

A new micelle-based method to quantify the Tween 80[®] surfactant for soil remediation

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Abstract Tween 80[®] is a surfactant widely employed to enhance remediation of contaminated soils. Actually, there are few convenient and selective methods to quantify Tween 80[®] at low concentrations. Here, we report a new and simple quantification method to monitor Tween 80[®] analysis. Our method is based on the enhancement of the fluorescence of 6-(*p*-toluidino)naphthalene-2-sulfonic acid (TNS) by formation of micelles with Tween 80[®]. Results show a linear calibration curve with a correlation coefficient R^2 of 0.99, a detection limit of 0.13 mM and a quantification limit of 0.19 mM. This method showed better performances compared to actual methods such as UV absorbance and total organic carbon measurements. In addition, we demonstrated that the measurements using this new technique are impacted only at 3.5 % maximum by the presence of oxidation by-products formed during oxidation of Tween 80[®] by the electro-Fenton process or by hydrophobic organic contaminants present in solution. Fluorescence measurements of soil washing solution with real contaminated soil show almost no impact on Tween 80[®]-TNS micelle analysis. The analytical method proposed for Tween 80[®] analysis could replace the currently used conventional method because it is quite simple, highly sensitive and more selective.

Keywords Micelle · Fluorescence quantification · Soil organic matter · Hydrophobic organic contaminants · By-products · Electro-Fenton

1 Introduction

Surface-active agents or “surfactants” are amphiphilic molecules having both a hydrophobic (apolar group) tail and a hydrophilic (polar group) head (Rosen 2004). When dissolved in water at low concentrations, surfactant molecules exist as monomers. When the concentration of the surfactant increases, there is a critical concentration beyond which surfactant monomers start aggregating to form self-assemblies called micelles. The concentration at which micelle formation occurs is known as the critical micelle concentration (CMC). CMC is a function of surfactant structure, composition of the solution, temperature, ionic strength and the presence and types of organic additives in the solution (Edwards and Liu 1994; Rosen 2004). Depending on the nature of the hydrophilic group, surfactants can be classified as anionic, cationic, zwitterionic and non-ionic (Rosen 2004).

Surfactants have several applications, not only in the soap and detergent industry but also in medicine, and as extracting agents in chemistry and in environmental technology, especially in soil and groundwater remediation (Mulligan et al. 2001; Paria 2008).

In surfactant-enhanced remediation of contaminated soil, anionic and non-ionic surfactants are mostly used (Mulligan et al. 2001) especially to extract hydrophobic organic contaminants since they are strongly sorbed to soil. These pollutants are also known to be persistent in the environment and have a potential toxicity effect (Gascon et al. 2013). Among the non-ionic surfactants, which are better solubilizing agents than anionic and cationic ones because of their lower CMC value, their lower sorption into soil

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(Paria 2008) and their better cost-effectiveness (Alcantara et al. 2008; Wang and Keller 2008), Tween 80[®] is widely studied and employed (Gomez et al. 2010; Lopez-Vizcaino et al. 2012; Torres et al. 2012). Moreover, Tween 80[®] is getting more and more interesting since it can enhance also phytoremediation of contaminated soils (Gao et al. 2007). Furthermore, a more recent study shows the potential benefit of Tween 80[®] in contaminated soil bioremediation by enhancing the interaction between organic pollutants and bacteria (Zhang and Zhu 2012).

It seems to be very interesting to quantify the surfactant evolution during soil remediation process, in particular, its sorption into soil and its degradation during a bioremediation process or a water treatment of soil washing/flushing solution containing such surfactant. Its ability to be reused during a soil washing/flushing treatment can then be studied. Several analytical methods already exist to quantify general surfactants like gas chromatography method, gravimetric method, flow-injection methods and dynamic surface tension detection (Young and Synovec 1996). These methods are based on the liquid–liquid extraction and have low sensitivity and selectivity (Yang et al. 2000). Few techniques were developed to quantify non-ionic surfactants and especially Tween 80[®]. These are colorimetric measurements, cobalt thiocyanate active substances method and potassium picrate active substances method (Yeom et al. 1995), direct UV absorbance at a wavelength of 234 nm (Ko et al. 1998; Ko and Schlautman 1998; Zhu and Zhou 2008) and total organic carbon (TOC) (Ahn et al. 2008). These methods are not satisfying when studying solutions containing other organic molecules (like organic pollutants, other organic matter or oxidation by-products) that can absorb in the same range of wavelength and whose carbon is also taken into account in TOC values. The high performance liquid chromatography method (with derivatization of the stationary phase) was also experimented using a complexing agent such as phenyl isocyanate to produce a UV-active derivative upon reaction with the ethoxylate group. However, at low concentrations (below 0.6 g L⁻¹), the accuracy of measurement was unacceptable (Yeom et al. 1995). One other method was developed to quantify Tween 60 surfactant based on fluorescence enhancement of tetraphenylporphyrin (Yang et al. 2000). However, this method is not selective and efficient enough when it is applied for Tween 80[®] quantification. That is the reason why in this study, a new fluorimetric method to quantify Tween 80[®] is suggested. This is a quick, simple and highly sensitive method, which is more selective to Tween 80[®]. It is based on the enhancement of the fluorescence of 6-(*p*-toluidino)naphthalene-2-sulfonic acid (TNS) by forming Tween 80[®]–TNS micelles. According to the best of our knowledge, such a method has never been reported in the literature. TNS is a compound already used for cyclodextrin

(host/guest molecules) quantification by fluorescence (Hanna et al. 2005).

In the present study, surfactant fluorimetric quantification is carried out. It is based on the theory about micelle formation and fluorescence detection. Comparisons were performed between UV absorbance, TOC and fluorescence measurement methods of Tween 80[®] during electro-Fenton degradation in the presence of a hydrophobic organic contaminant representative from the polycyclic aromatic compound family, namely phenanthrene. The electro-Fenton process is an emerging advanced oxidation process that consists of a coupling between electrochemistry and Fenton process (Eq. 1) since the Fenton's reagent is electrochemically in situ generated (Oturán 2000).



The electro-Fenton process appears to be a good alternative technique compared to the classical chemical Fenton process. It permits to minimize the use of H₂O₂ reagent that is generated in situ and continuous regeneration of soluble iron (Fe²⁺, Fe³⁺ or iron oxides) from a catalytic amount added initially to the solution (Sirés et al. 2007) if needed.

Since the fluorescence measurements of this study are done in the humic acid-like region (Chen et al. 2003), it is also interesting to study the impact on fluorescence of soil organic matter extracted during a soil washing process in the presence of Tween 80[®]. Figure 1 schematizes the main objectives of the present study.

2 Materials and methods

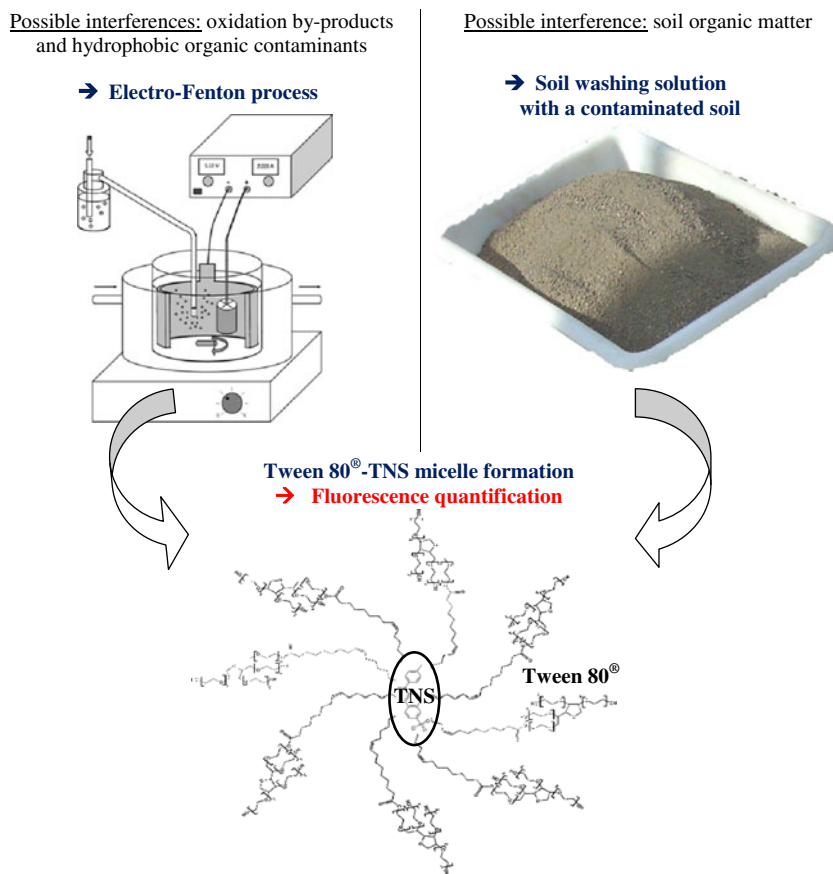
2.1 Chemicals

Tween 80[®] (polyoxyethylene (20) sorbitan monooleate; C₆₄H₂₄O₂₆; molar weight, 1,310 g mol⁻¹), TNS (6-(*p*-toluidino)naphthalene-2-sulfonic acid sodium), phenanthrene (>99.5 %), methanol (>99.9 %, analytical grade) and sodium sulphate were purchased from Aldrich (USA). Heptahydrated ferrous sulphate (FeSO₄·7H₂O), and sulfuric acid were supplied by Acros (USA) at analytical grade. In all experiments, deionised water from a Millipore Simplicity 185 (resistivity >18 MΩ cm) system was used.

2.2 Oxidation treatment

Electro-Fenton experiments were performed at room temperature (22±1 °C), in a 0.40-L undivided glass electrochemical reactor at current controlled conditions. The cathode was a 150-cm² carbon-felt piece (Carbone-Lorraine, France). The anode was a 5-cm-high cylindrical (i.d.=3 cm) Pt grid, which is centred in the cell and

Fig. 1 Schematic representation of possible interferences studied on Tween 80[®] quantification by fluorescence spectroscopy in the presence of TNS (6-(*p*-toluidino)naphthalene-2-sulfonic acid). Phenanthrene is added as representative organic pollutants present in contaminated soils. Electro-Fenton treatment of the Tween 80[®]-phenanthrene mixture was performed in order to study the interference of oxidation by-products. Soil washing experiment was accomplished with the aim of studying the impact of soil organic matter on fluorescence determination



surrounded by cathode covering the inner wall of the cell. An inert electrolyte (Na_2SO_4 at 0.150 M) was added to the medium. Since too much foam is formed during the bubbling system, the solutions containing Tween 80[®] were not saturated with O_2 . The electrochemical cell is monitored by a power supply HAMEG 7042-5 (Germany) and applied current was set to 1,000 mA. Solutions were stirred continuously by a magnetic stirrer. A heat exchanger system was used to keep the solution at constant room temperature by using freshwater. The pH of initial solutions was set at the optimal value of 3.0 (± 0.1) by the addition of aqueous H_2SO_4 (1 M) solution. In these experiments, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added at catalytic amount (0.2 mM). Tween 80[®] (750 mg L^{-1}) was used in the presence of phenanthrene in excess (17 mg L^{-1} initially).

2.3 Soil washing process

The polluted soil was sampled from a polycyclic aromatic hydrocarbon- and aliphatic hydrocarbon-contaminated site. Before its utilization, the soil was sieved under 2 mm and homogenized by a sample divider (Retsch, Germany). The soil has the following particle size distribution: clay ($< 2 \mu\text{m}$), 19.7 %; fine silt (2–20 μm), 23.3 %; coarse silt (20–50 μm), 7.5 %; fine sand (50–200 μm), 12.3 %; coarse sand (200–2000 μm), 37.1 %. It has the other following characteristics:

pH (water), 8.3; organic matter content, 4.71 %; total polycyclic aromatic hydrocarbon (16 compounds) content, 730 mg kg^{-1} ; aliphatic hydrocarbon (C10-C40) content, 850 mg kg^{-1} .

The soil washing experiment was performed in a 500-mL bottle at a soil/liquid ratio equal to 10 % (40 g/400 mL). A Tween 80[®] solution (10 g L^{-1}) was used, and the mixture was rotated in a Rotoshake RS12 (Gerhardt, Germany) at ten rotations per minute for 24 h. Then, the particles settled for 12 h, and the supernatant was filtered with a 0.7- μm glass microfiber filter (Whatman GF/F, England). The supernatant was diluted 15,000 times and analysed by excitation-emission matrix fluorescence spectroscopy, with or without adding TNS compound ($1.7 \times 10^{-6} \text{ M}$).

2.4 Analytical procedures

All absorbance determinations were carried out with a PerkinElmer (USA) Lambda 10 UV/vis spectrometer. Calibration curve of Tween 80[®] was performed at a wavelength of 245 nm that is found to be the optimal wavelength giving the maximal absorbance intensity.

The TOC values were determined by catalytic oxidation using a Shimadzu (Japan) V_{CSH} TOC analyser. Calibrations were performed by using the potassium hydrogen phthalate

solutions as standard. All samples were acidified to pH 2 with H_3PO_4 (25 %) to remove inorganic carbon. The injection volumes were 50 μL . All samples values are given with a coefficient of variance below to 2 %.

The Tween 80[®] concentration was proposed to be determined with fluorescence (Kontron Instruments SFM 25 spectrofluorometer, USA) by analysing the Tween 80[®]-TNS micelles formed with excitation and emission wavelengths of 318 and 428 nm, respectively. Since TNS is photosensitive, TNS and the diluted samples are therefore stored in dark conditions at room temperature (22 ± 1 °C).

With the aim of studying the possible interferences of phenanthrene, its oxidation by-products and soil organic matter, excitation–emission matrix fluorescence spectroscopy analyses were performed. The samples were first diluted with ultrapure water at the same dilution factor to be comparable. Fluorescence spectra of the sample were measured using a Shimadzu (Japan) RF-5301 PC spectrofluorophotometer. Spectra were collected with subsequent scanning of emission spectra from 220 to 550 nm by varying the excitation wavelength from 220 to 450 nm at 12-nm increments using high sensitivity. The software Panorama Fluorescence 2.1 was employed for handling excitation–emission matrix data.

The phenanthrene degradation was followed by reversed-phase high performance liquid chromatography coupled with a diode array detector from Dionex (USA). The detection was carried out at the wavelength of 249 nm. The mobile phase was a mixture of water/methanol (22:78 v/v) at the flow rate of 0.8 mL min^{-1} (isocratic mode), giving 6.9 min of retention time for phenanthrene. A reversed-phase C-18 end-capped column (Purospher[®], Merck, Germany), placed in an oven set at 40 °C, was used.

3 Results and discussion

3.1 Tween 80[®] quantification

3.1.1 Theory

It is assumed that the surfactant does not complex with (i.e. solubilize) the substrate TNS, except when the former is in the form of micelles and that complexation between the substrate and the micelle is in a 1:1 stoichiometric ratio. To establish a relation between fluorescence measured and the concentration of surfactant in solution, one can start from the partitioning model of the organic compounds between micelles and monomeric solution, which quantifies the surfactant solubilization. The micelle phase/aqueous phase

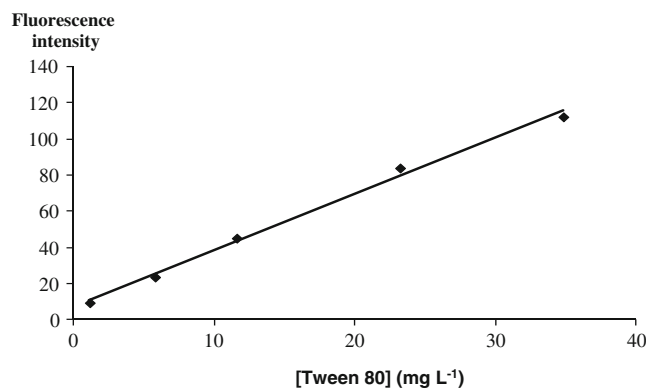


Fig. 2 Calibration curve of Tween 80[®] determined by fluorescence (excitation–emission, 318–428 nm) in the presence of TNS (6-(p-toluidino)naphthalene-2-sulfonic acid) (5×10^{-5} M). The suggested linear model between the fluorescence measurement of the Tween 80[®]-TNS micelles and Tween 80[®] concentration fits well ($R^2=0.995$) the experimental calibration curve ($F=3.1123 (\pm 0.12) \times [\text{Tween } 80^{\circledR}] + 7.1849 (\pm 2.33)$)

partition coefficient (K_{mw}) is based on the mole fraction ratios, i.e. the ratio of the mole fraction of the compound in the micellar pseudophase (X_{m}) to the mole fraction of the compound in the aqueous pseudophase (X_{a}). K_{mw} also can be defined as (Paria 2008):

$$K_{\text{mw}} = \frac{X_{\text{m}}}{X_{\text{a}}} = \frac{C_{\text{m}}}{C_{\text{a}}} = \frac{S - S_{\text{CMC}}}{(C_{\text{S}} - \text{CMC} + S - S_{\text{CMC}})(S_{\text{CMC}} V_{\text{w}})} \quad (2)$$

where C_{m} is the concentration of the hydrophobic solute in the micelle, C_{a} is its concentration in the aqueous phase, CMC is the critical micelle concentration, S is the apparent solubility of the organic compound at surfactant concentration C_{S} ($C_{\text{S}} > \text{CMC}$), S_{CMC} is the apparent solubility of the organic compound at the CMC, V_{w} is the molar volume of water, i.e. $1.805 \times 10^{-3} \text{ L mol}^{-1}$ at 22 °C.

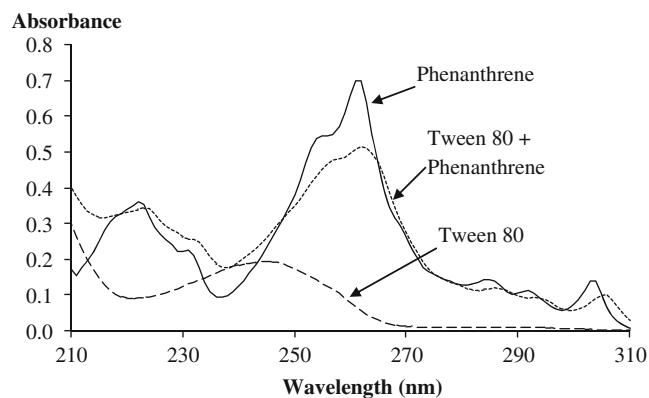


Fig. 3 UV absorbance spectra of Tween 80[®] (750 mg L^{-1}), phenanthrene (2 mg L^{-1}) and Tween 80[®] (750 mg L^{-1}) with phenanthrene (2 mg L^{-1}). An overlap between each spectrum is observed, which restrains the use of this method to quantify Tween 80[®]

Fig. 4 Excitation–emission matrix spectra of electro-Fenton treatment of phenanthrene (2 mg L⁻¹) with Tween 80[®] (750 mg L⁻¹) initial solution at initial treatment (a and b) and after 2 h of treatment (c and d) without TNS (a and c) and with TNS (b and d), where TNS is 6-(p-toluidino)naphthalene-2-sulfonic acid. [Fe²⁺]=0.2 mM, [Na₂SO₄]=0.150 M, V=400 mL, pH 3, Pt anode and I=1,000 mA. There is almost no impact of phenanthrene and oxidation by-products on fluorescence of the TNS–Tween 80[®] complex

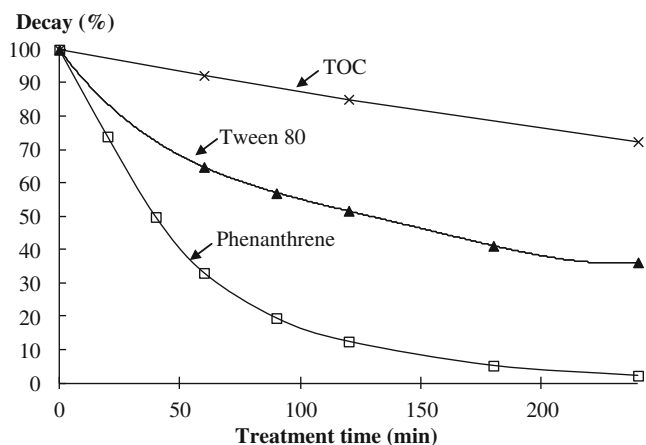
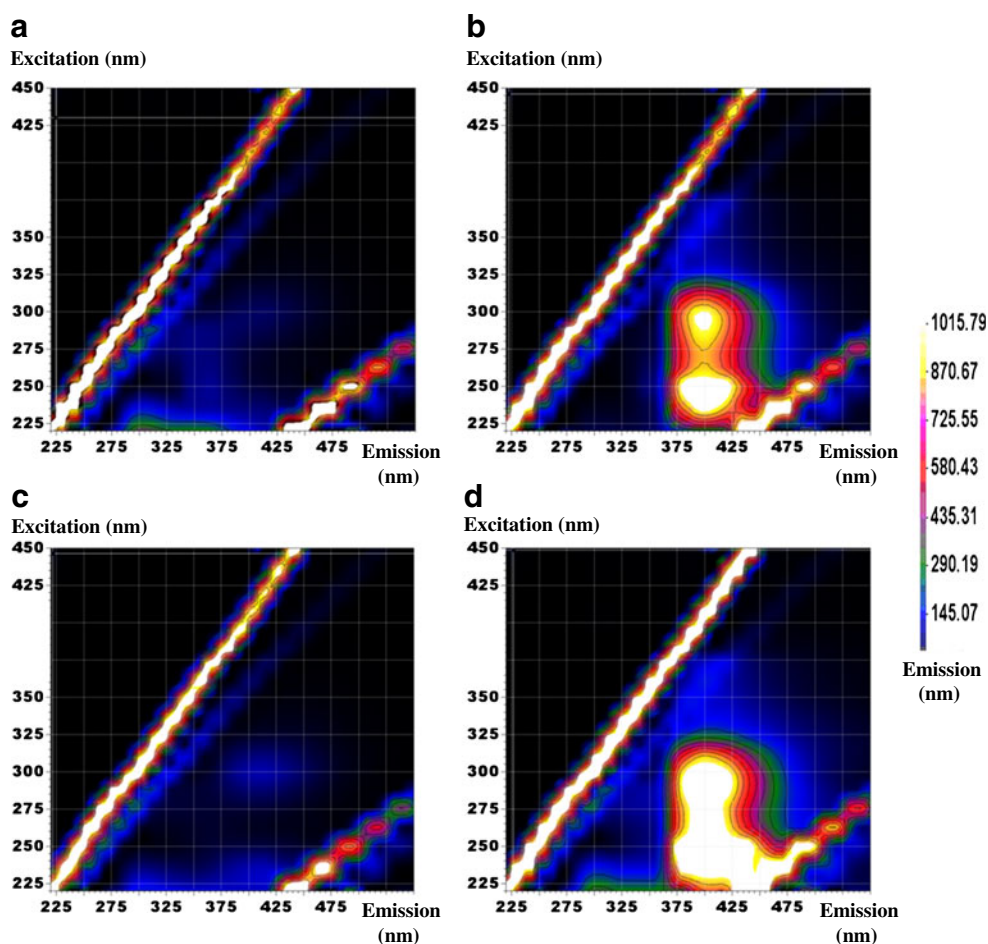


Fig. 5 TOC values (multiplication signs) and degradation kinetic of Tween 80[®] (750 mg L⁻¹) (filled triangles) and phenanthrene (17 mg L⁻¹) (empty squares) during electro-Fenton treatment. [Fe²⁺]=0.2 mM, [Na₂SO₄]=0.150 M, V=400 mL, pH 3, Pt anode and I=1,000 mA. Tween 80[®] decay determined by fluorescence method follows the pseudo-first-order kinetic model ($k_{app}=0.0056 \text{ min}^{-1}$; $R^2=0.971$), even in the presence of phenanthrene and oxidation by-products. TOC values take into account all the carbons present in the solution. Thus, all the Tween 80[®] and oxidation by-products are considered, which lead to a higher value compared to fluorescence data

As the concentrations of surfactant and TNS are low, the following Eqs. (3) and (4) can be written (Rouessac et al. 2004):

$$F = kI_0S \quad (3)$$

$$F_0 = kI_0S_{CMC} \quad (4)$$

where F and F_0 are the emission fluorescence referred to S and S_{CMC} , respectively; k is a constant (depending on the equipment and the compounds studied) and I_0 is the radiation intensity of excitation.

The fluorescence of the surfactant (Tween 80[®]) alone is considered to be equal to zero (data not shown).

By replacing relations (3) and (4) in Eq. (2), we can get a linear Eq. (5) between F and C_s :

$$F = a \times C_s + b \quad (5)$$

$$\text{with } a = \frac{F_0 V_W K_{mv} k I_0}{k I_0 - K_{mv} F_0 V_W} \text{ and } b = F_0 - \frac{F_0 V_W K_{mv} k I_0}{k I_0 - K_{mv} F_0 V_W} CMC$$

3.1.2 Calibration curve

Different excitation and emission wavelengths were investigated with the spectrofluorometer, and finally, the

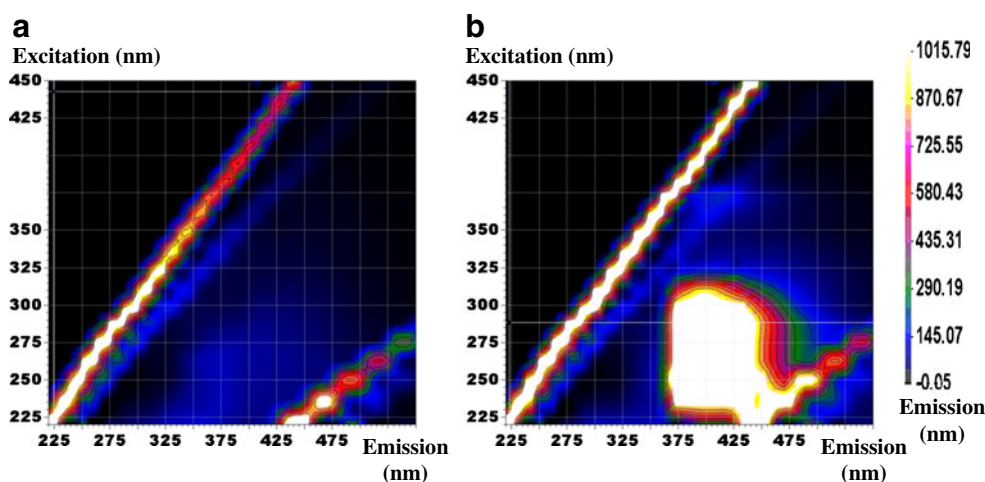


Fig. 6 Excitation–emission matrix spectra of soil washing solution by using Tween 80[®] (10 g L⁻¹) without the addition of TNS (*a*) and in the presence of TNS (1.7 × 10⁻⁶ M) (*b*), where TNS is 6-(*p*-toluidino)naphthalene-2-sulfonic acid. Organic matter content, 4.71 %; total polycyclic aromatic compounds (16), 730 mg kg⁻¹;

aliphatic hydrocarbons (C10–C40), 850 mg kg⁻¹; pH of soil washing solution, 8.0; soil/liquid ratio, 40 g/400 mL; contact time, 24 h. There is almost no impact (<4.0 %) of soil organic matter and organic pollutants initially present on real contaminated soil on fluorescence of the TNS–Tween 80[®] complex

highest sensibility was obtained at 318 nm for excitation and 428 nm for emission. Each sample was diluted in TNS (5 × 10⁻⁵ M). By plotting the emission fluorescence as a function of the Tween 80[®] concentration, a good *R*² value was reached (Fig. 2).

According to the good fitting (*R*²=0.995) of the calibration curve, this fluorimetric method was then used in the following experiments. As expected, the linear curve does not intercept the ordinate axis. According to the model, this value corresponds to the fluorescence of TNS alone and depends also on the CMC and other parameters described above. It is noticed that the calibration curve is also relevant for Tween 80[®] concentration below the CMC (15.7 mg L⁻¹; Rosas et al. 2011) in contrast to the assumption considered in the model. It was mentioned by several authors that only few surfactant monomers (below CMC) are able to slightly solubilize hydrophobic organic molecules (Edwards and Liu 1994; Deshpande et al. 1999).

The fluorimetric method provided, for Tween 80[®] analysis, a detection limit of 0.13 mM (0.10 mg C L⁻¹) and a quantification limit of 0.39 mM (0.30 mg C L⁻¹). Comparatively, the detection limit and the quantification limit were 3.18 mM (2.44 mg C L⁻¹) and 9.64 mM (7.40 mg C L⁻¹), respectively, for the UV absorption method and 0.27 mM (0.21 mg C L⁻¹) and 0.85 mM (0.65 mg C L⁻¹), respectively, for the TOC method. The detection limit and quantification limit were calculated according to Zhu et al. (2012) and Oliveri and Di Bella (2011), respectively. These results highlight clearly the advantage of the proposed fluorimetric method.

3.2 Comparison between different methods for Tween 80[®] quantification during oxidative degradation

Figure 3 illustrates the UV absorbance spectra of Tween 80[®], phenanthrene and Tween 80[®] in the presence of phenanthrene. It highlights the overlap between each spectrum, which restrains the use of this method to quantify Tween 80[®]. The same behaviour was observed during Tween 80[®] degradation alone, since some oxidation by-products absorb in the same range of wavelength (data not shown). For that reason, UV absorbance was not selected for measurement in electro-Fenton degradation.

Figure 4 represents excitation–emission matrix spectra of electro-Fenton treatment of phenanthrene (2 mg L⁻¹) with Tween 80[®] (750 mg L⁻¹) initial solution at first before treatment and then after 2 h of treatment with or without TNS. The more the colour is warm, the higher the fluorescence intensity is. It can still be considered that Tween 80[®] has no fluorescence without the presence of TNS and that the fluorescence of TNS alone is negligible. It is obvious that there is almost no impact of phenanthrene and oxidation by-products on fluorescence of the TNS–Tween 80[®] complex. Several other samples were analysed during all the treatments, and the percentages of fluorescence of phenanthrene and oxidation by-products were not more than 3.5 % compared to the fluorescence of the TNS–Tween 80[®] complex.

Figure 5 depicts the electro-Fenton degradation of Tween 80[®] in the presence of phenanthrene as a hydrophobic organic contaminant representative. Its oxidative degradation during electro-Fenton treatment was followed by TOC and fluorescence measurements. Since TOC values take into account all

the carbons present in the solution, all the Tween 80[®], phenanthrene and oxidation by-products are considered, leading to a higher value compared to fluorescence data. It is also important to note that the degradation of Tween 80[®] quantified by fluorescence can follow a pseudo-first-order kinetic model ($k_{app}=0.0056 \text{ min}^{-1}$; $R^2=0.971$), which is also notified with phenanthrene degradation ($k_{app}=0.016 \text{ min}^{-1}$; $R^2=0.994$) (Fig. 5). This kinetics model was largely observed in oxidative degradation studies in which hydroxyl radicals are involved (Brillas et al. 2009). This can also ensure the quality of the fluorescence measurements.

3.3 Interference of soil organic matter on fluorescence detection

It is demonstrated that humic acid-like substances show fluorescence intensity in the following region: excitation, 250–360 nm/emission, 380–480 nm (Chen et al. 2003). Since humic substances represent generally 70 to 90 % of the soil organic matter, their contribution to fluorescence signal should be assessed. Figure 6 depicts excitation–emission matrix spectra of soil washing solution from real contaminated soil. The fluorescence of soil washing solution without TNS was much lower than in the presence of TNS and represents only 4.0 % of the fluorescence of the Tween 80[®]–TNS mixture. By still considering that Tween 80[®] and TNS have a negligible fluorescence if they are not in the same solution, it can be assumed that soil organic matter does not interfere significantly on Tween 80[®]–TNS complex fluorescence in the operated diluted ratio. This is probably due to the high sensitivity of the method.

4 Conclusion

For this new Tween 80[®] fluorimetric analysis method, with an excitation–emission wavelength of 318–428 nm, the suggested linear model between fluorescence measurement of Tween 80[®]–TNS micelles and Tween 80[®] concentration fits well ($R^2=0.995$) the experimental calibration curve ($F=3.1123 (\pm 0.12) \times [\text{Tween } 80^{\text{®}}] + 7.1849 (\pm 2.33)$). This method has a detection limit of 0.13 mM and a quantification limit of 0.39 mM. The UV absorbance and TOC analysis have demonstrated much lower performance and selectivity than the fluorescence quantification proposed when it is aimed to follow the decay of Tween 80[®]. Such lower performance is due to interference with other organic compounds present in solution (oxidation by-products, phenanthrene). The degradation curve of Tween 80[®] during the electro-Fenton process determined by the fluorescence method follows the pseudo-first-order kinetic model ($k_{app}=0.0056 \text{ min}^{-1}$; $R^2=0.971$), even in the presence of hydrophobic organic compounds and

oxidation by-products. The fluorescence intensities of phenanthrene and by-products are insignificant in this range of concentration (<3.5 %). Soil organic matter has a negligible impact (<4.0 %) due to the operated diluted ratio and the high sensitivity of this method. These results validate the performance of the fluorescence quantification of Tween 80[®] surfactant by using TNS compound.

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References

- Ahn CK, Kim YM, Woo SH, Park JM (2008) Soil washing using various nonionic surfactants and their recovery by selective adsorption with activated carbon. *J Hazard Mater* 154:153–160. doi:10.1016/j.jhazmat.2007.10.006
- Alcantara MT, Gomez J, Pazos M, Sanroman MA (2008) Combined treatment of PAHs contaminated soils using the sequence extraction with surfactant-electrochemical degradation. *Chemosphere* 70:1438–1444. doi:10.1016/j.chemosphere.2007.08.070
- Brillas E, Sires I, Oturan MA (2009) Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry. *Chem Rev* 109:6570–6631. doi:10.1021/cr900136g
- Chen W, Westerhoff P, Leenheer JA, Booksh K (2003) Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolved organic matter. *Environ Sci Technol* 37:5701–5710. doi:10.1021/es034354c
- Deshpande S, Shiau BJ, Wade D, Sabatini DA, Harwell JH (1999) Surfactant selection for enhancing ex situ soil washing. *Water Res* 33:351–360. doi:10.1016/S0043-1354(98)00234-6
- Edwards DA, Liu Z (1994) Surfactant solubilization of organic compounds in soil/aqueous systems. *J Environ Eng* 120:5–22. doi:10.1061/(ASCE)0733-9372(1994)120:1(5)
- Gao YZ, Ling WT, Zhu LZ, Zhao BW, Zheng QS (2007) Surfactant-enhanced phytoremediation of soils contaminated with hydrophobic organic contaminants: potential and assessment. *Pedosphere* 17:409–418. doi:10.1016/S1002-0160(07)60050-2
- Gascon M, Morales E, Sunyer J, Vrijheid M (2013) Effects of persistent organic pollutants on the developing respiratory and immune systems: a systematic review. *Environ Int* 52:51–65. doi:10.1016/j.envint.2012.11.005
- Gomez J, Alcantara MT, Pazos M, Sanroman MA (2010) Remediation of polluted soil by a two-stage treatment system: desorption of phenanthrene in soil and electrochemical treatment to recover the extraction agent. *J Hazard Mater* 173:794–798. doi:10.1016/j.jhazmat.2009.08.103
- Hanna K, Chiron S, Oturan MA (2005) Coupling enhanced water solubilization with cyclodextrin to indirect electrochemical treatment for pentachlorophenol contaminated soil remediation. *Water Res* 39:2763–2773. doi:10.1016/j.watres.2005.04.057
- Ko SO, Schlautman MA (1998) Partitioning of hydrophobic organic compounds to sorbed surfactants. 2. Model development/predictions for surfactant-enhanced remediation applications. *Environ Sci Technol* 32:2776–2781. doi:10.1021/es971076f

- Ko SO, Schlautman MA, Carraway ER (1998) Partitioning of hydrophobic organic compounds to sorbed surfactants. 1. Experimental studies. *Environ Sci Technol* 32:2769–2775. doi:10.1021/es971075e
- Lopez-Vizcaino R, Saez C, Canizares P, Rodrigo MA (2012) The use of a combined process of surfactant-aided soil washing and coagulation for PAH-contaminated soils treatment. *Sep Purif Technol* 88:46–51. doi:10.1016/j.seppur.2011.11.038
- Mulligan CN, Yong RN, Gibbs BF (2001) Surfactant-enhanced remediation of contaminated soil: a review. *Eng Geol* 60:371–380. doi:10.1016/S0013-7952(00)00117-4
- Oliveri IP, Di Bella S (2011) Highly sensitive fluorescent probe for detection of alkaloids. *Tetrahedron* 67:9446–9449. doi:10.1016/j.tet.2011.09.100
- Oturan MA (2000) An ecologically effective water treatment technique using electrochemically generated hydroxyl radicals for in situ destruction of organic pollutants: application to herbicide 2, 4-D. *J Appl Electrochem* 30:475–482. doi:10.1023/A:1003994428571
- Paria S (2008) Surfactant-enhanced remediation of organic contaminated soil and water. *Adv Colloid Interface Sci* 138:24–58. doi:10.1016/j.cis.2007.11.001
- Rosas JM, Vicente F, Santos A, Romero A (2011) Enhancing p-cresol extraction from soil. *Chemosphere* 84:260–264. doi:10.1016/j.chemosphere.2011.03.071
- Rosen MJ (2004) *Surfactants and interfacial phenomena*, 3rd edn. Wiley, New York
- Rouessac F, Rouessac A, Cruché D (2004) *Analyse chimique—Méthodes et techniques instrumentales modernes*. Dunod, Paris
- Sirés I, Garrido JA, Rodríguez RM, Brillas E, Oturan N, Oturan MA (2007) Catalytic behavior of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ system in the electro-Fenton degradation of the antimicrobial chlorophene. *Appl Catal B Environ* 72:382–394. doi:10.1016/j.apcatb.2006.11.016
- Torres LG, Lopez RB, Beltran M (2012) Removal of As, Cd, Cu, Ni, Pb, and Zn from a highly contaminated industrial soil using surfactant enhanced soil washing. *Phys Chem Earth* 37–39:30–36. doi:10.1016/j.pce.2011.02.003
- Wang P, Keller AA (2008) Particle-size dependent sorption and desorption of pesticides within a water-soil-nonionic surfactant system. *Environ Sci Technol* 42:3381–3387. doi:10.1021/es702732g
- Yang RH, Wang KM, Xiao D, Yang XH, Li HM (2000) A selective optical chemical sensor for the determination of Tween-60 based on fluorescence enhancement of tetraphenylporphyrin. *Anal Chim Acta* 404:205–211. doi:10.1016/S0003-2670(99)00715-1
- Yeom IT, Ghosh MM, Cox CD, Robinson KG (1995) Micellar solubilization of polynuclear aromatic hydrocarbons in coal tar-contaminated soils. *Environ Sci Technol* 29:3015–3021. doi:10.1021/es00012a019
- Young TE, Synovec RE (1996) Enhanced surfactant determination by ion-pair formation using flow-injection analysis and dynamic surface tension detection. *Talanta* 43:889–899. doi:10.1016/0039-9140(95)01762-3
- Zhang D, Zhu L (2012) Effects of Tween 80 on the removal, sorption and biodegradation of pyrene by *Klebsiella oxytoca* PYR-1. *Environ Pollut* 164:169–174. doi:10.1016/j.envpol.2012.01.036
- Zhu L, Zhou W (2008) Partitioning of polycyclic aromatic hydrocarbons to solid-sorbed nonionic surfactants. *Environ Pollut* 152:130–137. doi:10.1016/j.envpol.2007.05.001
- Zhu H, Fan J, Lu J, Hu M, Cao J, Wang J, Li H, Liu X, Peng X (2012) Optical Cu^{2+} probe bearing an 8-hydroxyquinoline subunit: high sensitivity and large fluorescence enhancement. *Talanta* 93:55–61. doi:10.1016/j.talanta.2012.01.024