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A tetracycline-selective fluorescent biosensor using anthranilic acid immobilized on a glutaraldehyde-coated eggshell membrane†

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Rapid and efficient detection of tetracycline (Tc) by immobilizing a fluorescent probe on a chemical sensor or biosensor is of great importance to scientific practice. In this study, an eggshell membrane (ESM) was modified for the quantification of Tc by immobilizing anthranilic acid (AA) on the membrane with glutaraldehyde as a cross-linking agent. The fluorescence emission peak of the ESM was effectively covered by AA as a fluorophore, and then the fluorescent intensity of AA could be efficiently quenched in the presence of Tc by the fluorescence inner filter effect (FIFE). The immobilization conditions (*e.g.* AA concentration and glutaraldehyde concentration) were optimized. The fluorescence sensor had a linear working range of 10 ng mL^{-1} to 1 μg mL^{-1}, while the detection limit for Tc was 10 ng mL^{-1}. The proposed biosensor exhibited low detection limits, high sensitivity and selectivity, as well as excellent stability and regeneration. This biosensor was also successfully applied for the determination of Tc in food samples.

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1. Introduction

Tetracycline (Tc) is a class of wide-spectrum antibiotics used against microorganism infections. Because of its broad antibacterial spectrum and high effectiveness, Tc has been used in a wide variety of food-producing animals.[1,2] However, the extensive use of Tc has resulted in serious problems regarding infections and high bacterial resistance,[3] while the residues of Tc remaining in milk or meat could directly cause allergic reactions in some hypersensitive individuals.[4]

In recent years, significant efforts have been made towards developing materials and methods for the detection of Tc, such as high performance liquid chromatography (HPLC),[5] capillary electrophoresis,[6] terahertz spectroscopy[7] and fluorescence methods.[2] Moreover, due to easy sample preparation and high sensitivity, fluorescence methods have received considerable attention and been broadly applied in analysis.[8–10] Additionally, fluorescent probes used to detect Tc mainly include quantum dots like CdTe,[11] Mn-doped ZnS,[12] CdTe–SiO_2-MIPs[13] and metal-organic coordination polymers like europium ion (Eu^{3+})-based fluorescence detection.[14–17] These fluorescence methods are sensitive and highly specific, but certain drawbacks still exist. For example, quantum dots and polymers are expensive and complicated to synthesize. In order to achieve cheap and rapid determination for Tc, we found that Tc can efficiently quench the fluorescence intensity of anthranilic acid (AA) due to the fluorescence inner filter effect, but the high detection limit (7.8×10^{-7} mol L^{-1}) makes this method unsuitable for trace-detection of Tc. In order to improve the detection sensitivity, we take the application of solid surface fluorescence into account. In contrast to the solution-phase fluorescence measurement, solid membrane-based sensors have more favorable advantages in practice. For example, membrane-based sensors can concentrate analytes,[18] fix reactants, achieve real-time and continuous measurements, as well as be regenerated by a simple washing procedure.[19] It has been reported that some biomaterials, such as bamboo inner shell membranes,[20] silk,[21] collagen,[22] and eggshell membranes,[23] were applied as platforms for fabrication of biosensors.

The eggshell membrane (ESM) is a natural biomembrane with an interconnected fibrous structure. The membrane has exhibited great potential as a new biomaterial for the determination of Tc.[24] The ESM has long been treated as a waste material, but has gained increased attention due to its intrinsic characteristics, such as abundant functional groups for chemical modification, high surface area for adsorption, good stability in aqueous media, and non-toxicity.[24–26] Thus the ESM could be employed as a platform for immobilization of fluorescent probes with the assistance of cross-linking agents. Many researchers have proven that the ESM could be successfully applied as a sorbent to remove heavy metal ions such as Au(I, III),[27] Cr(II), Cd(II), Cu(II)[28] and Hg(II)[29] or organic dyes like malachite green,[30] eosin B[31] and Congo red.[32] The ability of the

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ESM to capture heavy metal ions or organic dyes demonstrates the coordination interaction and covalent bonding between the ESM and adsorbates. On the other hand, the ESM can also be employed as a biosensor, for example, the immobilization of glucose oxidase and DNAzyme on ESMs for determining glucose concentration and hydrogen peroxide, respectively, has been studied.[33,34] Thus it can be seen that the biotemplating abilities of ESMs have been widely applied in enzyme immobilization with the purpose of achieving catalysis. However, immobilizing fluorescent probes on ESMs for direct detection of Tc with high sensitivity has not been reported.

In the present study, as a fluorescent probe, AA was robustly immobilized on a glutaraldehyde-coated ESM for efficient and recyclable detection of tetracycline. Glutaraldehyde can act as a cross-linking agent, while its aldehyde groups endow it with a specific affinity for common groups such as amino groups and hydroxyl groups, thus synergistically constructing a stable linkage between ESM fibers and AA. Moreover, Tc could greatly quench the fluorescence intensity of AA, as a result the concentration of Tc can be detected by calculating the fluorescence difference (ΔF). Furthermore, we also examined the linear working range in Tc determination as well as the stability and regeneration of the biosensor in continuous detection. To the best of our knowledge, this is the first presentation of immobilizing AA on the surface of an ESM for efficient fluorescence detection of Tc, and this biosensor could be applied to the rapid and sensitive determination of Tc existing in foods and the environment.

2. Materials and methods

2.1. Chemicals and reagents

Tetracyclines including tetracycline hydrochloride, oxytetracycline (OTC), chlortetracycline (CTC), and doxycycline hyclate (DOXC), as well as cysteine (Cys) and histidine (His) were purchased from Sigma (St. Louis, USA) and used without further purification. Anthranilic acid, glutaraldehyde solution (25%, w/w) in water, trichloroacetic acid, citric acid monohydrate, disodium hydrogen phosphate and Na_2EDTA were supplied by Beijing chemical Reagents (Beijing, China). Fresh eggshells were obtained from De Qingyuan Co. Ltd (Beijing, China).

Unless indicated otherwise, all chemicals were of analytical reagent grade and used without further purification. Ultra-pure water was prepared in the lab using a Milli Q (Millipore Company, USA) water treatment device.

2.2. Instrumentation

An F-7000 fluorescence spectrophotometer (HITACHI Instruments, Japan) with a xenon discharge lamp and a scaffold was used. All pH measurements were performed on a pH meter (METTLER TOLEDO Instruments, Shanghai, China). SEM images were recorded using a JSM-6360 scanning electron microscope (JEOL Instruments, Japan). All of the measurements were performed at room temperature at about 298 K.

2.3. Preparation of the ESM

The ESM was carefully stripped from the ultrapure water-washed eggshells. It was then immersed in ultrapure water at 277 K for 1 h followed by rinsing with ultrapure water 10 times to remove most of the albumen. The cleaned ESM was finally stored in ultrapure water at 277 K for further use.

2.4. Preparation of a glutaraldehyde-coated ESM with immobilized AA

The ESM was cut into pieces (1×1 cm) with a clean scissor. An aliquot of 20 μL for optimal concentration of AA was pipetted and smeared evenly on the membrane surface. After approximately 20 min at 277 K, the membrane was taken out and 10 μL for optimal concentration of glutaraldehyde was applied evenly on it. Then the membrane was retained for 2 h at 277 K. Finally the glutaraldehyde-coated ESM with immobilized AA was obtained after repeated rinsing with ultrapure water to remove uncross-linked AA.

2.5. Procedure for the determination of Tc

Aliquots of 10 μL for different concentrations of Tc were spread evenly on the 1×1 cm glutaraldehyde-coated ESM with immobilized AA which was prepared in Section 2.4. After 5 min at room temperature, the concentration of Tc was subsequently analyzed with the fluorescence measurement performed at Ex/Em = 360/430 nm.

2.6. Analytical application

The proposed method was applied to detecting Tc in four different kinds of eggs purchased from local markets including 2 domestic eggs and 2 free ranging eggs. An aliquot of 5 g whole egg was homogenized and mixed with 5 mL Na_2EDTA–Mcllvaine buffer.[35] After the mixture was centrifuged at $9333 \times g$ 10 min, the supernatant was separated and the residue was extracted repeatedly with 5 mL Na_2EDTA–Mcllvaine buffer for five replications by vortex. Then the supernatants were pooled and mixed with 5 mL of 5% trichloroacetic acid (TCA).[36] After the mixture was centrifuged, the supernatant was diluted to a constant volume of 50 mL and filtered with rapid filter paper. Finally the filtrate was collected for further use.

An aliquot of 10 μL sample filtrate was taken and evenly applied on the membrane biosensor, and then the Tc in samples would be determined with the same procedures in Section 2.5.

3. Results and discussion

3.1. SEM images of the ESM

In order to know the microstructure of the ESM before and after the cross-linking reaction, the ESM with and without glutaraldehyde and AA were prepared for SEM, and all samples were sputter-coated with gold. The surface morphology of the cleaned ESM shown in Fig. 1(a) indicates that the ESM is a highly cross-linked network with fibers arranged in layers. In Fig. 1(b), cross-linking protein fibers of the inner ESM are not

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clearly visible due to the presence of an even coating of glutaraldehyde on the ESM. As for the outer ESM coated by glutaraldehyde (Fig. S1†), although its fiber structure cannot be completely covered by the crosslinker, some mantles of glutaraldehyde can obviously be seen on the protein fibers. The morphological difference between the ESM and glutaraldehyde-coated ESM with immobilized AA suggests that the ESM can be modified by linking with glutaraldehyde through amino groups of ESM proteins.[37] Therefore the biosensor can be fabricated with AA immobilized on the ESM with the linkage of glutaraldehyde.

3.2. Optimizing the conditions for the detection of Tc

3.2.1 Effect of the concentration of AA. As the luminescence reagent in this system, the concentration of AA should be optimized to improve the biosensor response. The effect of AA concentration in the range of 10 μg mL^{-1} to 5600 μg mL^{-1} was investigated. The results showed that the optimal concentration of AA was 5000 μg mL^{-1}.

As illustrated in Fig. 2, upon the concentration of AA up to 5600 μg mL^{-1}, the fluorescence response at Ex/Em = 360/430 nm increased at first, and then reached its maximum when the AA concentration was above 5000 μg mL^{-1}, indicating that the active sites for the cross-linking reaction are almost saturated with 5000 μg mL^{-1} AA. On the other hand, the fluorescence intensity of the ESM at Ex/Em = 280/340 nm was gradually decreased with the addition of AA, and was entirely covered when the concentration of AA was above 4000 μg mL^{-1}, also suggesting that AA has been evenly immobilized on the membrane. Furthermore, for the stability of the biosensor, the concentration of AA should be below 5700 μg mL^{-1} which has been known as its solubility in water at 298 K. Above all, 5000 μg mL^{-1} AA was chosen as the optimal concentration in the immobilization process.

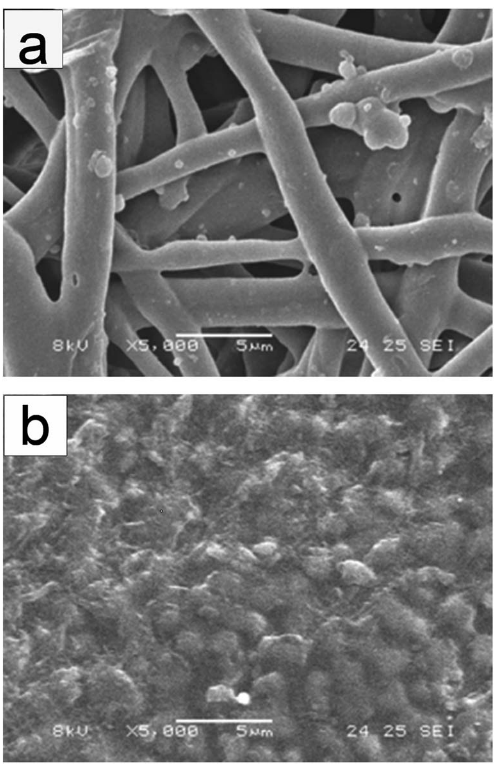

Fig. 1 SEM images of ESM before and after cross-linking with glutaraldehyde and AA:ESM, ×5000 (a); glutaraldehyde-coated inner ESM with immobilized AA, ×5000 (b).

3.2.2 Effect of the concentration of glutaraldehyde. As a cross-linking agent, glutaraldehyde has the effect to link AA with ESM fibers through covalent bonding.[37] To find the optimal concentration of glutaraldehyde, the fluorescent response of AA on Ex/Em = 360/430 nm was studied when 20 μL of 2.5%, 5%, 10%, 15%, 20%, and 25% glutaraldehyde were cross-linked with the ESM, respectively.

Without glutaraldehyde, the fluorescent intensity was very weak and unstable. This can be attributed to the fact that without glutaraldehyde, the majority of AA is physically adsorbed on the ESM, and could de-adsorb easily.[37] However, with the addition of glutaraldehyde, the fluorescent intensity of AA increased simultaneously with the fluorescence decrease of the ESM, and reached the maximum when the concentration of glutaraldehyde was 25% (w/w) (Fig. 3), indicating that glutaraldehyde could cross-link with AA and quench the fluorescence of the ESM at the same time. This may due to the fact that the microenvironment of tryptophan in the ESM is changed by hydrophilic glutaraldehyde.[38] The hydrophilic nature of glutaraldehyde also increases the ability of the ESM to retain water, thus reducing the possibility of biosensor drying. Furthermore, considering that the highest concentration of generally used glutaraldehyde is 25% (w/w), the optimized concentration of glutaraldehyde was chosen as 25% (w/w).

According to the above results, the optimized procedure for preparing the membrane biosensor was that 10 μL of 5000 μg mL^{-1} AA was immobilized on the ESM coated with 20 μL of 25% glutaraldehyde.

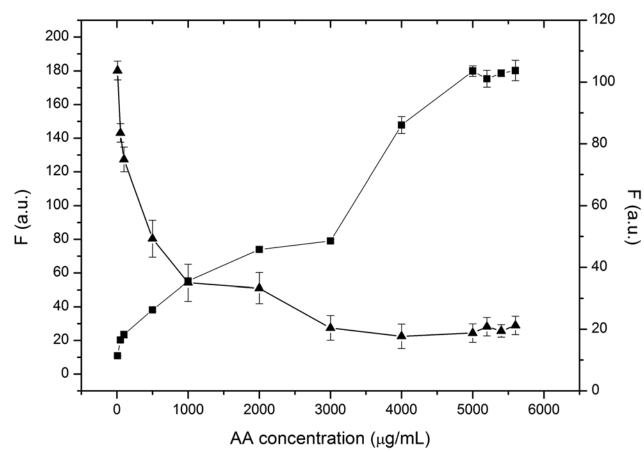

Fig. 2 Effect of AA concentration on the fluorescent intensity at Ex/Em = 360/430 nm (■) and Ex/Em = 280/340 nm (▲). Glutaraldehyde concentration, 25% (w/w); temperature, 277 K; immobilization time, 20 min. Error bars represent one standard deviation for six measurements.

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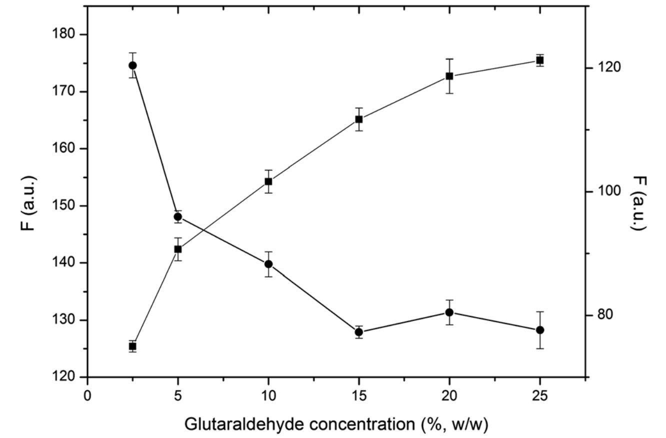

Fig. 3 Effect of glutaraldehyde concentration on the fluorescence intensity at Ex/Em = 360/430 nm (■) and Ex/Em = 280/340 nm (●). AA concentration, 5000 μg mL^{-1}; temperature, 277 K; immobilization time, 2 h. Error bars represent one standard deviation for six measurements.

3.3. Fluorescence detection of Tc by glutaraldehyde-coated ESM with immobilized AA

Under the optimal conditions given above, the fluorescent emission intensity of AA was gradually reduced upon the addition of Tc (Fig. 4(b)), suggesting that the fluorescence of AA could be efficiently quenched by Tc. The quench mechanism may be attributed to the fluorescence inner filter effect.[39] It could be found in Fig. 4(a) that the absorption spectrum of Tc (λ_{abs} = 355 nm) has an almost complementary overlap region with the excitation spectrum of AA (λ_{ex} = 360 nm), so the fluorescence excitation of AA will be modulated by the adsorption change of Tc, thus the addition of Tc could be efficiently converted to fluorescence quenching signals of AA, achieving fluorescence analysis of Tc.

As illustrated in Fig. 5, the calibration graph of fluorescent difference before and after quenching (ΔF) *versus* Tc concentration was linearly in 10 ng mL^{-1} to 1 μg mL^{-1} ($R^2 = 0.9984$) while the detection limit of Tc was 10 ng mL^{-1}. To the best of our knowledge, there has been no study reporting the detection of Tc by AA as a fluorescent probe, so we compared the developed method with other fluorescent sensors for analyzing Tc, and the presented method provides a comparable linear range and detection limit for Tc (Table S1†). Although the sensitivity of the developed method is lower than that of the methods performed by carbon dots and gold nanoparticles, its advantage is that the presented sensor can achieve a cheaper, simpler and faster determination. Thus this biosensor could be satisfactorily applied to the trace quantization of Tc.

3.4. Selectivity of the glutaraldehyde-coated ESM with immobilized AA to Tc over other reagents

In order to evaluate the selectivity of the biosensor to Tc, 100 ng mL^{-1} foreign reagents such as oxytetracycline (OTC), chlortetracycline (CTC), doxycycline hyclate (DOXC), cysteine (Cys) and histidine (His) were spread, respectively, onto the membrane.

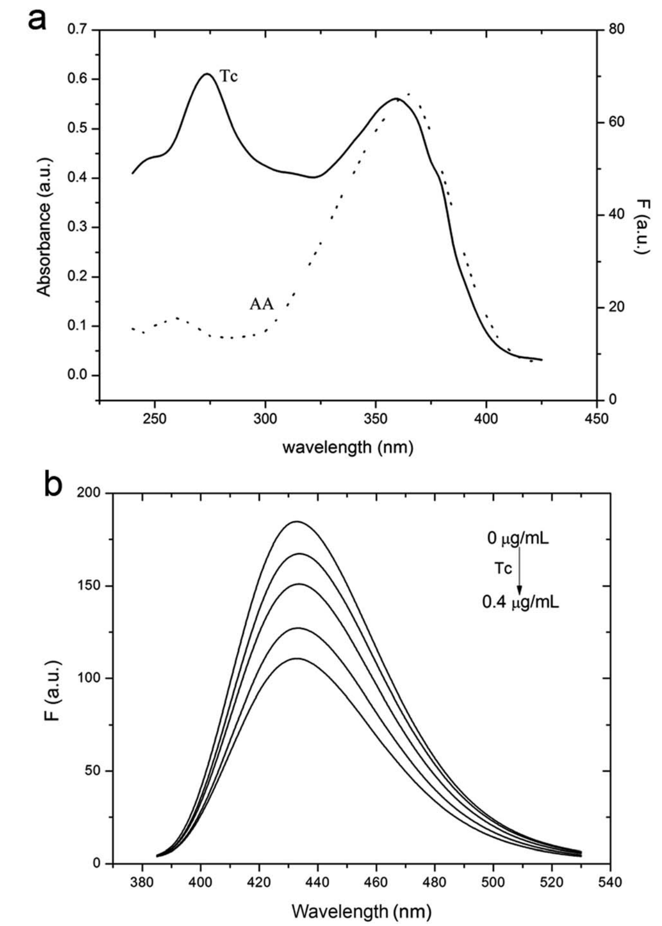

Fig. 4 Fluorescence excitation spectrum of 1000 μg mL^{-1} AA at Em = 430 nm (—) and absorption spectrum of 40 μM Tc (—) (a); fluorescence emission spectrum of 5000 μg mL^{-1} AA upon the addition of Tc. Excitation was performed at 360 nm (b).

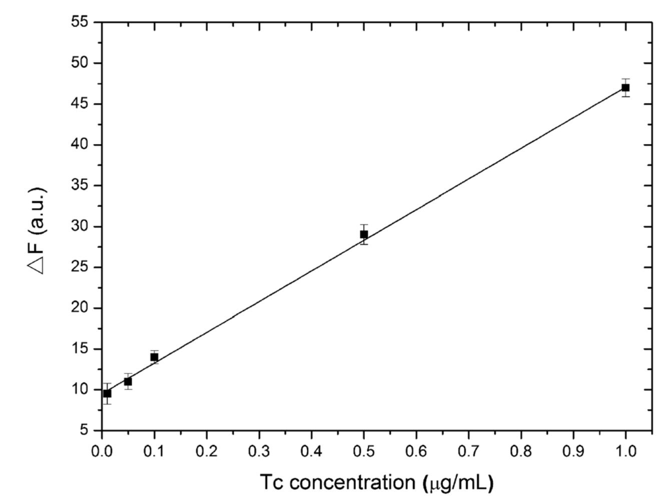

Fig. 5 Fluorescent difference (ΔF) of the biosensor at Ex/Em = 360/430 nm as a function of Tc concentration. AA concentration, 5000 μg mL^{-1}; glutaraldehyde concentration, 25% (w/w); temperature, 20 °C; reaction time, 5 min. Error bars represent one standard deviation for five measurements.

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Table 1 Fluorescence response ratio and tolerance of other reagents compared to Tc

Foreign reagents	Response ratio (%)	Tolerance limit (fold)
OTC	0.5	10
CTC	0.5	10
DOXC	0.6	8.3
Cys	<0.1	>50
His	0.3	16.7

Table 2 Recovery rate of Tc determination in different egg samples by the biosensor

Added (ng mL^{-1})	Found (ng mL^{-1})	Recovery (%)
50	53.67 ± 1.01	107.34%
100	98.47 ± 0.97	98.47%
200	204.22 ± 1.36	102.11%
400	402.61 ± 1.85	100.65%
800	795.90 ± 1.31	99.49%

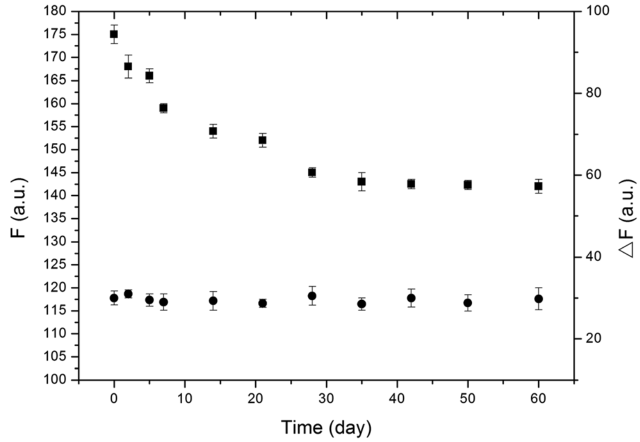

Fig. 6 Fluorescent intensity of biosensor at Ex/Em = 360/430 nm during 60 days as a representation of biosensor stability (■). Tc concentration, 50 ng mL^{-1}; storage temperature, 277 K. Fluorescent difference (ΔF) of biosensor at Ex/Em = 360/430 nm during 60 days as a representation of regeneration (●). Tc concentration, 50 ng mL^{-1}; storage temperature, 277 K. Error bars represent one standard deviation for six measurements.

Among the testing species, OTC, CTC and DOXC were mainly investigated because their absorption values are at about 360 nm. The response ratio[39] for each foreign reagent compared to Tc at Ex/Em = 360/430 nm and the tolerance limit[40] considered as the interfering concentration causing fluorescent reduction higher than ±5% are listed in Table 1. It can be found that both amino acids (Cys and His) and tetracyclines (OTC, CTC, and DOXC) had little interference for the detection of Tc, showing good selectivity of the developed method to Tc over other reagents.

3.5. Application of glutaraldehyde-coated ESM with immobilized AA in egg samples

Under the optimized conditions, four kinds of egg samples sold in local markets were analyzed by the proposed method. There was no Tc determined from all samples. In order to verify the feasibility of the method, we designed the recovery experiment by addition of 50, 100, 200, 400, and 800 ng mL^{-1} Tc, and the results are shown in Table 2. The recovery of different additions of Tc was all within 100 ± 10%, indicating Tc in samples could be efficiently and accurately detected. Moreover, the RSD was 2.85% when the added concentration of Tc was 200 ng mL^{-1}, which could prove the good reproducibility of the method.

3.6. Stability and regeneration of the glutaraldehyde-coated ESM with immobilized AA

In order to determine the long-term stability, the biosensor was stored at 277 K and it retained 80.6% original fluorescent response even after two months (Fig. 6). The ESM protein would probably be decomposed by the effect of microbial metabolism and water evaporation, which results in the activity decrease of the biosensor. Regeneration was assessed by measuring the fluorescent response of the biosensor with 50 ng mL^{-1} Tc spread on it, then the biosensor was treated with ultrapure water for sufficient washing and stored at 277 K for repeated use. It was found that the ΔF value of the biosensor was still stable even after 11 successive uses over two months (Fig. 6). Thus, the above results prove the excellent stability and complete regeneration of the modified membrane, which makes the biosensor suitable for actual applications.

4. Conclusions

In this paper, a glutaraldehyde-coated ESM with immobilized AA was applied to detect Tc in aqueous media. Under optimized conditions, the quantification of Tc using a fluorescence method was satisfactory in a linear range of 10 ng mL^{-1} to 1 μg mL^{-1}, with a detection limit of 10 ng mL^{-1} Tc. The biosensor and the analytical method have the advantages of low detection limits, high sensitivity and selectivity, as well as excellent stability and regeneration. And the biosensor and method could be used to achieve efficient and rapid detection of trace Tc in foods and the environment.

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