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Nanosilica-based molecularly imprinted polymer nanoshell for specific recognition and determination of rhodamine B in red wine and beverages☆

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ABSTRACT[1]

A new and facile rhodamine B (RhB)-imprinted polymer nanoshell coating for SiO_2 nanoparticles was readily prepared by a combination of silica gel modification and molecular surface imprinting. The RhB-imprinted polymers (RhB-MIPs) were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, and UV–vis spectroscopy; the binding properties and selectivity of these MIPs were investigated in detail. The uniformly imprinted nanoparticles displayed a rather thin shell thickness (23 nm) with highly effective recognition sites, showing homogenous distribution and monolayer adsorption. The maximum MIP adsorption capacity (Q_m) was as high as 45.2 mg g^{-1}, with an adsorption equilibrium time of about 15 min at ambient temperature. Dynamic rebinding experiments showed that chemical adsorption is crucial for RhB binding to RhB-MIPs. The adsorption isotherm for RhB-MIPs binding could also be described by the Langmuir equation at different temperatures and pH values. Increasing temperature led to an enhanced Q_m, a decreased dissociation constant (K'_d), and a more negative free energy (ΔG), indicating that adsorption is favored at higher temperatures. Moreover, the adsorption capacity of RhB was remarkably affected by pH. At pH > 7, the adsorption of RhB was driven by hydrogen bonding interactions, while at pH < 7 electrostatic forces were dominant. Additionally, the MIPs also showed specific recognition of RhB from the standard mixture solution containing five structurally analogs. This method was also successfully employed to determine RhB content in red wine and beverages using three levels of spiking, with recoveries in the range of 91.6–93.1% and relative standard deviations lower than 4.1%.

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1. Introduction

Rhodamine B (RhB), a highly water-soluble synthetic industrial azoic dye [1], is extensively used for fluorescent labeling and food coloring due to its fastness, low cost, and stability. However, it is an allergen affecting the human respiratory system, skin, and brain [1,2]. Moreover, rhodamine B was also found to be toxic and carcinogenic in multiple feeding tests of rats and mice [3]. Currently, enrichment and measurement of trace amounts of rhodamine B in complex food matrices is still a demanding task, requiring extensive pretreatment to extract and purify the title analytes prior to analysis. The analytical methods most commonly used for the determination of rhodamine B are liquid chromatograph-mass spectrometer (LC–MS)[4], high performance liquid chromatography (HPLC) [5], UV–vis spectroscopy [6], and fluorescence spectrometry [7,8], which are combined with sample pretreatment methods, such as liquid-liquid extraction (LLE), solid-phase extraction (SPE), etc. Since classical SPE sorbents (C_8, C_{18}, etc.) [9,10] mainly rely on non-selective hydrophobic interactions, this can lead to a partial co-extraction of interfering substances. In order to remove those co-extractants, further purification is nec-

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[1] Rhodamine B, RhB; RhB-imprinted polymers, RhB-MIPs; liquid-liquid extraction, LLE; solid-phase extraction, SPE; molecularly imprinted polymers, MIPs; nanoparticles, NPs; transmission electron microscopy, TEM; lemon yellow, Ly; chrysoidine, Chd; orange II, Org; sunset yellow, Sy; tetraethyl orthosilicate, TEOS; ethylene glycol dimethacrylate, EGDMA; azobisisobutyronitrile, AIBN; methacrylic acid, MAA; 3-methacryloxypropyl trimethoxysilane, γ-MPS; non-imprinted polymers, NIPs.

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essary. As a result, sample pretreatment becomes time-consuming and suffers from a lack of selectivity due to analyte loss.

Molecularly imprinted polymers (MIPs) are attractive synthetic materials that are customized for a given target and possess specific selectivity and high affinity [11,12]. Other MIP advantages include ease of preparation, low cost, physicochemical stability [13], etc. At present, MIPs are widely applied in chromatography [12,13], catalysis [14,15], chemical sensing [16,17], drug delivery [18], and solid-phase extraction [19,20]. However, MIPs fabricated by the conventional process of bulk or precipitation polymerization have limited practical applications due to certain inherent defects, such as irregular shapes or sizes, and a heterogeneous distribution of binding sites [21,22]. These defects lead to most binding sites being embedded in the bulk of the material. Consequently, these internal binding sites are hardly accessible and result in slow mass transfer. Hence, the reproducibility process would not consume plenty of eluent but also be exhausting due to the difficulty of template removal.

Recently, surface imprinting techniques based on a variety of supports, such as alumina membranes [23], TiO_2 [24], SiO_2 [25–30], Fe_3O_4 [31,32], Fe_3O_4@TiO_2 [33], Fe_3O_4@SiO_2 [34], and Fe_3O_4@chitosan [35] have been exploited. The generated recognition sites are mainly distributed on the imprinted layer on the surface of the supports, helping to overcome or alleviate the problem of mass transfer. Chen et al. [26] prepared a hollow MIP shell with a ca. 40 nm thickness, displaying high monodispersity and a uniform spherical shape. The imprinted shell could selectively separate estradiol in spiked milk samples with high recoveries of 97.0% and 94.8%. Sadeghi et al. [27] prepared molecularly imprinted sol-gel polymer surfaces for solid-phase extraction of florfenicol from meat samples. The maximum adsorption capacity and equilibrium adsorption time were found to be 64.9 mg g^{-1} and 250 min, respectively. However, the great challenge is still posed by the existence of heterogeneous binding sites on most molecularly imprinted surfaces, restricting their actual application in various aspects [28].

The latest studies indicate that more thinly imprinted shells could result in remarkably improved accessibility of the recognition sites and elevated binding capacity and kinetics. For example, Fu et al. [29] synthesized protein-imprinted polymer nanoshells (ca. 16 nm thick) on vinyl-modified silica nanoparticles (NPs) by using lysozyme as a model protein template and a Cu^{2+} chelating complex as a functional monomer. The imprinted particles reached equilibrium adsorption within 40 min, with maximum lysozyme binding capacities as high as 49.6 mg g^{-1}. Subsequently, these authors have also reported an enhanced protein-imprinted layer (nanosized thickness) on magnetic chitosan submicrospheres, which reached selective rebinding capacities of up to 129.8 mg g^{-1}, and the equilibrium adsorption time for lysozyme was shortened to ca. 5 min [35]. Additionally, these homogenously distributed nanoshell binding sites showed monomolecular layer adsorption for analytes, which may be a vital contribution to fast mass transfer.

Recently, RhB-imprinted polymer surfaces have been successfully used for the extraction and determination of rhodamine B in food matrices. Sun et al. [30] prepared particles with RhB-imprinted surfaces using γ-MPS-modified silica gel as carrier material. The results showed that the binding sites of the imprinted shell were heterogeneously distributed (according to Scatchard analysis), with the equilibrium adsorption time exceeding 2 h. Su et al. [31] synthesized a core-shell magnetic RhB-imprinted polymer, which was used as a solid-phase extraction material for the determination of rhodamine B illegally added to foods, with recoveries in the range of 74.87–101.6%. The Fe_3O_4@MIPs showed fast adsorption equilibrium (ca. 30 min) and significant selectivity ($\alpha = 1.88$). However, the Scatchard analysis for Fe_3O_4@MIPs did not result in a single linear curve, but consisted of two linear parts with different slopes ($r > 0.97$). The results showed that the binding sites were also heterogeneously distributed in the Fe_3O_4@MIPs shell. Ji et al. [32] reported structurally similar Fe_3O_4@MIPs, which were used as dispersed solid-phase extraction adsorbents for wine samples. The method had a short analysis time (ca. 30 min) and relatively high selectivity for rhodamine B. These properties, involving binding site distribution, elution of template, binding capacity, and mass transfer are principally dependent on the molecularly imprinted shell thickness. To the best of our knowledge, no reports discussing the relationship between imprinted shell thickness and imprinted efficiency for all known core-shell RhB-imprinted polymers exist.

Herein, we report a rapid, versatile, controllable, and economical approach to synthesizing new polymer nanoshells with RhB-imprinted surfaces of desired homogeneity based on relatively low-cost vinyl-modified SiO_2 NPs. The RhB-imprinted microspheres were characterized by Fourier transform infrared spectroscopy, transmission electron microscopy (TEM), and X-ray diffraction. The resulting RhB-imprinted polymers (RhB-MIPs) exhibited faster kinetics, selective affinity for the title template, and satisfactory reproducibility. Additionally, the adsorption performance and selectivity of the sorbents for five different azo dyes have been systematically evaluated. The RhB-MIP-assisted extraction coupled with HPLC was successfully applied to the preconcentration and detection of RhB in red wine and beverage samples at trace levels. Compared to previously reported RhB-imprinted materials, the MIPs showed a much shorter equilibrium adsorption time, higher target selectivity, and better durability, accounting for the rapid separation and high measurement sensitivity.

2. Experimental

2.1. Chemicals and materials

Lemon yellow (Ly), chrysoidine (Chd), orange II (Org), sunset yellow (Sy), and RhB were purchased from Aladdin Reagent Co., Ltd. (China). Tetraethyl orthosilicate (TEOS) and ethylene glycol dimethacrylate (EGDMA, ≥98%) were obtained from Aladdin Reagent Co., Ltd. (USA). Azobisisobutyronitrile (AIBN) was obtained from Kelong Chemical Co., Ltd. (Chengdu, China). Methacrylic acid (MAA) was acquired from Guangfu Fine Chemical Research Institute (Tianjin, China). 3-Methacryloxypropyl trimethoxysilane (γ-MPS) was purchased from Xiya Reagent Co., Ltd. (Chengdu, China). Ammonium acetate was purchased from Shisihewei Chemical Co., Ltd. (Shanghai, China). Analytical grade anhydrous toluene, acetonitrile, methanol, ethanol, and acetic acid were exclusively purchased from Zhiyuan Chemical Reagent Co., Ltd. (Tianjin, China). HPLC grade acetonitrile and methanol were purchased from Fisher (Pittsburgh, PA, USA). Distilled and ultrapure water was purified using a Milli-Q system (Millipore Corporation, U.S.). All chemicals were sourced from commercial suppliers and used without further purification.

2.2. Instrumentation and conditions

FTIR spectra were measured in KBr on a Vertex70 instrument (Bruker, Germany). The morphology of the imprinted and non-imprinted nanoparticles was characterized by TEM (JME-1230, operating at 100 kV). UV–vis spectra were recorded on a UV-2450 spectrometer (Shimadzu, Japan). Chromatographic separations and analysis were performed on a Waters ACQUITY UPLC H-class system (Waters, USA) equipped with an HSS T3 column (2.1 mm × 150 mm) and a photodiode array detector.

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