



Contents lists available at ScienceDirect

# Journal of Chromatography A

journal homepage: [www.elsevier.com/locate/chroma](http://www.elsevier.com/locate/chroma)



## Mixed hemimicelle solid-phase extraction based on magnetic halloysite nanotubes and ionic liquids for the determination and extraction of azo dyes in environmental water samples

Wei Liu<sup>a</sup>, Meriem Fizir<sup>a</sup>, Fan Hu<sup>a</sup>, Ang Li<sup>a</sup>, Xuanhong Hui<sup>a</sup>, Jun Zha<sup>b,\*</sup>, Hua He<sup>a,c,d,\*\*</sup>

<sup>a</sup> Department of Analytical Chemistry, China Pharmaceutical University, 24 Tongjia Lane, Nanjing 210009, China

<sup>b</sup> Vocational and Technical College of Guizhou Minzu University, Guiyang, Guizhou 550025, China

<sup>c</sup> Key Laboratory of Biomedical Functional Materials, China Pharmaceutical University, Nanjing 210009, China

<sup>d</sup> Key Laboratory of Drug Quality Control and Pharmacovigilance, China Pharmaceutical University, Ministry of Education, 639 Longmian Avenue, Nanjing, 211198, Jiangsu Province, China

### ARTICLE INFO

#### Article history:

Received 30 January 2018

Received in revised form 26 March 2018

Accepted 27 March 2018

Available online xxx

#### Keywords:

Magnetic halloysite nanotubes

Ionic liquid

Mixed hemimicelles

Azo dyes

Solid phase extraction

### ABSTRACT

An effective and greener mixed hemimicelles magnetic solid phase extraction (MHMSPE) based on magnetic halloysite nanotubes (MHNTs) and ionic liquid (IL) is developed for the simultaneous enrichment and determination of anionic azo dyes in a spiked environmental water sample. In this MHMSPE, the formation of C<sub>16</sub>mimBr with mixed hemimicelles on the surface of MHNTs leads to the retention of analytes by strong hydrophobic, p-p and electrostatic interactions. This MHMSPE technique combines the advantages of MHNTs and mixed hemimicelles. Zeta potential data demonstrated that mixed hemimicelles were formed in [C<sub>16</sub>mimBr]/[MHNTs] ratios of the range from 0.15 to 1.33. Different important factors affecting the preconcentration of analytes were investigated and optimized by response surface methodology and one variable at a time. Under the optimum conditions, the limits of detection (LOD) for methyl red and methyl orange (MR and MO) were 0.042 and 0.050 μg L<sup>-1</sup> in samples, respectively. The accuracy of the method was assessed by recovery measurements on a spiked sample, and good recoveries 85–87% for MR and 89–93% for MO, with preconcentration factors of 481 and 524, respectively. The low relative standard deviations from 1.6–3.1% for tap water and 2.5–5.4% for lake water was achieved. So far as we know, this is the first development of a mixed hemimicelles SPE based on MHNTs and IL for the extraction of trace anionic azo dyes in environment water samples.

© 2018 Elsevier B.V. All rights reserved.

### 1. Introduction

Industrial wastewater treatment is one of the major current environmental issues. For coloring of textile, cosmetics, and paper, the manufacturing industry still uses water-soluble dyes that are lethal to living organisms. The common of anionic dyes, including azo dyes such as methyl red and methyl orange examined in this present work, could not be biochemical oxidized. Because the degradation of azo dyes under anaerobic conditions produces aromatic amine, *o*-toluidine or aminobiphenyl type compounds,

which have been prohibited due to their toxicity and carcinogenicity [1]. Therefore, they are removed from wastewaters by physical or chemical treatment. One of the most valuable and inexpensive methods for removal of dyes out of wastewaters is solid-phase extraction (SPE) with inorganic or organic sorbents of natural or synthetic origin, such as activated carbon (AC) [2], silica beads, zeolites [3] and clay nanotubes [4].

Halloysite nanotubes (HNTs) is clay aluminosilicate mineral which chemical properties are similar to the structure of kaolinite. However, halloysite can intercalate a monolayer of water molecules giving a basal spacing near 10 Å. The general stoichiometry of halloysite is Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>.nH<sub>2</sub>O [5], and has a similar geometry to carbon nanotubes [6] with an external diameter of 30–190 nm, lumen diameter of 10–100 nm, and length of about 500–1000 nm [7]. The crystal structure of layered silicate in halloysite are formed by two building blocks: (I) sheets of corner sharing (SiO<sub>4</sub>) tetrahedra and (II) sheets of edge sharing (AlO<sub>6</sub>) octahedral (Fig. 1). On the (SiO<sub>4</sub>) sheets, the tetrahedra apices are all pointing in the

\* Corresponding author at: Vocational and Technical College of Guizhou Minzu University, Guiyang, Guizhou 550025, China

\*\* Corresponding author at: Department of Analytical Chemistry, China Pharmaceutical University, 24 Tongjia Lane, Nanjing 210009, China. fax: +86 025 86185008.

E-mail addresses: [chajun@126.com](mailto:chajun@126.com) (J. Zha), [dochehua@163.com](mailto:dochehua@163.com), [jcb315@163.com](mailto:jcb315@163.com) (H. He).

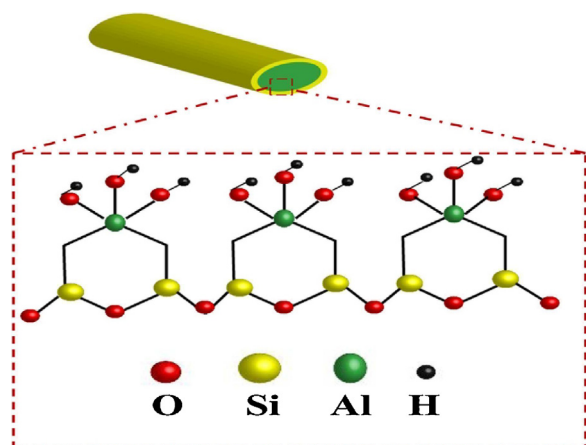


Fig. 1. The structure of HNTs.

same direction. The dispersion ability of HNTs is due to the low density of OH groups on its outer surface and charged properties as well, which provides the possibility for the preparation of HNTs/composites [8]. Recently, HNTs have gained rapidly growing interest due to their strong interactions, stability under acidic conditions, good dispersibility [9], lack of swelling, and large surface area [10]. In contrast with other nanosized materials, especially carbon nanotubes, HNTs are abundantly available in low price [8], and HNT are greener materials for they are not hazardous toward the environment. For these reason, this natural biocompatible nanomaterial could be a promising candidate for the nanosized support and nanoarchitectural composites. Varying degrees of success have been gained in the application of HNTs to extract and preconcentrate a variety of compounds, such as organic pollutants [11–13], drugs [14], metals [15,16], proteins [17]. Due to the dual nature of the pristine HNTs outside is negative and the inner lumen is positive (pH 3–8) [9], adsorption of ionized or surfactant-type analytes onto or inside HNTs surface is mainly driven by electrostatic interaction and ions-exchange. As HNTs is mesoporous and macroporous nanomaterial as well, the adsorption of aromatic or hydrophobic analytes took place into the cavities and pores of HNTs. However, for this kind of analytes HNTs usually gives poor extraction performance for lacking of adsorption capacity [4]. Therefore, chemical modification to increase the uptake of hydrophobic-anionic type analytes is highly desired.

During last years, a potent solid-phase extraction technique termed mixed hemimicelles [18] based on the formation of supramolecular self-assembly sorbents was developed [19]. In this method, sorbents prepared by adsorption of ionic surfactants or ionic liquids such as cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS) or 1-hexadecyl-3-methylimidazolium bromide ( $C_{16}mimBr$ ) on the surface of mineral oxides [20] sorbents, such as alumina [21], silica, titanium oxide [22], graphene oxide GO [23], carbon nanotubes (CNTs) [24] and ferric oxyhydroxides [20,25]. The adsolubilization of analytes with different nature was achieved into different polarity regions formed by hemimicelles and/or admicelles aggregates. Adsolubilization is a phenomenon in which organic compounds can incorporate in the surfactant-adsorbed layer on adsorbents [26,27]. Hemimicelles and/or admicelles provide two kinds of mechanisms for the retention of analytes, hydrophobic or chain-chain interactions for hydrophobic analytes provided by hydrocarbon part of surfactant, while electrostatic interaction or hydrogen bonding is the main mechanism adsorption of the ionic analytes by its polar groups [28]. Numerous significant advantages were gained using hemimicelles in the SPE procedure, for instance, high enrichment factor, low discarding costs, and low solvent usage. Therefore, the mixed

hemimicelles magnetic solid phase extraction (MHMSPE) method is a substitute technique for samples pretreatment.

For large volume samples, the reported mixed hemimicelles assembly SPE method may cause a moderately low extraction capacity and time-consuming because of the comparatively small specific surface area of the micro-particle sorbents used [29]. These limitations could be overcome by applying nanosized material sorbents to SPE for the pretreatment of complex matrix samples, some research groups discovered that nanosized sorbents had excellent extraction capacities [30]. However, some drawbacks of this dynamic extraction mode in SPE column were noted such as high backpressure, making it very complicated to adopt elevated flow rates when the static batch approach was used. Furthermore, the nanosized SPE adsorbents often generated a very low filtration rate [24]. To maintain the advantages of nanosized SPE sorbents and to defeat their defects, the use of magnetic nanomaterials as adsorbents for this kind of SPE is a promising alternative as the enrichment time shortened greatly by the application of an external magnetic field.

Nowadays, magnetic halloysite nanotubes (MHNTs) have attracted great attention in the research community in virtue of their size and physico-chemical properties. In order to obtain high specific surface area and high saturation magnetization, particular attentions have been going to mix iron oxide nanoparticles with halloysite nanotubes (HNTs) for composite preparation, and various MHNTs synthesis approaches have been reported. Yanfang Xie et al. prepared magnetic HNT- $Fe_3O_4$  by co-precipitation method using  $FeCl_3 \cdot 6H_2O$  and  $FeSO_4 \cdot 7H_2O$  as precursors [31]. Jianming Pan et al. used thermal decomposition method to synthesis MHNTs using  $Fe(acac)_3$  as precursors [6]. Same researchers group used a polyol-medium solvothermal method approach to attach  $Fe_3O_4$  nanoparticles onto HNTs. The cations of iron (III) bind the negatively charged HNTs in aqueous solution.  $Fe(OH)_3$  partially transformed into  $Fe(OH)_2$  because of the reductive environment provided by ethylene glycol at high temperature, and finally  $Fe_3O_4$  nanoparticles were formed through dehydration [32]. Jinsong He et al. also used simple solvothermal method to synthesis MHNTs using  $Fe(NO_3)_3 \cdot 9H_2O$  as iron salt [33]. However, the further development of mixed hemimicelles on the surface of MHNTs for SPE of trace amounts of dyes in environmental water remains a challenge. Compared to magnetic graphene oxide (MGO), MHNTs synthesized directly from naturally available HNTs and without any tedious pretreatment procedure or modification which needs time and using hazardous solvents such as preparing GO by hummer method [34]. Regardless to the proprieties of HNTs and its low price, reasons mentioned above are the only motivation that led us to choose MHNTs as nanosized support for mixed hemimicelles.

Mixed hemimicelles SPE based on surfactant coated magnetic materials for determination of dyes have been studied, such as SDS coated  $Fe_3O_4$ NPs to form mixed hemimicelles for the extraction of Rhodamine B and Rhodamine 6G (RB and R6G) in environment water samples [35], and illegal cationic dye in food samples [36]. Moreover, researchers also attempted to apply CTAB coated  $Fe_3O_4$  nanoparticles ( $Fe_3O_4$ NPs) for adsorption of MO dye [37]. These all demonstrated MHMSPE is an excellent method for adsorption and preconcentration in complex matrix samples. However, researches are all devoted to the study of the extraction and enrichment of small volume samples and surfactant of SDS and CTAB has a certain toxicity for it will cause secondary pollution of environmental water samples. Thus, the preconcentration of analytes in large volume water samples and find a greener and effective surfactant applied in MHMSPE is urgently needed.

Room Temperature Ionic liquids (RTILs) are organic salts, usually named as compounds completely consisting of ions with melting point below or equal  $100^\circ C$  [38,39]. They are classified as green solvents because of their unique and novel physicochemi-

Download English Version:

<https://daneshyari.com/en/article/7608219>

Download Persian Version:

<https://daneshyari.com/article/7608219>

[Daneshyari.com](https://daneshyari.com)