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Research paper

Bifunctional monomer molecularly imprinted sol-gel polymers based on the surface of magnetic halloysite nanotubes as an effective extraction approach for norfloxacin

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ABSTRACT

An effective magnetic surface imprinted polymer with high adsorption ability and selectivity has been designed. Three magnetic halloysite nanotubes combined with molecularly imprinted polymer (MMIP) composites were fabricated. Halloysite nanotubes (Hal nanotubes) were us as supporting matrix, norfloxacin (NOR) as template molecules, Aminopropyltriethoxysilane (3-APTES) and Methacryloxypropyltrimethoxysilane (MTEOS) used as monomers and tetramethyl orthosilicate (TEOS) as cross linker through a one-pot sol-gel polymerization. The resulting MMIP were characterized by various techniques. The adsorption isotherms, adsorption kinetics and selective recognition of MMIP were investigated in detail. The imprinted polymers with bifunctional monomer possess the highest adsorption capacity (312.08 $\mu g \cdot mg^{-1}$) and the best select factor (5.41). After optimization of solid phase extraction (SPE) condition, imprinted polymer with bifunctional monomer possess the best extraction ability and can be successfully applied into the extraction of norfloxacin in lake water. In addition, the SPE-ultraviolet method established possesses good accuracy and precision. Hydrochloric acid (9:1/v:v) could be used as the best elution and the magnetic imprinted polymer could be reused for at least seven times.

1. Introduction

Nowadays, SPE is considered as the gold standard among all conventional sample enrichment techniques (Samanidou et al., 2016; Ansari and Karimi, 2017) used for the cleanup of complex matrices and preconcentration of the target analyte (Fang et al., 2013). A cleaner extract that is free of matrix interferences is the main goal of the SPE. However, the traditional SPE adsorbents (C8, C18, etc.) based on nonselective hydrophobic reaction not only can retain target compounds but also can concentrate other compounds present in the matrix (Ansari and Karimi, 2017), which may interfere with the analysis. Thus, the lack of selectivity arises, that causes co-extraction of matrix interference components with a target analyte (Soledad-Rodriguez et al., 2017). Hence, an adsorbent with high selectivity and specificity for the target analyte such as MIP is required to overcome this problem.

Molecular imprinting is a well-established and simple technique for synthesizing molecularly imprinted polymers (MIP) with specific molecular recognition properties (Wang et al., 2017a). MIP is fully synthetic polymeric materials produced around the target molecule (template). To generate imprints with certain selectivity, a prepolymer is simply polymerized in the presence of the desired target molecule. When the polymer is cured two things happen simultaneously. First, functional groups in the prepolymer orient towards their counteracting partners in the template. Second, the polymer is cross-linked resulting in “freezing” the orientation of the functional groups. This orientation remains even when the template is washed away from the material (Schirhagl, 2014), leaving behind cavities suitable to recognize and rebind the molecule again. They can be selective for both shape and chemical functionality (Poma et al., 2015). Owing to the chemical, mechanical, and thermal stability together with high selectivity for the template molecules (Poma et al., 2013), MIP have been utilized for a wide variety of applications, including in chromatography, solid phase extraction(Wang et al., 2017b; Barciela-Alonso et al., 2017), drug-controlled release(Zaidi, 2016; Dramou et al., 2013), and sensor devices

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(Bou-Maroun et al., 2017; Zamora-Galvez et al., 2016), where the MIP act as a ‹artificial antibodies›. By preparing the MIP film on a solid-support substrate, Surface imprinting has been considered as one of the most promising strategies to improve mass transfer and reduce permanent entrapment of the template (Luo et al., 2017; Barati et al., 2017). In previous investigations, SiO_2 (Li et al., 2013), GO (Luo et al., 2014, 2017), CNTs (Xiao et al., 2013) and Fe_3O_4 (He et al., 2014) have been widely used in the surface-imprinting process.

Halloysite nanotubes (Hal nanotube) are clay aluminosilicate mineral. Their deposits are found in China, Australia, USA, New Zealand, Brazil and France (Leporatti, 2017). Halloysite are structurally and chemically similar to those of kaolinite, and has a molecular formula of $Al_2Si_2O_5{\cdot}(OH)_4{\cdot}nH_2O$, possessing a naturally occurring unique tubular structure on the nano-scale which has a similar geometry to carbon nanotubes (Pan et al., 2011; Shu et al., 2015). The length of halloysites is within a micrometer range (0.4–1 μm), inner lumen diameter is 10–70 nm and outer (overall) diameter is 20–200 nm (Yuan et al., 2015). The majority of the external morphology of Hal nanotubes consists of siloxane groups (Si—O—Si); whereas, there are many functional groups (hydroxyl group, Al—OH) lining the internal surface of Hal nanotubes (Peixoto et al., 2016; Yang et al., 2016; Pandey et al., 2017). Recently, Hal nanotubes have gained growing interest because of their strong interactions, stability under acidic conditions, lack of swelling, and large surface area (Pan et al., 2012a,b). In contrast with other nanosized materials, especially carbon nanotubes, Hal nanotubes are readily obtainable, much cheaper and possessing large reserves in China (Lvov and Abdullayev, 2013). Therefore, Hal nanotubes could be a promising candidate for the nanosized support.

Magnetic nanoparticles (MNPs) have been broadly used as adsorbent due to their strong magnetism (Ben Aissa et al., 2017). In order to pass up the aggregation of MNPs and obtain a high specific surface area, the combination of inorganic materials (halloysite nanotubes) with magnetic nanoparticles has recently attracted immense interest to produce magnetic clay nanotubes (Xie et al., 2011; Zhang et al., 2012, 2014), which possess both the easy separation ability and excellent mechanical properties. Combining the advantages of imprinted polymer and magnetic halloysite nanotubes, efficient adsorbent materials with specific recognition ability, large adsorption capacity and magnetic separation would be designed. It is quite expected that magnetic halloysite nanotubes would also be a promising support for preparing surface imprinted materials. Magnetic halloysite nanotubes based MIP composites have been successfully produced in recent years (Pan et al., 2011, 2012a,b; Dai et al., 2014; Zhu et al., 2015; Xie et al., 2016). The resulting magnetic Hal nanotubes/MIP composites exhibited not only faster adsorption and desorption dynamics, but also higher binding capacity. However, the obtained magnetic Hal nanotubes/MIP composites are generally dispersed in solution and their recovery after adsorption process still remains a concern.

The sol-gel process, which has been a method for the production of ceramic materials for decades (Tsai and Syu, 2011) is becoming more important because it provides rather convenient and simple means to incorporate heat-sensitive materials including organic molecules and active proteins (Lofgreen et al., 2011). The reasons to use sol-gel silica for molecular imprinting are numerous. The simple fabrication process, eco-friendly reaction solvent (aqueous solution), mild conditions (Chang et al., 2016). Sol-gel technology provides a simple way to produce a three dimensional silicate network with high porosity, excellent physical rigidity due to the highly cross-linked structure of silica, which allows the creation of delicate imprint sites with the potential for a high selectivity compared to more flexible organic polymers, chemical inertness and thermal stability (Deiminiat et al., 2017). This makes it a robust matrix for a wide variety of applications and chemical environments. Silica exhibits minimal swelling in the presence of solvents. This attribute, too, allows it to maintain the shape and size of imprint cavities. Silica is also remarkably compatible with aqueous and biological systems and is able to successfully encapsulate enzymes and antibodies without damaging their activity. This template fidelity is likely a major contributing factor to the success of early silica imprinting work (Lofgreen and Ozin, 2014). In the process of MIP synthesis, in order to strengthen the multi-noncovalent interactions between the template and functional monomers, bifunctional MIP is the best choice due to their high adsorption capacity and selectivity (Wu et al., 2016).

This work aims to develop a novel surface imprinting technology. The silylating agent was applied in order to form more rigid cavities with the sol-gel method. Adsorption performance was further studied with the help of Scatchard model and intra-particle research combined with adsorption isotherm and kinetic process. MMIP applied in solid phase extraction coupled with UV (MISPE-UV) method has been established after optimization of conditions, and validated for the detection of norfloxacin in lake waste water.

2. Experimental parts

2.1. Materials and instruments

Halloysite clay was supplied from DanjiangKou, China. Norfloxacin, Ethylene glycol dimethacrylate (EGDMA), Aminopropyltriethoxysilane (3-APTES), Methacryloxypropyltrimethoxysilane (METOS), and tetramethyl orthosilicate (TEOS) were obtained from Aladdin Industrial Corporation (Shanghai, China). Ferric chloride hexahydrate (Fe^{3+}) and dimethyl sulfoxide (DMSO) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ferrous sulfate heptahydrate (Fe^{2+}), ammonium hydroxide ($NH_3{\cdot}H_2O$) and acetic acid were obtained from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). All these chemicals and solutions used for an analytical grade.

UV–visible spectrophotometer (UV-1800) and Fourier-transform infrared spectrophotometer (FT-IR-8400S) were purchased from Shimadzu (Kyoto, Japan). FEI Tecnai G2F20 transmission electron microscope (TEM) was used to characterize the morphology of the materials. The magnetic properties were tested by an LDJ 9600-1 vibrating sample magnetometer (VSM) operating at room temperature with applied fields up to 10 kOe.

2.2. Synthesis of magnetic halloysite nanotube

The magnetic Hal nanotubes support was synthesized according to the previous reported method (Fizir et al., 2017; Riahi-Madvaar et al., 2017). Crude Hal nanotubes were sieved and then dried at 100 °C in an oven for 12 h. 2.5 g of halloysite powder was suspended in 150 mL of deionized water by sonication for 15 min, and then 4.8 g of $FeCl_3{\cdot}6H_2O$ and 2.4 g of $FeSO_4{\cdot}7H_2O$ were added. The mixture was stirred for 10 min at 60 °C in N_2 atmosphere. Subsequently, 50 mL (25%) of ammonia solution was added drop wise into the mixture solution. The addition of the base to the Fe^{2+}/Fe^{3+} salt solution resulted in the immediate formation of black precipitates of magnetic Hal nanotubes. Then, the resulting reaction mixture was aged for 4 h at 70 °C. The magnetic Hal nanotubes were separated by an external magnetic field and washed for several times sequentially with water. Finally, the magnetic Hal nanotubes were dried in vacuum at 60 °C.

2.3. Synthesis of the MMIP

In a typical procedure, 0.12 g of magnetic Hal nanotubes and NOR were dispersed in 100 mL of ethanol and subjected to ultrasonication for 30 min. 310 μL APTES (or METOS) and 1.4 mL TEOS were then added to the above dispersion and the pH of the mixture was adjusted to ~9.3 with $NH_3{\cdot}H_2O$ (28 wt%). The obtained reaction solution was subsequently stirred for 24 h at room temperature. The resulting product was collected by a magnet and washed with water: hydrochloric acid (9:1/v:v) for several times to extract the template until the NOR molecules could not be detected. The final MMIP composite was