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Tetracycline selective electrode based on molecularly imprinted polymer particles

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Abstract

Tetracycline selective electrode using molecularly imprinted polymer particles as quasi-ionophore was constructed the first time, and its performance was carefully characterized. Due to the specific recognition of tetracycline by the particles, the selectivity coefficients for routine interferences were less than 10^{-4}. Benefited from the absence of tetracycline in the sensitive membrane and the optimized composition of the inner filling solution, the limit of detection of the electrode was reduced to about 2.5×10^{-8} mol/L. It exhibited a good electrode slope 57.6 mV/decade near the theoretical Nernstian one, with a wide linear working range from 6.0×10^{-8} to 1.0×10^{-3} mol/L. The fabricated electrode should be used in pH 2–4, response time of which was less than 200 s when the concentration of tetracycline was higher than 1.0×10^{-6} mol/L and no more than 30 min at the concentration of 1.0×10^{-8} mol/L.

Keywords: Ion selective electrode; Molecular imprinting polymer; Quasi-ionophore; Tetracycline

Tetracycline (TC) is still commonly used in veterinary medicine for both therapeutic and prophylactic purposes in food-producing animals and fishes. Due to its public health impact, many methods have been developed to determine it in various matrices, among which chromatographic ones are the most widely used. Potentiometry was also applied to do it using TC selective electrode with TC–tetraphenylborate or TC–phosphotungstate ion-pair as electroactive substance [1,2]. However, it was not so successful because the detection limits of the electrodes were higher than 10^{-6} mol/L. Reasons were reported [3] that ion flux from the membrane to the sample solution would appear once the analyte concentration is lower than 10^{-6} mol/L, which results in the concentration of the analyte adjacent to the sensitive membrane is higher than that in the bulk solution, *i.e.*, the detection limit could not be further lowered. Molecularly imprinted polymer (MIP) has been widely used as solid-phase extraction materials, and MIP films were used to construct chemosensors recently [4,5]. However, using MIP particles as *quasi*-ionophore to fabricate a selective electrode has never been reported. In this work, TC selective electrode using MIP particles as *quasi*-ionophore was constructed the first time, and its performance was carefully characterized.

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1. Experimental

TC as template, ethylene glycol dimethacrylate (EGDMA) as cross-linker, dibutyl phthalate (DBP) as plasticizer and poly(vinylchloride) (PVC, selectophore, high molecular weight) were purchased from Fluka. Methacrylic acid (MAA) as functional monomer, 2,2′-azobisisobutyronitrile (AIBN) as initiator, acetic acid and lanthanum nitrate ($La(NO_3)_3{\cdot}6H_2O$) were purchased from the China National Medicines Co. Ltd. Methanol and tetrahydrofuran (THF) of HPLC grade were purchased from Aldrich. Water was obtained from a Millipore water system. EGDMA was distilled and AIBN was recrystallized before use.

TC (0.1 mmol), $La(NO_3)_3{\cdot}6H_2O$ (0.1 mmol) and MAA (0.066 mL) were dissolved in 5 mL of methanol–water (9:1, v/v). Then, 0.944 mL of EGDMA and 12 mg of AIBN were added and dissolved by sonicating. Nitrogen was bubbled to degas the mixed solution for 10 min prior to sealing it. The polymerization was performed in a 60 °C water bath for 24 h. Then, the molecularly imprinted polymer (MIP) particles were collected, washed repeatedly with methanol–acetic acid (9:1, v/v) in a soxhlet apparatus till they turned white, dried at 45 °C for 10 h, and finally obtained.

Above-mentioned MIP particles (122 mg), DBP (128 mg) and PVC (100 mg) were added into 2 mL of THF and stirred for 1 h. The obtained mixture was then poured into a glass ring (7.0 cm i.d.) fixed on a glass plate to form a membrane with the thickness of about 0.5 mm.

The electrode was fabricated as follows: a disk of 4-mm diameter was punched from the membrane and glued to plasticized PVC tubing with THF/PVC slurry. The inner filling solution was 10^{-3} mol/L tetracycline hydrochloride, 10^{-2} mol/L NaCl, and 10^{-2} mol/L $CaCl_2$. The tip of an Ag–AgCl wire was immersed in this solution to serve as an inner reference electrode. The obtained electrode was conditioned in 10^{-8} mol/L tetracycline hydrochloride solution for 12 h. It was washed by 0.001 mol/L hydrochloric acid for 5 min and water for 5 min successively prior to each determination.

Electromotive force (EMF) was measured at ambient temperature in the galvanic cell: SCE//KCl salt bridge// sample solution/membrane/inner filling solution/Ag–AgCl with a SDC-III potentiometer (Nanjing SangLi Electronic Equipment Factory). The morphology of MIP particles was studied by HITACHI S-3400N scanning electron microscope (SEM).

2. Results and discussion

Water-compatible MIP particles targeting TC was synthesized with La^{3+} as mediator. It was proposed that this novel strategy could substantially improve the specific binding capacity of MIP particles targeting the template molecules [6]. The SEM image of the prepared MIP particles was presented in Fig. 1. It was readily observed that they were very uniform with the diameter of 3–4 μm, which is redound to their homogeneous disperse in the mixture solution of DBP, PVC and THF.

The ionic response of the TC selective electrode using MIP particles as *quasi*-ionophore was measured in hydrochloric acid (pH 3). Calibration curves were obtained by gradual dilution of the sample with hydrochloric acid

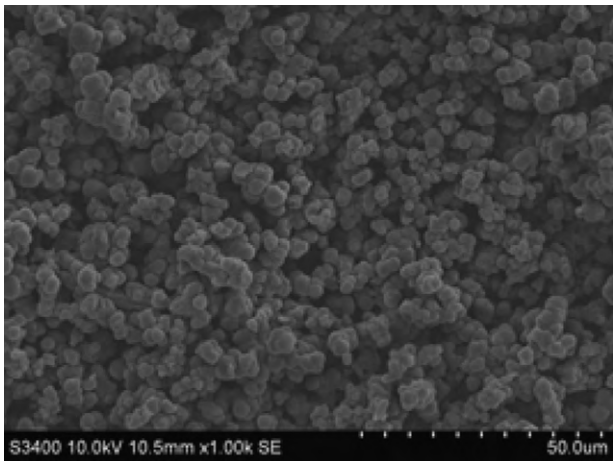

Fig. 1. The SEM image of the MIP particles.