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Hollow fiber supported ionic liquid membrane microextraction for preconcentration of kanamycin sulfate with electrochemiluminescence detection

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ABSTRACT

Three-phase hollow fiber based liquid phase microextraction (HF-LPME) was developed for the preconcentration of kanamycin sulfate combined with electrochemiluminescence detection. The extractant was 1-octyl-methylmidazolium hexafluorophosphate ([OMIM]PF_6). A hollow fiber supported liquid membrane was used between phosphate buffer solution (PBS) containing analyte (kanamycin sulfate) as donor phase and aqueous solution (pH 10) as acceptor phase. The effects of various parameters on the extraction efficiency were studied, such as pH of ECL working solution, extraction temperature, pH of donor phase, extraction time and salt content of sample. Under the optimized conditions, the linear range was 0.002–0.1 μg mL^{-1}, and the limit of detection (LOD) was 0.00067 μg mL^{-1}. No expensive equipment is necessary to perform this assay which makes it a viable replacement.

1. Introduction

Kanamycin sulfate (KAM) (Fig. 1) belongs to an important group of aminoglycosides used to prevent infections, treat diseases and promote growth. As a second-line treatment of mycobacterium tuberculosis, it has narrow therapeutic rang and is potentially oto-and nephrotoxic like other aminoglycosides [1]. Aside from this application, kanamycin is currently only used for treatment of mastitis in dairy cattle [2] and as a growth promoter in animal food [3]. However, antibiotic misuse could bring many problems. It received considerable public attention after the fast-grown chicken in restaurants in 2012. Recently, an article from Chinese Science Bulletin reported that there are 68 kinds of antibiotics in surface water in China [4–9]. The concentrations are far above these in other countries. It could be a danger to health to drink the water regularly. To protect public health and food safety, many countries and groups have established the criteria of Maximum Residue Limits (MRLs) for KAM [10–12].

Many analytical techniques are available to determine KAM, for example, HPLC–UV [13], immunosensor [14], liquid chromatographic method with pulsed electrochemical detection [15], DNA aptamer sensor [16], cantilever array sensor [17], solid-phase extraction and capillary electrophoresis [18], capillary zone electrophoresis [19], surface plasmon resonance light-scattering [20]. The HPLC and LC methods require expensive apparatus and professional operators. DNA aptamer sensor and immunosensor requires complex pretreatment. Solid-phase extraction and capillary electrophoresis need to improve detection limit. Cantilever array sensor is complex and its sensitivity is not high enough.

Sample pretreatment and purification can decrease or eliminate the interference of matrixes for real samples. To miniaturize traditional liquid–liquid extraction, a new solvent minimized extraction method named liquid-phase microextraction (LPME) [21] has attracted increasing attention for its effectiveness, cheapness, simplicity, and cleanup ability [22–27]. In this concept, the analytes are extracted from aqueous samples, through a thin layer of organic solvent (several microlitres) immobilized within the pores of a porous hollow fiber, and into an acceptor solution inside the lumen of the hollow fiber; when acceptor phase is an aqueous phase the procedure is known as three-phase HF-LPME. The analytes are firstly extracted into a supported liquid membrane sustained in the pores of a hydrophobic porous hollow fiber (HF), and later into an acceptor solution placed inside the lumen of the fiber. HF-LPME uses a porous-walled polypropylene hollow fiber to stabilize and protect the organic phase, to enhance the mechanical robustness and the extraction efficiency [28,29]. There are considerable researches about driving force for the extraction of target analytes by HF-LPME [30–33]. This technique can provide a high analyte preconcentration and excellent sample cleanup, with the advantages that the fiber can be disposable after use because of its low price.

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Room temperature ionic liquids (RTILs), resulting from the combination of organic cations and various anions, exhibit negligible vapor pressures at room temperature, good extractability for various organic compounds, and excellent thermal stability. Therefore, RTILs, regarded as a novel type of green solvents, have recently been used as alternatives to common organic solvents in many fields [34,35], including separation and enrichment in analytical chemistry [36–38].

The electrogenerated chemiluminescence (ECL) can be defined as a luminescent chemical reaction, light is emitted only when an appropriate potential is applied to an electrode in contact with a solution. The solution contains an appropriate luminescent compound [39]. $Ru(bpy)_3^{2+}$ is by far the most widely used ECL luminophore due to its unique photochemical, photo-physical, ECL properties and solubility in a variety of solvent media [40].

To the best of our knowledge, there is no ECL method that has been developed for the determination of trace KAM in dairy or water to date. In this work, a strong ECL enhancement due to KAM at a glass carbon electrode (GCE) in a $Ru(bpy)_3^{2+}$ solution was demonstrated. The sensitivity achieved by this ECL method is very high among the reported methodologies [13–20]. The enhancement mechanism of KAM to the ECL of $Ru(bpy)_3^{2+}$ was also discussed. This work reports the combination of HF-LPME and ECL for the analysis of kanamycin sulfate, by using ionic liquid $[OMIM]PF_6$ as solvent for extraction of KAM prior to electrochemical luminescence detection. Based on the enhancement behavior, the newly developed method HF-LPME–ECL was successfully applied to the determination of kanamycin sulfate in milk powder and water sample.

2. Experimental section

2.1. Apparatus

An electrochemistry workstation (CHI660B, Chenhua Instruments Co. Ltd., Shanghai, China) combined with BPLC Ultra weak luminescence Analyzer (Institute of Biophysics, Chinese Academy of Sciences, Beijing, China) was used to perform cyclic voltammetry and to control the cell potential during ECL experiments. The voltage of the photomultiplier tube (PMT) was set at 800 V. The cell contains a platinum counter electrode, a saturated calomel reference electrode (SCE) and a glassy carbon working electrode. All electrodes are mounted within a tailor-made quartz cell. Because the ECL performance of glassy carbon working electrode was dependent on its pretreatment history, the electrode was polished with 0.05 μm α-Al_2O_3 powder just before each experiment. To obtain the ECL signal, the working electrode was activate through a potential step from −0.1 to 0.6 V.

2.2. Reagents and materials

1-Butyl-3-methylimidazolium hexafluorophosphate $[BMIM]PF_6$, 1-hexyl-3-methy- limidazolium hexafluorophosphate $[HMIM]PF_6$, and 1-otyl-3-methylimidazolium hexafluorophosphate $[OMIM]PF_6$ were purchased from Shanghai Chengjie Chemical Co. Ltd. Polypropylene hollow fiber membrane (1 mm I.D., 200 μm wall thickness, 0.45 μm pore size) was obtained from Faculty of Chemical Engineering, Ningbo University, China. The water used for the solutions was purified by the Milli-Q system (Millipore Inc.; 18 MΩ cm).

$Ru(bpy)_3Cl_2{\cdot}6H_2O$ and tripropylamine (TPrA) were purchased from Sigma Chemical Company, USA. Pharmaceutical grade kanamycin sulfate (KAM, 95%) was obtained from Aladdin Reagent Co. Ltd. All other reagents were of analytical grade, and purchased from Shanghai Chemical Reagent Co. Ltd. (Shanghai, China). Phosphate buffer solution (PBS) containing 0.2 mol L^{-1} sodium phosphate monobasic and 0.2 mol L^{-1} phosphate dibasic, was used as the working solution for the ECL measurement. $Ru(bpy)_3^{2+}$ complex solution was prepared using phosphate buffer with TPrA concentration at 0.5 mol L^{-1}. The phosphate buffer was prepared by mixing 0.2 mol·L^{-1} NaH_2PO_4 and 0.2 mol L^{-1} Na_2HPO_4. KAM standard solutions were prepared using buffer solution with the kanamycin content ranging from 2×10^{-3} to 0.1 μg mL^{-1} and maintained at 4 °C.

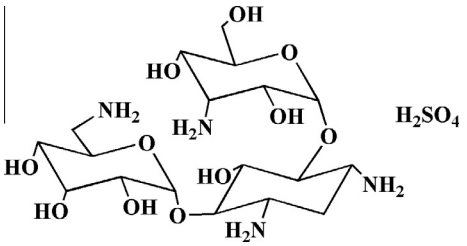

Fig. 1. Structure of kanamycin sulfate.

2.3. Extraction procedures

The hollow fiber was cut into small segments with length of 2 cm, washed with acetone in ultrasonic bath and dried in the air. The fiber segments were soaked with ionic liquid $[OMIM]PF_6$ to impregnate the pores for 5 min in ultrasonic bath. A 25 μL syringe was employed to introduce 10 μL of acceptor phase (pH 10 aqueous solution) into the lumen of each segment, and both ends of the hollow fiber were sealed. Then the fiber was submerged into the sample solution in a glass beaker. After stirring for 0.5 h at 300 rpm, the fiber was taken out, one of the ends was cut and the acceptor phase was extracted using a HPLC syringe and directly injected into the cell without further manipulation (Fig. 2). Each segment of hollow fiber was used only for a single extraction to avoid contamination.

2.4. ECL detection

A 2 μL of 0.001 mol L^{-1} $Ru(bpy)_3^{2+}$, 2 μL of 1 mol L^{-1} TPrA and 10 μL of the pretreated acceptor solution or KAM real sample solution were added into the ECL cell, and then 1 mL of 0.2 mol L^{-1} phosphate buffer (pH = 8) solution was added. The curves of ECL intensity versus applied potential (ECL–E) and the signal changes of current versus an applied potential (i.e. CV) were recorded (Fig. 3A). A cyclic voltammetry was scanned in the range of 0–1.2 V with the scan rate of 100 mV s^{-1}.

2.5. Determination of KAM in real samples

Milk powder and surface water samples were collected and used for the determination of KAM using the method described

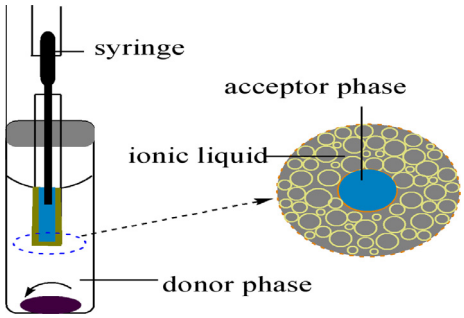

Fig. 2. The schematic plot of liquid–liquid–liquid phase microextraction (LLLME) based on hollower fiber supported ionic liquid membrane.