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A novel flow-through fluorescence optosensor for the sensitive determination of tetracycline

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ABSTRACT

A flow-through fluorescence optosensor with Sephadex G-50 microbeads as solid support is developed for the sensitive determination of tetracycline (TC). The fluorescent TC derivative encapsulated in CTAB micelle structures is retained onto the surface of the microbeads packed into a fluorescent flow cell in a flow system, followed by measurement of the native fluorescence of the TC derivative on the bead surface. The retained TC derivative is easily stripped off with DI water from the bead surface by breaking-down the micelle structure. This offers a convenient and effective way for the regeneration of the used solid support with DI water as a carrier. Under the optimal conditions, a linear calibration graph is obtained within a range of 3–500 $\mu g\,L^{-1}$, along with a detection limit of 1.0 $\mu g\,L^{-1}$. The present solid surface fluorescence optosensor provides a 22-fold improvement on the detection sensitivity for TC in comparison with that derived by fluorescence detection in aqueous medium. The feasibility of this flow-through fluorescence optosensor is evaluated by analyzing TC in a commercial drug tablet and surface water samples.

1. Introduction

Tetracyclines (TCs) are a group of broad spectrum antibiotics showing activity against Gram-positive/Gram-negative bacteria [1] and are widely used in the prevention and treatment of infectious diseases or as food additives for growth promotion in animal husbandry [2]. Tetracycline residues induced by the widespread usage are often encountered in animal-derived food products, such as meat, milk, honey etc., ground water or surface water contaminated by animal manure or sanitary wastewater, and now becoming a serious problem since it might cause toxicity or allergic reactions to some hypersensitive individuals [3]. In addition, long-term consumption of foodstuffs containing TC residues might result in a risk of spreading of drug-resistant microorganisms [4].

TCs are released to the aquatic environment via different pathways, and have been found in surface waters in China [5]. Therefore, it is of great importance to develop sensitive and accurate quantification procedures to determine the TC content in environmental water samples for the aim of protecting human health. Up to now, various analytical methodologies including immunoassays [6,7], fluorimetry [8,9], chemiluminescence [10,11], HPLC [3,12], and CE [13,14] etc. have been successfully used for the quantification of TCs. Solid-surface fluorescence (SSF) is a kind of detection technique based on the retention or spotting of the analyte on an appropriate solid support, and then perform direct spectrometric measurements on the surface of solid phase [15]. In comparison to conventional fluorescence strategies in aqueous medium, a significant improvement on the detection sensitivity is usually obtained in SSF protocols due to the improved emission efficiency of fluorescence molecules on the solid surface, resulting from the isolating and collision-restricting of the excited molecules [16]. The generation of flow injection analysis (FIA) offers an excellent platform for the SSF measurement and a "flow-through optosensor" based on the hyphenation of FIA and SSF has been successfully developed by Ruzicka and Hansen [17]. By packing solid materials inside the flow cell, successive monitoring the spectral changes of the surface of solid materials could be obtained and regeneration of the solid surface is easily achieved via the flexible and powerful fluid manipulations of FIA. Most importantly, the continuous flow of sample solution through the solid phase packed in the flow cell contributes substantially to the retention of the species of interest or analytes on the surface of the solid materials and thus leads to an increase of the detectable analyte in a confined region, which eventually results in a pronounced improvement on the detection sensitivity [18,19].

Though the main applications of flow-through optosensor were focused firstly toward inorganic analytes [20], recent research efforts indicated that the flow-through optosensors could be readily applied in pharmaceutical analysis as a very promising tools with remarkable analytical features, i.e., improved sensitivity and selectivity compared with the respective conventional spectro-

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scopic procedures [18,21]. In this present work, a flow-through fluorescence optosensor for the sensitive determination of tetracycline is developed. Sephadex G-50 microbeads are used as the solid support and the fluorescent TC derivative, i.e., CTAB micelle structures, is on-line preconcentrated onto the surface of the solid material in a sequential injection flow system. The native fluorescence of the derivative on the solid surface is measured for the purpose of quantification. The regeneration of the microbeads is realized by stripping of the retained TC derivatives from the solid surface by DI water carrier.

2. Experimental

2.1. Chemicals

A 100 mg L^{-1} of tetracycline stock solution is prepared by dissolving appropriate amount of tetracycline hydrochloride (Amresco, USA) in DI water and stored under dark at 4 °C for future use.

A microbead suspension is prepared by putting 10 mg of Sephadex G-50 beads (50–150 μm, Pharmacia, USA) into 400 μL of DI water and stood for overnight.

A 3 mmol L^{-1} solution of cetyltrimethylammonium bromide (CTAB, Beijing Aoboxing Biotech Co., Ltd, Beijing, China) is prepared in 0.05 mol L^{-1} NaOH.

Other chemicals used include Triton X-100, Tween 80, sodium dodecyl benzene sulfonate (SDBS), sodium dodecylsulfate (SDS), hydrochloric acid and ethylene diamine tetraacetic acid (EDTA) are all purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and at least of analytical reagent grade. DI water of 18 MΩ cm is used throughout.

2.2. Instrumentation

A FIAlab-3000 sequential injection system (FIAlab Instruments Inc., Medina, WA, USA) with a 2.5 mL syringe pump (SP) and an 8-port selection valve are employed for sample introduction and fluidic delivery. All the external channels are made of narrow-bore PTFE tubing (0.75 mm inner diameter) connected to the selection valve with PEEK nuts/ferrules (Upchurch Scientific, Oak Harbor, WA, USA).

An F-7000 Fluorescence Spectrophotometer (Hitachi High-Tech Co., Japan) equipped with a Hellma Model 176.751-QS flow cell of 100 μL internal volume and a 0.5 cm quartz cuvette is used for the flow-through and batch fluorescence measurement.

Both the fluorescence spectrophotometer and the sequential injection system are controlled by a single computer in order to synchronize the sample pre-treating process and the fluorescence measurement.

Scanning electron micrographs (SEM) of Sephadex are obtained by using a SSX-55 scanning electron microscope (Shimadzu, Japan). FT-IR spectra are recorded on a Nicolet 6700 FT-IR Spectrometer (Thermo Fisher Scientific Inc., USA) adopting an ATR mode.

2.3. Samples and sample pretreatment

The commercial TC tablets are carefully ground for homogenization. 0.5590 g of the homogenized powder is transferred into a glass beaker and dissolved with 150 mL HCl (0.01 mol L^{-1}). The obtained solution is then filtered through a 0.45 μm hybrid fiber membrane filter and the filtrate is diluted to 1000 mL for analysis.

Surface water samples are collected from Nan-Hu Lake and Hun-He River (Shenyang, China). The water samples are first filtered through a 0.45 μm membrane filter, afterwards, 0.02 mol L^{-1} EDTA is added in the filtrate to prevent the complexation of TC with divalent cations [22].

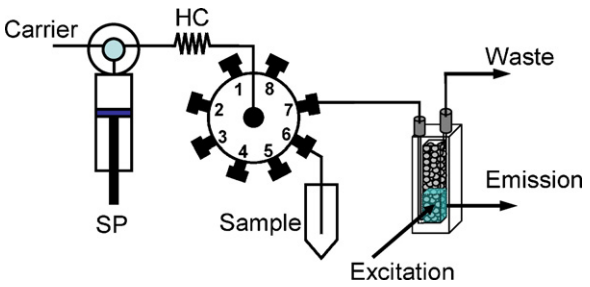

Fig. 1. Schematic diagram of the flow-through optosensor for the determination of tetracycline. SP: syringe pump; HC: holding coil.

10 μL of sample solution is mixed with 9.99 mL of 3 mol L^{-1} CTAB solution in a beaker. The mixture is then heated in a boiling-water bath for 40 min to facilitate the hydrolysis of TC under alkali medium. After cooling down, the hydrolyzed solution is used for analysis.

2.4. General procedure

2.4.1. Batch mode

20 mg of Sephadex microbeads are mixed with 3 mL hydrolyzed solution and incubated at room temperature for 40 min. After removal of the liquid phase, the microbeads are transferred to a quartz cuvette for solid-phase surface fluorescence measurement. The fluorescence intensity is recorded at 410 nm by excitation at 340 nm. Both the excitation and emission slit are set at 5 nm.

2.4.2. Flow-through mode

400 μL of the Sephadex G-50 beads suspension are first introduced into the Hellma flow cell (100 μL internal volume). The outlet of the cell is blocked with small amount of glass wool to form a packed microcolumn. The flow cell is then incorporated into the flow system as illustrated in Fig. 1

500 μL of carrier (DI water) is first aspirated into the syringe pump, 1000 μL of sample solution is aspirated from port 6 into the holding coil subsequently at a flow rate of 100 μL s^{-1}. The sample solution is then dispensed via port 7 to flow through the flow cell at 5 μL s^{-1} to facilitate the retention of TC derivative onto the surface of the solid support. The fluorescence of the solid support is recorded with $\lambda_{ex}/\lambda_{em}$ = 340 nm/410 nm. Afterwards, the retained TC derivative is stripped from the solid surface by using DI water as a carrier.

For the purpose of comparison, control measurements are performed following exactly the same procedure as described herein except for that no microbeads packing in the flow cell.

3. Results and discussion

3.1. Hydrolysis of tetracycline

The intrinsic fluorescence of TC is too weak to facilitate direct fluorescence detection, while the hydrolyzed derivative of TC under alkali medium is found to be strongly fluorescent. Therefore, a large number of fluorescent protocols for the quantification of TC have been developed based on the monitoring of the fluorescence behaviors of TC derivatives [15,23]. In the present study, an alkali hydrolysis procedure is adopted to obtain the fluorescent TC derivative in NaOH solution. The effect of NaOH concentration on the fluorescence intensity of the derivative is investigated within a range 0.03–0.07 mol L^{-1}. The experimental results indicated an increase of the fluorescence intensity with the increase of NaOH concentration up to 0.05 mol L^{-1}, and thereafter a decline is observed when even higher NaOH concentrations are employed. In

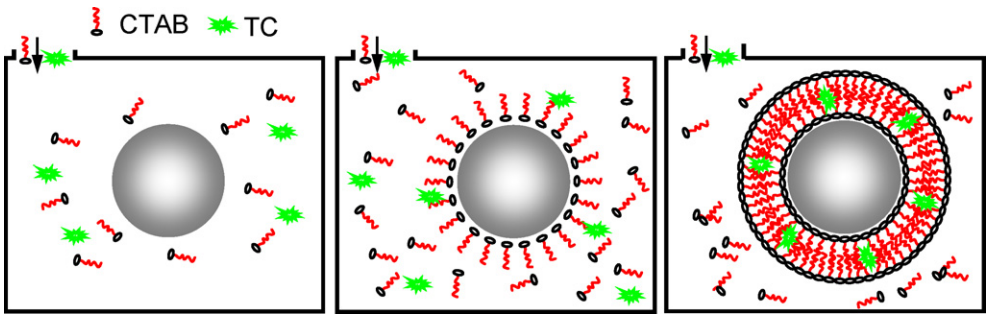

Fig. 2. Illustration of the retention of tetracycline derivative on the solid support.

the present study, a 0.05 mol L^{-1} NaOH is suitable for the purpose of performing tetracycline hydrolysis and generating fluorescent derivative.

3.2. CTAB micelle of TC derivative and its adsorption on Sephadex G-50

Surfactant is a kind of fluorescence sensitizer widely adopted in fluorescence detection [24]. The surfactant micelles formed over critical micelle concentration are well organized structure, offering a favorable circumstance for the fluorescent analyte encapsulated inside to reduce the vibrational motions and increase the rigidity, which eventually led to the improvement on fluorescence efficiency. The enhancement effect of various kinds of surfactants including nonionic surfactants (Triton X-100, Tween 80), anionic surfactants (SDBS, SDS) and cationic surfactant CTAB for TC derivative have been investigated and the results indicated that an effective fluorescence enhancement could generally be obtained by using CTAB as the sensitizer.

It has been well demonstrated that aggregates of hemimicelles and admicelles are usually formed when the adsorption of ionic surfactants onto the surface of the solid substrates takes place [25–28]. Hemimicelles is a monolayer of surfactants adsorbed head-down on the oppositely charged surface of the solid substrates, while the hydrocarbon tail-groups protruding into the solution with strong lateral interaction among themselves. These hydrophobic interactions among hydrocarbon chains of the surfactant molecules eventually lead to the formation of admicelles as bilayers [29].

Sephadex G-50 is a negatively charged resin under certain circumstances [30,31]. In the present study, when the hydrolyzed tetracycline derivative flowing through the Sephadex G-50 microcolumn inside the flow cell, the head of CTAB is prone to adsorb on the surface of the Sephadex G-50 microbeads via electrostatic

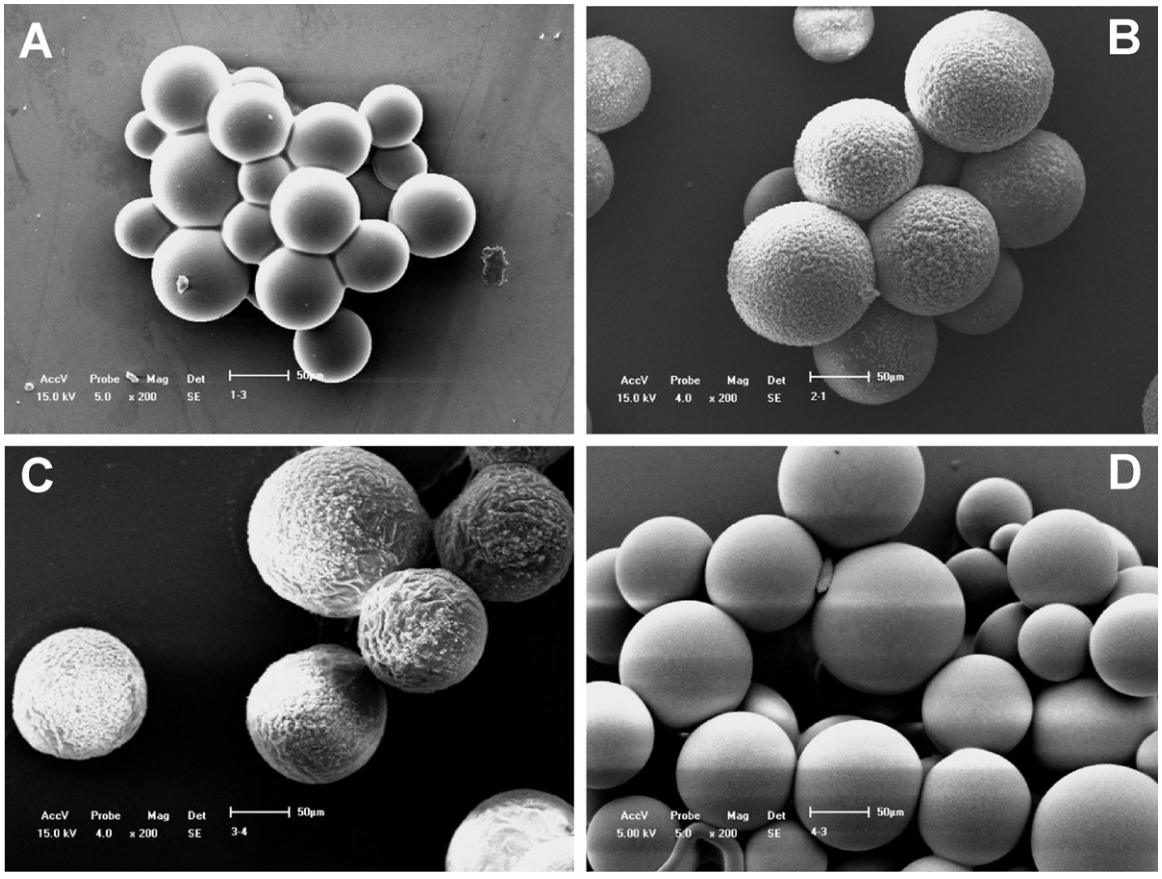

Fig. 3. SEM images of the native Sehpadex G-50 microbeads (A), Sephadex G-50 micorbeads after adsorption of CTAB (B), Sephadex G-50 micorbeads after adsorption of CTAB together with tetracycline (C), Sephadex G-50 micorbeads after adsorption and elution (regeneration) with DI water as eluent (D).

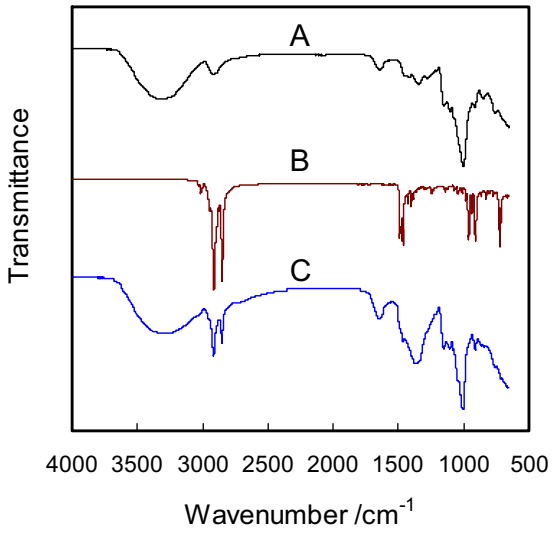

Fig. 4. FT-IR spectra of Sephadex G-50 microbeads (A), CTAB (B), and Sephadex G-50 microbeads after CTAB retention (C).

interaction as illustrated in Fig. 2. When increasing the amount of CTAB, the formation of hemimicelles is initiated with the head groups toward the surface and at the same time the TC derivative is retained by the hydrocarbon tail of CTAB via hydrophobic interaction [25]. Thereafter, the lateral hydrophobic attraction and the head group repulsion among CTAB molecules led to the orientation of newly adsorbed molecules to form admicelle, and the tail groups are prone to form a hydrophobic core to provide sites capable of encapsulating the TC derivatives [32]. These well organized and ordered hemimicelle and admicelle structures are helpful to improve the rigidity of the TC derivative molecules and reduce its vibrational motions [33], resulting in the enhancement of the emission efficiency of TC derivative. Most importantly, the increased amount of CTAB micelle structures offered a favorable microenvironment for the retention of the TC derivative and resulted in its preconcentration on the surface of the solid support, which eventually led to a substantially enhanced fluorescence signal.

Fig. 3 showed SEM images of the Sephadex G-50 microbeads at different operation conditions. It could be observed that the surface of the native Sephadex G-50 microbeads is very smooth (Fig. 3A), while it becomes rough after the adsorption of CTAB or CTAB micelles encapsulated TC derivative took place (Fig. 3B–C). The FT-IR spectra (Fig. 4) indicated that the characteristic absorption bands of CTAB, i.e., the asymmetric and symmetric stretching vibration of CH_2 at 2918 cm^{-1} and 2850 cm^{-1}, are clearly observed in the spectrum of Sephadex G-50 after adsorption. These well demonstrated that CTAB is efficiently retained on the surface of the solid support.

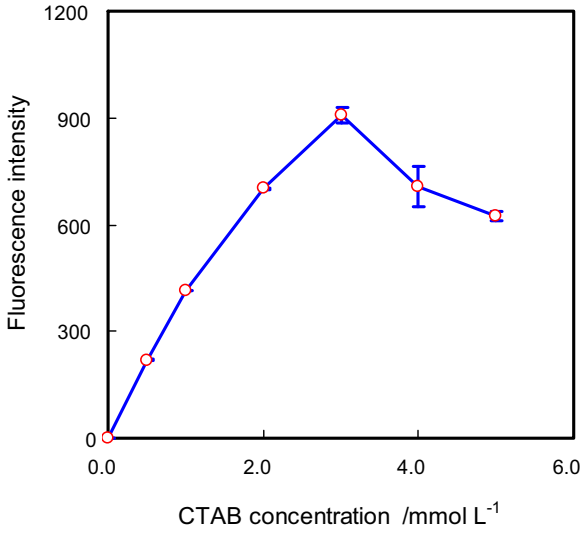

Fig. 5. The effect of CTAB concentration on the fluorescence intensity. TC: 50 μg L^{-1}, 1000 μL; Loading flow rate: 5 μL s^{-1}; eluent: 1200 μL DI water; elution flow rate: 10 μL s^{-1}.

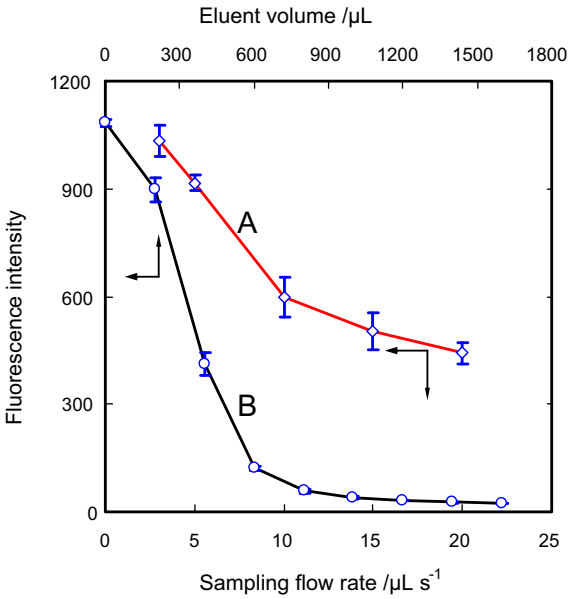

Fig. 6. The effect of sample loading flow rate and the volume of eluent (DI water) on the fluorescence intensity. TC: 50 μg L^{-1} 1000 μL; eluent: DI water; elution flow rate: 10 μL s^{-1}.

The retention efficiencies of different concentrations of TC on the surface of the Sephadex G-50 microbeads are investigated and the experimental data are fit with the Langmuir model [34]. Under the optimal conditions, the maximum retention capacity is derived to be 125 mg g^{-1}.

Fig. 5 showed the effect of the CTAB concentration on the fluorescence intensity. The results indicated that no TC derivative is retained on the solid support in the absence of CTAB. The fluorescence intensity increased with the CTAB concentration up to 3 mmol L^{-1}, probably due to the fact that more TC derivative is retained or encapsulated by the CTAB micelle structures. When the CTAB concentration exceeds 3 mmol L^{-1}, a decline of the fluorescence is observed. This might be attributed to the fact that CTAB molecules started to form micelles in the bulk aqueous solution at high CTAB concentration and the formed micelles in aqueous phase caused redistribution of the TC derivatives [35], which led to a decline of TC derivative concentration on the surface of the solid substrate. Therefore, a CTAB concentration of 3 mmol L^{-1} is suitable for the present system.

Table 1
The characteristic performance data of the present flow-through fluorescence optosensor for the determination of TC.

Sample volume	1000 μL
Enrichment factor	22
Precision (RSD, $n = 11$)	3.8%
Detection limit (3σ, $n = 11$)	1.0 μg L^{-1}
Linear range	3–500 μg L^{-1}
Regression equation	$I_f = 13.09C_{TC}$(μg L^{-1}) + 177.33

Table 2
Determination of TC in a drug tablet and surface water samples ($n = 3$).

	Given (mg/tablet)	Found (mg/tablet)	Spiked	Recov.(%)
Tablet	0.25	0.23 ± 0.01	0.20 mg	97.5 ± 2.1
Nan-Hu lake water	–	–	10 μg L^{-1}	98.6 ± 5.7
Hun-He river water	–	–	10 μg L^{-1}	94.8 ± 5.5

3.3. Effect of the flow variables

The effect of sample loading flow rate on the adsorption of TC is investigated within a range of 3–20 μL s^{-1}, the results are showed in Fig. 6A. It illustrated that the readout is indeed decreased with the increase of the flow rate within the range investigated. As discussed previously, the retention of TC derivative is realized via the formation of CTAB micelles, thus a certain period of time is needed to adsorb sufficient CTAB molecules on the surface of the microbeads for the formation of the necessary micelle structures, thus a lower flow rate is certainly favorable for the accumulation of CTAB on the solid support. In practical applications, for the comprehensive consideration of the analysis time, i.e., sample throughput, and the detection sensitivity, a sample loading flow rate of 5 μL s^{-1} is appropriate for the ensuing experiments.

Although organic solvents are able to disrupt the surfactant aggregates, they are not employed as eluent in the present study considering their significant effect on the deformation of the Sephadex G-50 microbeads. This will definitely destroy the illuminating area for the fluorescence detection and eventually deteriorate the reproducibility of the system. As electrostatic interaction is the main driving force for the retention of CTAB molecules and the adsorption took place in an alkali medium, the strip of the retained TC derivative could be facilitated by changing the pH value or regulating the CTAB concentration on the solid surface to disrupt the micelle structures. Therefore, the stripping efficiency by using DI water as eluent is investigated and the results suggested that satisfactory elution could be achieved. Fig. 3D showed the SEM image of the microbeads after elution. A smooth surface similar to that of the native Sephadex G-50 microbeads is observed, indicating the entire removal of the micelle structure from the surface of the solid support. The volume of elutent is further studied in a range of 0–1800 μL and the results are given in Fig. 6B. It is obvious that an eluent volume of 1200 μL is sufficient for the regeneration of the solid support in the present study.

3.4. The effects of foreign species

In order to evaluate the practical applicability of the present procedure for the determination of TC in real samples, the potential interfering effects of some species frequently encountered in real-world samples are investigated by analyzing a standard solution containing 50 μg L^{-1} TC and various amounts of coexisting species. The experiments indicated that within a ±5% error range, 50 mg L^{-1} of K^+, Cl^-, PO_4^{3-}, glucose and BSA; 25 mg L^{-1} of SO_4^{2-}; 10 mg L^{-1} of Mg^{2+}, Ca^{2+} and Zn^{2+}; 5 mg L^{-1} of Cu^{2+} and Al^{3+} do not interfere with the determination. For the drug tablet and the surface water samples, the contents of the above mentioned coexisting species are usually lower than the tolerant concentration levels (or appropriate dilution of the sample solution can be made), therefore the present protocol can be readily exploited directly.

3.5. Analytical performance and validation of the optosensor

The characteristic analytical performance data of the flow-through optosensor for the determination of TC are summarized in Table 1. A calibration curve is obtained within a range of 3–500 μg L^{-1}, along with a detection limit of 1.0 μg L^{-1}. Fig. 7 illustrated the recorded fluorescence spectra of tetracycline at the same concentration in aqueous solution and on the solid surface. It is worth mentioning that this solid surface fluorescence optosensor provides a 22-fold improvement on the detection sensitivity for TC in comparison with that derived by using fluorimetric protocol with detection in aqueous medium.

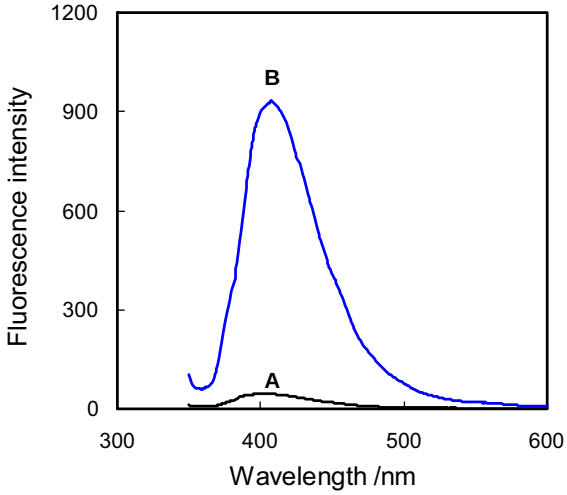

Fig. 7. The recorded fluorescence spectra of tetracycline in aqueous solution (A) and on the solid surface (B). TC: 50 μg L^{-1}.

The experiments also showed that no obvious decline of fluorescence intensity to 50 μg L^{-1} of tetracycline on the solid phase was observed after more than 100 runs. This means that the lifetime of this flow-through optosensor is suitable for long-term operation.

The practical applicability of this flow-through optosensor is demonstrated by analyzing TC contents in a drug tablet. Table 2 illustrates that a reasonable agreement is achieved between the given value and the found content. In addition, spiking recoveries are performed for surface water samples. It can be seen from Table 2 that no TC is found in these surface water samples but favorable spiking recoveries are achieved.

4. Conclusions

A simple flow-through solid surface fluorescence protocol for the sensitive determination of tetracycline is developed. It has been demonstrated that solid surface fluorescence is an effective approach for the improvement of detection sensitivity for drugs or pharmaceuticals, in comparison with the conventional fluorescence strategy operated in aqueous medium. In addition, micelle structures formed on the surface of the solid support facilitates the preconcentration of the drug target of interest.

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