrated that its solubilization in water increased as a function of the concentration of Tween 20.[1] Consequently, micellar media also enhance the PIF signal of pesticides in aqueous solution.[17,18] Irace-Guigand *et al.*[19] found a LOD of between 330 – 920 ng mL^{-1} for four phenylurea herbicides by this method. In this work we associated, for the first time, the use of a micellar media and the PIF method for an oxidazion study.

The goal of this paper was to develop a micellar-enhanced photo-induced fluorescence method (ME-PIF) that is simple, robust and rapid for the detection of oxadiazon herbicide in aqueous solution. We first investigated the critical micellar concentration (CMC) of cetyl trimethylammonium choride (CTAC) and Tween 20 to maximize the oxadiazon solubility. We then determined the fluorescence characteristics and the kinetic formation of the photoproducts obtained by ME-PIF for oxadiazon, and the effect of the pH and the micellar agent concentration. At last we exposed the analytical performances obtained and conducted analytical applications.

Materials and Methods

Chemicals

Herbicide oxadiazon (Table 1), CTAC (cetyltrimethylammonium choride), Tween 20 and methanol were purchased from Sigma-Aldrich (St Quentin Fallavier, France). All of the reagents were

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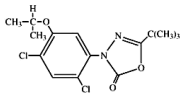
Table 1 Chemical properties of oxadiazon

Pesticide	Chemical structure	Formula	Molecular weight/ g mol^{-1}	Water solubility at 20°C/ mg L^{-1}
Oxadiazon		$C_{15}H_{18}Cl_2N_2O_3$	345.221	1.01

of analytical grade. Ultrapure water (Mro-MQ System form Millipore, Guyancourt, France) was used for the experimental work.

Apparatus

Excitation and emission fluorescence spectra are obtained on a Cary Eclipse fluorescence spectrophotometer (Varian-Agilent, Les Ulis, France) with an arc-Xenon lamp pulsed at 80 Hz as the excitation source. UV irradiation is produced by a broadband 125 W Hg lamp (Philips, Suresnes, France). Photoproducts were formed in 25 mL quartz tubes placed on an optical bench 4 cm from the mercury lamp.

Methods

Stock standard solutions of the pesticide (340 mg L^{-1}) were prepared in methanol. Working solutions were obtained by successive dilutions in water. Stock solutions of CTAC (0.1 mol L^{-1}) and Tween 20 (0.06 mol L^{-1}) were prepared with distilled water. Samples were collected from Penfeld river (Finistère district, France); from Brest tap water (Fance); from Senegal River, which irrigates one of the most important agricultural areas in Senegal and can be submitted to some pesticide pollution; and from Dakar seaside, which can be contaminated by effluents and induce fish contamination. The water samples were filtered through a filter disk (45 µm) in order to eliminate any organic suspended matter. To obtain natural water matrix samples free of organic contamination, traces of organic compounds were eliminated by preparative chromatography using a SPE C18 cartridge (LiChrolutRP-18E 200 mg 40 – 63 mm, Merck-Millipore, Molsheim, France). The cartridge was preconditioned with 5 mL of methanol, followed by 5 mL of ultrapure water, and then 50 mL of natural water samples were passed through the cartridge. The sample was then irradiated for the appropriate time in the quartz tubes. In all cases, the PIF intensity measurements were corrected for the background signal using the appropriate blank. Experiments were carried out in triplicate and expressed as mean values. The detection limit was calculated as the concentration of analyte giving a signal-to-noise ratio of 3, and the quantification limit as the concentration of analyte giving a signal-to-noise ratio of 10. We used the following formula with the slope of the calibration curve and σ the noise of a blank sample:

$$(\mathrm{LOD} = \frac{3\sigma}{\mathrm{slope}})\ (\mathrm{LOD} = \frac{10\sigma}{\mathrm{slope}}).$$

Results and Discussion

Photo-induced fluorescence properties

The oxadiazon PIF excitation and emission spectra in water, CTAC and Tween 20 are given in Fig. 1. The shape of the fluorescence spectra was similar in all media, and we obtained approximately the same excitation and emission wavelengths, the maximum of which are located, respectively, at 220 nm for the excitation and 300 nm for the emission (Table 2). The addition of CTAC increases 2.3 times the PIF intensity, and the addition of Tween 20 2.7 times. Also, we note in water and in Tween 20, a shoulder of the emission band appeared at 360 nm which intensity corresponding to the second excitation peak at 270 nm. Indeed, oxadiazon has heavy atoms in its structure, such as chlorine, which is a fluorescence inhibitor. Thus, even though the irradiation probably eliminated the heavy atoms of the original molecules, the absence of the 360 nm band in the CTAC may be due the cationic nature of the surfactant, which releases an anion Cl^- inducing probably a quenching effect.

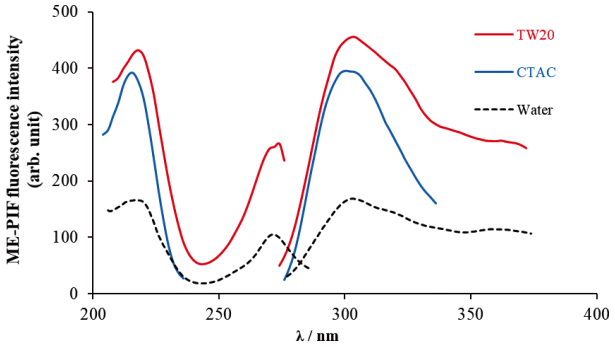


Fig. 1 PIF excitation and emission spectra of oxadiazon (10 µg L^{-1}) in water, CTAC and Tween 20.

Table 2 Fluorescence properties of the photoproduct and PIF optimal analytical conditions

Compound	Medium	pH	$\lambda_{ex}/\lambda_{em}$ (nm)	t_{irr}^{opt}/min
Oxadiazon	Water	6	220/300	5
	CTAC	7	220/300	7
	Tween 20	11	220/300	5

Optimization of the pH

We investigated the pH effect (from 1 to 13, adjusted using HCl and NaOH solutions) on the PIF intensity of the oxadiazon herbicide in the three media. The results presented in Fig. 2 and Table 2, indicate that the fluorescence intensity reaches a maximum at pH 7 in CTAC with a fluorescence intensity of four-times higher, and at pH 11 in Tween 20 with a fluorescence intensity of seven-times higher.

Tween 20 and CTAC concentration effects

The effect of two surfactants such as CTAC and Tween 20, was investigated in order to maximize the sensitivity in a solution containing 10 µg mL^{-1} of oxadiazon irradiated for 5 min. This concentration was chosen to be in the upper part of the domain of the study.

We first determined the CMC (*i.e.*: the concentration from which the micelles are formed) using concentrations of surfactants from 5×10^{-4} to 2×10^{-2} mol L^{-1} for CTAC and from 6×10^{-6} to 4×10^{-4} mol L^{-1} for Tween 20 (Fig. 3). By reference to the bibliography, the diameter of the micelles formed from CTAC was in the range of 8.1 nm and for Tween 20 in the range of 7.2 nm.

The results showed that until 5×10^{-3} and 7×10^{-5} mol L^{-1} for

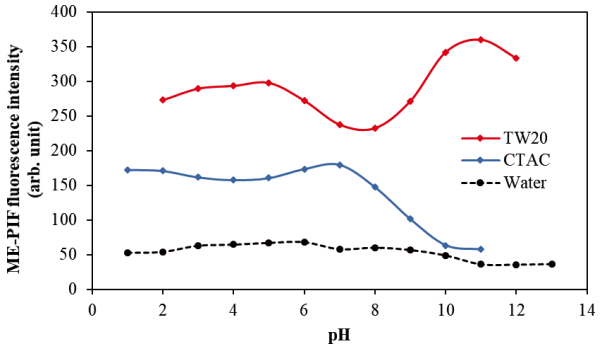


Fig. 2 Effect of the pH concentration on the PIF intensity for oxadiazon (10 µg mL^{-1}) in water, CTAC and Tween 20.

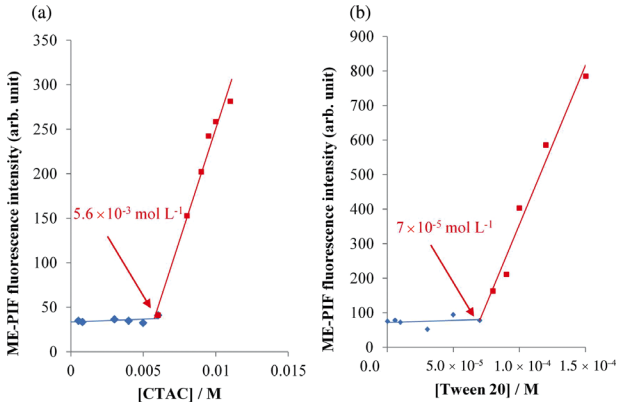


Fig. 3 Effect of CTAC (a) and Tween 20 (b) concentration on the PIF intensity for oxadiazon (10 µg mL^{-1}).

CTAC and Tween 20, respectively, the fluorescence intensity remained low (part I), meaning that the surfactants were in the monomeric state, and that we observed the low-fluorescence intensity of the oxadiazon PIF in water. Then, the fluorescence intensity increased rapidly as a function of the surfactant concentration corresponding to the micellization phase (part II), the pesticide progressively included in an apolar media increased its fluorescence quantum yield. The CMC corresponds to the crossing of the trend curves of phases I and II reported to the concentration. We obtained CMC values of 5.6×10^{-3} and 7×10^{-5} mol L^{-1} for CTAC and Tween.

The CMC of the surfactant depends on its nature (ionic or non-ionic), its hydrophilic group (type, size, counter-ion) and its lipophilic group (length, branching). Since Tween 20 is non-ionic and has a larger hydrophobic part, this facilitates the rapid formation of micelles and therefore favors the rapid molecules to self-aggregate, leading to a CMC of 7×10^{-5} mol L^{-1}. Unlike nonionic surfactants, as in the case of CTAC, the net charge in its hydrophilic group makes it much more difficult for micellization and leads to the higher CMC of 5.6×10^{-3} mol L^{-1}.

Thus, the working concentrations of 1.1×10^{-2} mol L^{-1} for CTAC (pH 11) and 1.5×10^{-4} mol L^{-1} for Tween 20 (pH 7) retained in oxadiazon determination, provided micellar enhancement factors (MEF) of 6 and 8 times to that in water (Fig. 3). Our results are in agreement with previous study which has shown that the presence of surfactants significantly increases the fluorescence intensity.[17-19] Indeed, Bautista *et al.*[17]

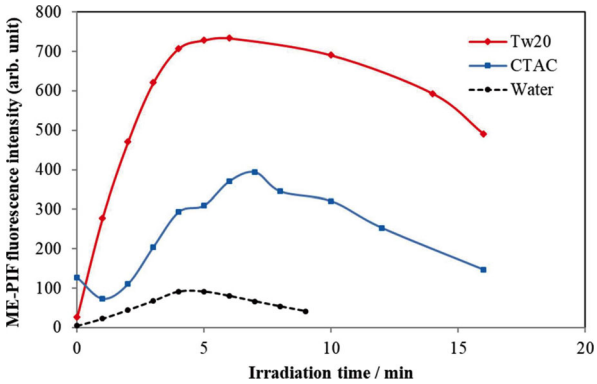


Fig. 4 Evolution of the ME-PIF signal in CTAC (pH 7), Tween 20 (pH 11) and water (pH 8) (λ_{ex} = 220 nm; λ_{em} = 300 nm) as a function of the irradiation time by the mercury lamp.

have found a CMC of 8×10^{-3} M, showing the exalting effect of CTAC in the same order of magnitude (in 6 times), during the quantitative analysis of some the phenylurea pesticides in water by photochemically-induced fluorescence. In a similar study, same CMC value of 8×10^{-3} M for CTAC was found by Guigand *et al.*[19] using flow-injection analysis micellar-enhanced photochemically induced fluorescence (FIA-MEPIF) method to improve the detection with sensitivity multiplicative factors varying over 1.6 to 18 fold. In their work, Berijani *et al.*[1] used a concentration of 5×10^{-5} M of Tween 20, which is close to the CMC (6×10^{-5} M), to enhance the extraction efficiency of oxadiazon in agriculture water samples.

Optimization of UV irradiation

The absence of native fluorescence of oxadiazon might be due, at least partially, to the following factors, inherent to its molecular structure (Table 1): the important flexibility of the molecule, with an obvious lack of rigidity, and therefore a tendency to be deactivated by thermal relaxation processes (collisions, *etc.*); the intramolecular heavy atom effect of the chlorine substituents, located on the benzene ring of this molecule, which generally produces a strong decrease of the fluorescence quantum yield. Therefore, the formed fluorescent photoproduct might result from a dechlorination photochemical reaction of oxadiazon.[22] The effect of UV irradiation on the fluorescence intensity depends strongly on the type of media, pH and micellar medium used.[1,23] We then chose pH 7 and 11 solutions, respectively, for CTAC and Tween 20, which correspond to the optimum the pH found in our previous results. The irradiation time was characterized by a regular increase of the PIF intensity, which reached a maximum at about 4 min in water, 5 min in Tween 20 and water and 7 min in CTAC (Fig. 4 and Table 2), followed by a progressive decrease of the PIF signal in all cases. This slight decrease of the fluorescence intensity indicates a disappearance of the photoproduct and, therefore its probable slow photolysis.

Analytical figures of merit

In order to evaluate the performance of the method, analytical merit values were determined with the ME-PIF method and compared with other results obtained by conventional PIF in aqueous media. Calibration curves were constructed by preparing samples in triplicate, containing increasing concentrations of each pesticide. The study was performed in the concentrations ranges of 2 – 11 µg mL^{-1} in water,

0.006 – 4 μg mL^{-1} in CTAC and 0.01 – 8 μg mL^{-1} in Tween 20. The UV irradiation time was set to five minute in water and Tween 20 and seven minute in CTAC. The excitation and emission intensity were measured at respectively 220 and 300 nm in all solvent (Fig. 5). Tween 20 and CTAC give the most sensitive result with slopes of 68.567 and 63.492 AU mL μg^{-1}, respectively; however, in water we obtained less sensitive results, about five-time lower, with a slope of 13.628 AU mL μg^{-1}. The linearity of the calibration curves was evaluated by variance analysis (Table 3). In all cases, the regression variance (V_{REG}) was significantly higher than the residual variance (V_{RES}) (p-value >5%), showing that the regression was significant. Moreover, the lack of a fit variance (V_{LOF}) was not significantly higher than the pure error variance (V_{PE}) (p-value >5%), indicating the good quality of the linear model. A Student's t test was employed to show that the intercepts of the calibration curves were not significantly different from zero (p value >5%) for the three media, except in water, which has a p-value of close to 0.4% (Table 4).

Low rather limits of detection (without preconcentration) obtained in Tween 20, CTAC and water were respectively 1, 2 and 160 ng mL^{-1} (Table 4). Compared to results obtained for other pesticides by classical PIF in an aqueous medium, we can notice a great improvement of the analytical performance of our method. For example, Muoz *et al.*[24] have found a LOD of between 70 and 460 ng mL^{-1} in acetonitrile-phosphate buffer 60:40 (v/v) for determination of four phenylurea herbicides, including diuron, isoproturon, linuron and neburon. Our values are also ten-times lower than the LOD obtained by Irace-Guigand *et al.*[19] (*i.e.*: between 330 – 920 ng mL^{-1}) for other pesticides in a micellar medium. Compared to the two precedent examples, our better results come from the selection of the optimal irradiation time, which is not possible by HPLC with post-derivation and by flow injection analysis. On the other hand, our LOD values are in the same range as those found by Coly *et al.*[18] by ME-PIF for chlorsulfuron, 3-rimsulfuron and sulfometuron-methyl using CTAC.

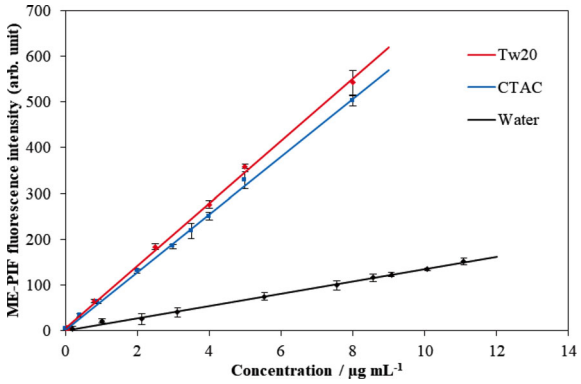


Fig. 5 Calibration curves of oxadiazon in water, CTAC and Tween 20.

Table 3 Evaluation of the linear functions of the ME-PIF method by variance analysis at a confidence level of 5%

		Water	CTAC	Tween 20
ANOVA 1	Regression variance	5.944×10^4	5.914×10^5	8.707×10^5
	Residual variance	31.4	104.4	123.904
	p-Value	0.000	0.000	0.000
ANOVA 2	Lack of fit variance	47.53	115.33	186.522
	Pure error variance	22.8	100.18	99.552
	p-Value	0.104	0.376	0.134

Analytical applications

The usefulness of this method was tested by recovery studies carried out on four different samples, subsequently fortified with 0.8 μg mL^{-1} of selected pesticide, and the standard addition method was used to evaluate the recovery rates. Thus, for the first time, the linearity of the standard addition curves were tested by a variance analysis (as explain in paragraph 3.5). In all cases, the regression was significant, without lack fit (at 5% confidence level), meaning that the linear model was validated. Then, the parallelism between the standard addition curves and the reference calibration curves was evaluated by a Student t test (Table 5). For this pesticide, the experimental Student t value (confidence level of 5%) was higher than the t calculated value, showing that the standard addition curves slopes are not significantly different from the calibration ones.

Table 4 Equations of the calibration curves, estimation of the quality of the intercept by comparing it to 0 by a Student t test, and comparison of the analytical performances of the new UV-PIF-LE method to the original DL-PIF one

	Water	CTAC[c]	Tween 20[d]
Slope	12.487	61.946	66.737
Intercept	11.285	4.064	7.276
Standard deviation of the intercept	2.070	3.142	2.807
p value (t test)	0.004	0.2078	0.0157
LOD/ng mL^{-1} [a]	160	2.0	1.0
LOQ/ng mL^{-1} [b]	483	6.4	3.4

a. LOD: limit of detection, calculated as the concentration of analyte giving a signal-to-noise ratio of 3.
b. LOQ: limit of quantification, calculated as the concentration of analyte giving a signal-to-noise ratio of 10.
c. [CTAC] = 1.1×10^{-2} mol L^{-1} at pH 11.
d. [Tween 20] = 1.5×10^{-4} mol L^{-1} at pH 7.

Table 5 Comparison between addition standard calibration curves slopes by a Student difference t test

	Oxadiazon in CTAC	Tap water	Seawater	Riverwater	Oxadiazon in Tween 20	Tap water	Seawater	Riverwater
Slope	63.49	64.73	64.2	63.525	68.57	69	68.18	69.87
STD	0.54	1.77	1.34	0.74	0.94	2.33	1.35	1.42
d.o.f	7	12	11	12	7	13	14	13
t_D	—	1.772	1.292	0.103	—	0.541	0.794	2.147
t (5%)	—	2.179	2.201	2.179	—	2.16	2.145	2.16
SD	—	NO	NO	NO	—	NO	NO	NO

STD: Standard deviation of the slope of the standard addition curve; d.o.f., degrees of freedom; t_D, calculated Student value of the difference between the two slopes; t, tabulated Student t value; SD, significant difference.

Method validation for applications

To validate the method, a recovery study was performed by spiking each water sample with an appropriate amount of oxadiazon. The recovery values obtained were very close to 100%, ranging from 90 to 110% in CTAC and 90 to 115% in Tween 20. The relative standard deviations vary between 4 and 9.6% in CTAC and from 3.6 to 7.9% in Tween 20 (Table 6). Our recovery results are in the same range as those obtained by Berijani *et al*. by classical fluorescence (*i.e.*: between 96 and 104%) using Tween 20 as a surfactant to enhance the determination oxadiazon in water samples.[1] Recovery between 97 and 108% were also obtained for the determination of dichlorophenoxyaceytic acid (2,4-D) and mecoprop in CTAC by Campana *et al.*[25] using the combination of a flow injection analysis (FIA) system with micellar-enhanced photochemically induced fluorescence (MEPIF) detection.

Table 6 Recovery values obtained in spiked river, tap and seawater samples for the determination of oxadiazon in CTAC and Tween 20

Medium	Added/ µg mL^{-1}	Found/ µg mL^{-1}	Recovery, %	Mean recovery, R_m, %	Recovery standard deviation, s(R), %
CTAC	Tap water				
	0.41	0.44	110		
	0.54	0.53	107		
	1.24	1.17	90	101	4
	2.40	2.32	96		
	3.40	3.44	101		
	3.92	3.93	100		
	Seawater				
	0.43	0.42	99		
	0.80	0.87	108		
	1.30	1.32	101	103	6.3
	2.40	2.52	105		
	3.40	3.86	99		
	3.90	4.45	105		
	Riverwater				
	0.41	0.39	99		
	0.81	0.87	109		
	1.10	1.12	102	103	9.6
	2.41	2.48	103		
	3.93	4.00	102		
	4.42	4.57	104		
Tween 20	Tap water				
	0.40	0.37	98		
	0.80	0.86	108		
	2.44	2.52	105	103	4.2
	3.90	3.86	99		
	7.20	7.34	103		
	Seawater				
	0.4	0.39	99		
	0.81	0.84	104		
	1.40	1.50	106	101	4.7
	4.42	4.44	100		
	8.41	7.98	94		
	Riverwater				
	0.40	0.40	100		
	0.83	0.77	96		
	1.40	1.27	90	99	3.6
	4.44	4.70	106		
	8.40	8.58	102		

In order to show the practical interest of the method in tap, sea and river-water samples we have done triplicates test points, at concentrations different from those in the calibration curves. The predicted concentration values obtained by reference to the calibrations curves are not significantly different from the real value by a Student *t* test (Table 7).

By the end, three blind tests were performed in tap, sea and river water samples. The concentration used for each blind test was different from those used for the calibration curves. Each test was performed in triplicate, then the concentrations of the unknown samples were computed in reference to the calibrations equations. The concentrations found for the blind samples are not significantly different from the real value by a Student *t* test (Table 7), which contributes to show the accuracy of the method.

Conclusion

In this work, we succeffuly developed a micellar enhaced photo-induced fluorescence method, for the determination of oxadiazon in water samples. We have improved the sensitivity of the previously published conventional PIF methods, by optimizing different parameters. Critical micellar concentrations (CMC) of 1.5×10^{-4} and 1.1×10^{-2} mol L^{-1} were obtained at the optimal pH for, respectively, Tween 20 (pH 11) and CTAC (pH 7). Thanks to the use of the micellar media and the PIF method, we have been able to develop a method that is simple, robust and rapid with a LOD of 1 ng mL^{-1} in Tween 20 and 2 ng mL^{-1} in CTAC, lower than many other classical fluorescence and PIF methods for pesticides determinations,[19,24] which confirm its good sensitivity. We have also avoided to use any preconcentration or extraction protocols before analysis. The relative standard deviation of less than 10% indicate good precision and appropriate repeatability of the method. The ME-PIF method allows to determine oxadiazon at low levels in natural water samples with satisfactory recovery (90 – 115%). These results testify the efficiency of ME-PIF in oxadiazon determination; therefore, it could be used for others pesticides and pollutants quantification in various environmental matrices.

Table 7 Test points: Comparison of the concentration of each test point, to the concentrations found by regression, by a Student *t* test

Sample	CTAC					Tween 20				
	Added/µg mL^{-1}	Found/µg mL^{-1}	t_D	t_S (5%)	SD	Added/µg mL^{-1}	Found/µg mL^{-1}	t_D	t_S (5%)	SD
Tap water	0.62	0.64 ± 0.02	1.531	2.302	No	0.62	0.65 ± 0.01	1.119	2.035	No
Seawater	0.72	0.74 ± 0.01	1.309	2.586	No	0.72	0.70 ± 0.08	1.580	2.852	No
Riverwater	0.71	0.73 ± 0.05	1.788	2.530	No	0.71	0.75 ± 0.05	1.320	2.231	No

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References

1. S. Berijani and G. Ahmadi, *Iran. J. Chem. Chem. Eng.*, **2014**, *33*, 41.
2. S. Miyake, Y. Hirakawa, T. Yamassaki, E. Watanabe, A. Harada, S. Iwasa, and H. Narita, *Anal. Sci.*, **2019**, *35*, 333.
3. I. Sbov, A. Khenlami Assandas, M. Catal Icarido, and J. Martnez Catatayud, *Anal. Sci.*, **2006**, *22*, 21.
4. C. Tomlin, "*The Pesticide Manual*", 16th ed., World Compendium, **2012**, British Crop Protectio Council, Farnham.
5. J. W. Wong, M. G. Webster, C. A Halverson, M. J. Hengel, K. K. Ngim, and S. E. Ebeler, *J. Agric. Food Chem.*, **2003**, *51*, 1148.
6. M. D. Gil-García, M. Martínez-Galera, P. Parrilla-Vázquez, A. R. Mughari, and I. M. Ortiz-Rodríguez, *J. Fluoresc.*, **2008**, *18*, 365.
7. A. Muñoz de la Peña, M. C. Mahedero, and A. Bautista-Sánchez, *Talanta*, **2003**, *60*, 279.
8. O. M. A. Mbaye, M. D. Gaye Seye, A. Coly, A. Tine, M. A. Oturan, N. Oturan, and J. J. Aaron, *Microchem. J.*, **2013**, *110*, 579.
9. P. A. Diaw, O. M. A. Mbaye, M. D. Gaye-Seye, J. J. Aaron, A. Coly, A. Tine, N. Oturan, and M. A. Oturan, *J. Fluoresc.*, **2014**, *24*, 1319.
10. S.-H. Zhu, H.-L. Wu, A.-L. Xia, Q.-J. Han, and Y. Zhang, *Anal. Sci.*, **2007**, *23*, 1173.
11. L. Burel, P. Giamarchi, L. Stephan, Y. Lijour, and A. Le Bihan, *J. Fluoresc.*, **2006**, *16*, 177.
12. P. A. Diaw, A. Maroto, O. M. A. Mbaye, M. D. Gaye-Seye, L. Stephan, A. Coly, L. Deschamps, A. Tine, J. J. Aaron, and P. Giamarchi, *Talanta*, **2013**, *116*, 569.
13. O. M. A. Mbaye, A. Maroto, M. D. Gaye-Seye, L. Stephan, L. Deschamps, J. J. Aaron, and P. Giamarchi, *Talanta*, **2015**, *132*, 909.
14. J. P. Bakhoum, O. M. A. Mbaye, P. Diaw, M. Mbaye, L. Cisse, D. Gaye-Seye, J.J. Aaron, A. Coly, B. Le Jeune, and P. Giamarchi, *Anal. Lett.*, **2019**, *52*, 2782.
15. J. P. Bakhoum, O. M. A. Mbaye, P. A. Diaw, M. Mbaye, L. Cisse, M. D. Gaye-Seye, J. J. Aaron, A. Coly, B. Le Jeune, and P. Giamarchi, *Spectrochem. Acta, Part A*, **2019**, *214*, 285.
16. G. N. Piccirilli, G. M. Escandar, F. C. Cañada, I. D. Merás, and A. M. de la Peña, *Talanta*, **2008**, *77*, 852.
17. A. Bautista, J. J. Aaron, M. C. Mahedero, and A. Muñoz de la Pena, *Analusis*, **1999**, *27*, 857.
18. A. Coly and J. J. Aaron, *J. Chem. Chem. Eng.*, **2009**, *28*, 33.
19. S. Irace-Guigand, E. Leverend, M. D. Gaye-Seye, and J. J. Aaron, *Luminescence*, **2005**, *20*, 138.
20. T. Nomura, Y. Asai, N. Murahashi, and K. Iwamoto, *Chem. Pharm. Bull.*, **2000**, *48*, 947.
21. E. S. Basheva, P. A. Kralchevsky, K. D. Danov, K. P. Ananthapadmanabhanb, and A. Lipsb, *Phys. Chem. Chem. Phys.*, **2007**, *9*, 5183.
22. Y. Guang-Guo and W. Brian, *Food Contam. Agricul. Wast.*, **1999**, *34*, 549.
23. M. C. Mahedero, A. Muñoz de la Peña, A. Bautista, and J. J. Aaron, *J. Incl. Phenom.*, **2002**, *42*, 61.
24. A. M. Peña, M. C. Mahedero, and A. Bautista-Sánchez, *J. Chromatogr. A.*, **2002**, *950*, 287.
25. A. M. G. Campana, J. J. Aaron, and J. M. B. Sendra, *Talanta*, **2001**, *55*, 531.