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Determination of dimetridazole using carbon paste electrode modified with aluminum doped surface molecularly imprinted siloxane

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ABSTRACT

For the first time, a simple and highly sensitive electrochemical dimetridazole (DMZ) sensor based on a carbon paste electrode modified with core-shell aluminum doped surface molecularly imprinted siloxane has been developed and tested. Because of aluminum doping, the surface imprinting sensor exhibits higher rebinding capacity, recognition ability and affinity for DMZ in comparison with the aluminum free and the non-imprinted ones. In addition, the as-prepared sensor shows good stability and satisfactory reproducibility for the determination of DMZ. Under optimal experimental conditions, the peak currents by differential pulse stripping voltammetry were found to vary linearly with DMZ concentrations in the range from 1.0×10^{-8} to 1.0×10^{-6} mol L^{-1} and 1.0×10^{-6} to 1.0×10^{-4} mol L^{-1}, with a detection limit of 3.6×10^{-9} mol L^{-1}. This sensor was successfully employed to detect DMZ in egg, milk powder, and pig feed samples with acceptable recoveries of 91.4% to 107.6%, which was verified by high performance liquid chromatography.

1. Introduction

Dimetridazole (DMZ, 1,2-dimethyl-5-nitroimidazole) is a 5-nitroimidazole type veterinary drug and has been used to treat diseases caused by bacterial and protozoal infections in poultry and swine [1,2]. It has also been used as a promoter to induce the growth of animals and to improve feed efficiency [3]. However, DMZ has been banned by many countries and areas from using in food producing animals [4–6], because of its mutagenic, carcinogenic and genotoxic side effects on humans [7–9].

Several methods have been developed for the detection of DMZ, including chromatographic techniques [10–13], immunoassay [14,15], and capillary electrophoresis [3,16]. However, these methods are not as simple as electroanalysis [17], which is an appropriate route for detecting DMZ because the nitro group in DMZ is electroactive. An extensive survey of the literature revealed that there is one report describing the determination of DMZ in pharmaceutical preparations using a supermolecular recognition-based electrochemical sensor [18]. Thus, it is still desirable but challenging to develop highly selective and sensitive electroanalytical methods for the determination of DMZ in different matrixes.

Molecularly imprinted polymer (MIP), as a key element of a sensor, can specifically recognize and rebind the target analyte as well as effectively overcome the interferences of closely related compounds [11]. An MIP-based sensor exhibits several remarkable advantages such as high selectivity, chemical stability, low cost and easy preparation, and has been received considerable concern over the past decades [19–23].

Among many methods for preparing MIP-based sensors [24–26], the surface molecular imprinting technique using a sol–gel process has been confirmed to possess much more effective recognition sites on the electrode surface than other approaches and then promote mass transfer kinetics [27,28]. To achieve surface imprinting, the simplest approach is imprinting molecules on surface of some solid substrates to obtain the core-shell structural MIPs [29–31]. Of various solid support materials, Fe_3O_4@SiO_2 nanoparticles is an excellent candidate because of its reliable chemical stability, compatibility with various modified agents, and the inherent properties of the magnetic element, which makes the resulting MIP be easily separated by an external magnet to facilitate the preparation process [32,33].

So far, molecular imprinting has mainly been established in a non-covalent way. The use of non-covalent interactions alone, such

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as polar, hydrogen bonding, and van der Waals forces, is limited for the formation of selective recognition sites. Thus, fabrication of MIP with metal coordinate interactions offers greater promise for producing more highly defined recognition sites [34,35]. Compared with non-covalent interactions utilized in MIPs, the coordinate interaction has higher strength, specificity, and directionality, which makes it more like a covalent interaction than hydrogen bond or electrostatic interaction [35]. The metal ion doped MIPs are mainly used in solid phase extraction [35–37] and catalyst [38], however, seldom in electrochemical sensors [39].

In our previous study [37], we synthesized a novel aluminum doped molecularly imprinted siloxane (MIS) with a core-shell structure using a surface imprinting technique. The resulted nanosorbent was then used for the selective solid phase extraction followed by spectrophotometric determination of DMZ. In continuation of our research on the applications of the Al(III) doped MIS to electroanalysis of interested analytes, in this work, we fabricated a carbon paste electrode (CPE) modified with the above mentioned MIS for selective recognition and trace determination of DMZ via differential pulse stripping voltammetry (DPSV). CPE is preferably selected as the working electrode because it usually offers a wide potential window, a low background current and facile renewability [40]. Above all, the sensitivity and selectivity of a CPE for detecting the target analyte can be improved easily by employing a wide variety of modifiers, such as MIPs [41,42], nanomaterials [43,44] and biomacromolecules [45,46]. The superior performance of the MIS modified carbon paste electrode (MIS-CPE) is demonstrated by the trace determination of DMZ in egg, milk powder and pig feed samples under optimized conditions. The developed method has been validated with high performance liquid chromatography (HPLC). To the best of our knowledge, this is the first instance where Al(III) doped MIS, in which the Lewis acid sites with a memory for DMZ were anchored to the silica matrix, has been employed to modify CPE for trace determination of DMZ in food and feed samples.

2. Experimental

2.1. Reagents

Graphite powder, paraffin oil, DMZ, ronidazole, metronidazole, 3-aminopropyltriethoxysilane (APTES), methyltrimethoxysilane (MTMOS), tetraethyl orthosilicate (TEOS), and aluminium chloride hexahydrate ($AlCl_3{\cdot}6H_2O$) were purchased from Aladdin Reagent Company (Shanghai, China). All the chemicals were of analytical reagent grade and used directly. Double distilled water (1.0 $\mu S\,cm^{-1}$) was used throughout all experiments. Milk power and fresh egg samples were obtained from local supermarkets. Pig feed samples were purchased from Innovation Biotech Co., Ltd (Hunan, China).

2.2. Instrumentation

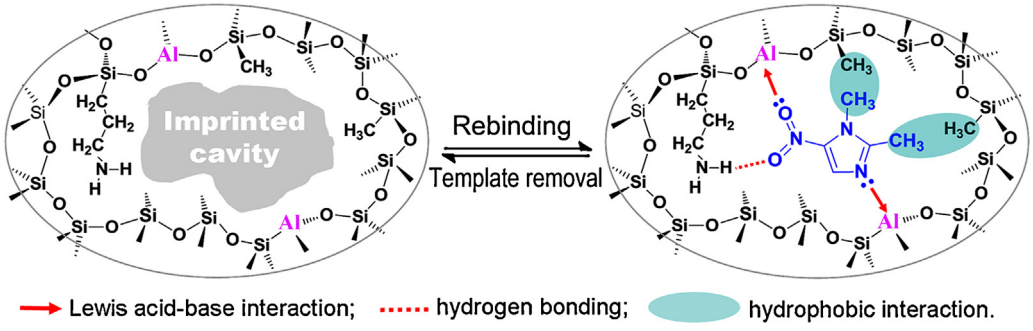
Electrochemical measurements were performed on a CHI 660 C electrochemical workstation (Chenhua Instrument, Shanghai, China) connected to a personal computer. A conventional three-electrode system was employed, consisting of a bare or a modified carbon paste electrode (2 mm in diameter) serving as a working electrode, a platinum wire as the counter electrode, and a saturated calomel electrode (SCE, 0.2415 V vs. SHE) as the reference electrode. All potentials reported in this article were referenced to the SCE. All measurements were carried out at room temperature (25 ± 2 °C). All solutions were deaerated with high-purity nitrogen for 10 min before each electrochemical experiment.

2.3. Preparation of dimetridazole-molecularly imprinted siloxane (DMZ-MIS)

Fe_3O_4 magnetic nanoparticles were prepared according to our previous report [37]. Five mmol of trisodium citrate dehydrate, 200 mmol of sodium nitrate, and 20 mmol of sodium hydroxide were dissolved in 90 mL of deionized water. The mixture was then heated to 100 °C until a clear solution was formed. Ten mL of 1.0 mol L^{-1} ferrous sulfate heptahydrate solution was added rapidly into the above solution which was kept at 100 °C for 1 h. After cooled down to room temperature, the precipitate was collected by a magnet and washed with deionized water for several times. Then the obtained black Fe_3O_4 magnetic nanoparticles were dried under vacuum at 60 °C for 6 h.

The core–shell Fe_3O_4@SiO_2 nanoparticles were synthesized via a sol-gel method [37]. Shortly, 0.5000 g as-prepared Fe_3O_4 were dispersed in a solution composed of 80.0 mL ethanol and 20.0 mL double distilled water by sonicating for 30 min. Then, 5.0 mL ammonia solution (25 wt%) and 4.0 mL TEOS were added successively. The resulting suspension was stirred and allowed to react for 6 h at room temperature. The obtained Fe_3O_4@SiO_2 was separated by a magnet, rinsed with double distilled water for several times, and dried under vacuum at 60 °C for 8 h.

The DMZ-MIS was prepared using our previously reported method [37] with minor modification. Briefly, 0.4000 g of Fe_3O_4@SiO_2 nanoparticles was dispersed in 30 ml ethanol by sonication for 30 min, followed by addition of 1.8 mmol (0.2540 g) of DMZ, 1.5 mL (6.4 mmol) of APTES, and 1.3 mL (9.1 mmol) of MTMOS sequentially. After the mixture was stirred for 20 min, 4.0 mL (17.9 mmol) of TEOS was added. Under stirring for another 10 min, 1.3 mL of 1.0 mol L^{-1} (1.3 mmol) $AlCl_3{\cdot}6H_2O$ and 1.0 mL of 0.01 mol L^{-1} hydrochloric acid solution were added, and allowed to react for 12 h at room temperature with agitation. Finally, the DMZ-MIS was obtained by magnetic separation, rinsed with ethanol, and dried under vacuum at 60 °C for 8 h. It has been proved [36] that Al



Scheme 1. Schematic representation of the specific recognition of DMZ by an imprinted cavity on the surface of the MIS matrix.