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Removal of sudan dyes from water with C_{18}-functional ultrafine magnetic silica nanoparticles

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ABSTRACT

In this study, the new C_{18}-functionalized ultrafine magnetic silica nanoparticles (C_{18}-UMS NPs) were successfully synthesized and applied for extraction of sudan dyes in water samples based on the magnetic solid-phase extraction (MSPE). The extraction and concentration were carried out in one step by blending C_{18}-UMS NPs and water samples. The sudan dyes adsorbed C_{18}-UMS NPs were isolated from the matrix easily with an external magnetic field. After desorption the quantitation of sudan dyes was done by ultra fast liquid chromatography (UFLC). Satisfactory extraction recovery can be obtained with only 50 mg C_{18}-UMS NPs. The effects of experimental parameters, including the amount of the nanoparticles, extraction time, pH value, desorption solvent, volume of desorption solvent and desorption time were investigated. The limits of detection for sudan I, II, III and IV were 0.066, 0.070, 0.12 and 0.12 ng mL^{-1}, respectively. Recoveries obtained by analyzing the six spiked water samples were between 68% and 103%.

1. Introduction

Sudans dyes are kind of coloring additives in fuels, waxes, plastics, floor and shoe polishes [1]. The dyes are harmful to human health. The International Agency for Research on Cancer (IARC) has classified the sudan dyes as category 3 carcinogens [2]. So it is banned in most countries using sudan dyes as additives in food products destined for human consumption at any level. Because of their low cost and the enhancement of products appearance, sudan dyes are still used in food stuffs unfortunately [3,4]. This illegal use is a severe danger for public health. Liu et al. extracted and separated sudan dyes in chilli powder by cloud point extraction [5]. Chailapakul et al. detected sudan dyes in soft drink with electrochemical detection [6]. Zhao et al. extracted sudan dyes in tomato sauce and sausage with molecularly imprinted polymers [7]. Recently, the biological method is widely applied to treatment of dyes in plant effluent. But it is not very effective to remove dyes. In some textile processing plants, the non-adsorbed dyes combined with the dispersing agents were sent to the treatment system [8]. This process may result in an increase of dyes in wastewater. Although dyes are released into the environment from various sources, there are very few researches about the sudan dyes in environment water.

In view of the low levels of sudan dyes in water samples and the complexity of the matrices, it is difficult to determine these compounds directly, so the pre-concentration and cleaning steps prior to their determination become necessary. At present, solid-phase extraction (SPE) is the most popular sample preparation method for isolating and pre-concentrating desired components from the sample matrix [9,10]. SPE has many obvious advantages compared with other extractions, such as simplicity, low consumption of organic solvent and high enrichment factor. In some cases, however, SPE still has some inherent limitations. Due to the limited rate of diffusion and mass transfer, the extraction time is usually very long when applied in the adsorption and separation of contaminant from large volume of environment samples. So it is necessary to develop new SPE method with short extraction time.

The magnetic separation technique based on small magnetic particles was introduced in 1973 and from then on more and more attentions have been paid to its development and application. Magnetic solid-phase extraction (MSPE) was first introduced by Safariková et al. in 1999 [11]. The new mode of SPE was based on the use of magnetic adsorbents or nanoparticles (NPs). The magnetic adsorbents are not packed into the SPE cartridge, but dispersed into the sample matrix. In MSPE, the target analytes from the complicated matrix are pre-concentrated based on the use of magnetic adsorbents, separated from the matrix under an external magnetic field and then readily dispersed into organic phase after removal of the magnetic field. MSPE has been widely applied in many fields including isolation, catalysis and environmental science based on its advantages, such as high extraction yield, large breakthrough volume and easiness of operation [12]. Fe_3O_4 NPs have been used as the most popular adsorbents in MSPE [13,14]. However, it should be point out that pure magnetic NPs (such as Fe_3O_4 NPs) are prone to form aggregates which may alter their magnetic properties and be oxidized, lost their magnetism easily when the pH is below 4.0.

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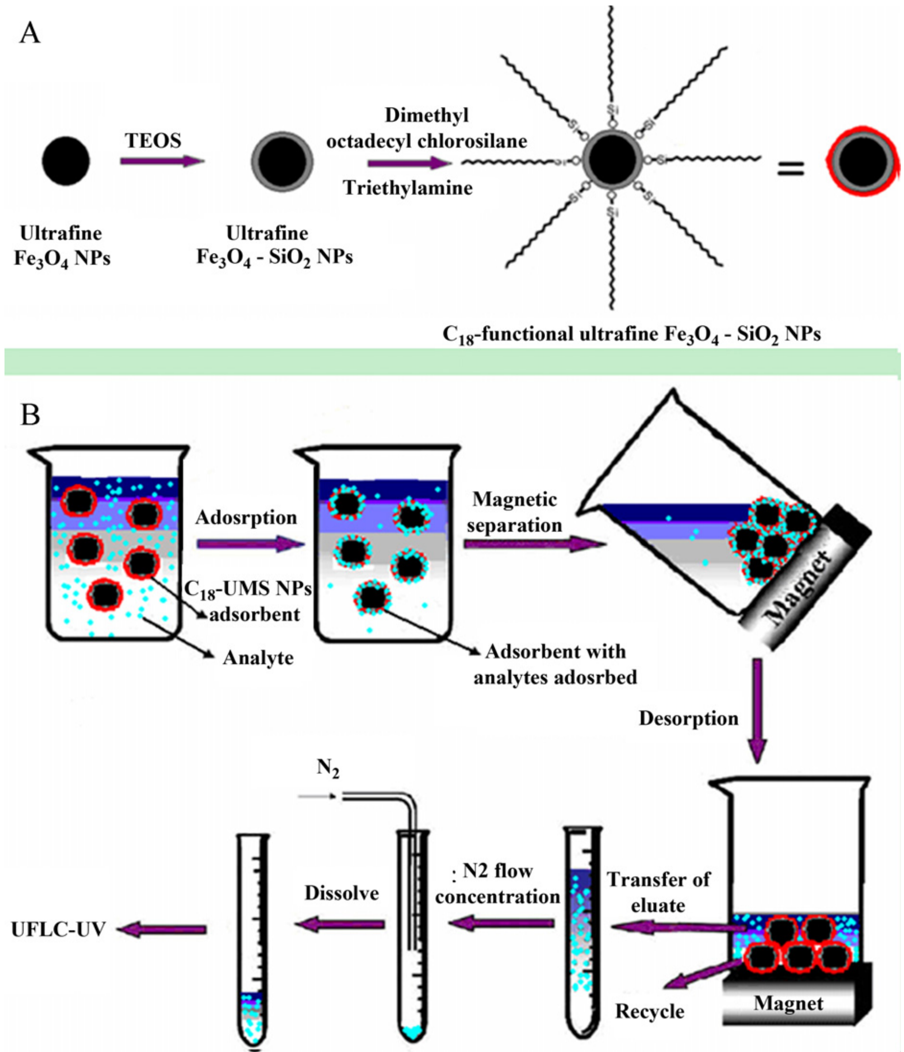

Fig. 1. Synthesis procedure of C_{18}-UMS NPs (A) and enrichment process of sudan dyes (B).

So it is indispensable to coat Fe_3O_4 NPs with a suitable protective coating.

Silica is a kind of the most popular material for protecting Fe_3O_4 NPs because of its stability under acidic condition, high thermal resistance and versatility in surface modification [15]. Furthermore, silica is also abundant and inexpensive. The unique magnetization characteristics of Fe_3O_4 NPs would not sacrificed when Fe_3O_4 NPs were coated with silica [16,17]. Zou et al. reported the extraction of glycopeptides with the superparamagnetic silica particles [18]. Specifically, the inner magnetic Fe_3O_4 NPs core has magnetic property, while the outer silica shows high chemical stability and biocompatibility. Moreover, the surface of magnetic particles coated with SiO_2 can be used to graft various desirable functional groups [19].

In recent years, a few papers have reported on the application of alkoxysilanes modified with magnetic NPs in isolation and purification. C_{18} is most widely used [20,21]. The adsorption ability of magnetic NPs is enhanced after the magnetic NPs are modified with C_{18} group by silylation reaction. C_{18} has been widely used for the pre-concentration of environmental organic pollutants because of its high adsorption ability, excellent stability and long lifetime. Shen et al. reported the application of C_{18} functionalized Fe_3O_4 NPs to the separation of organophosphorous pesticides in cabbage [22]. Ding et al. prepared C_{18} modified Fe_3O_4 NPs and investigated the efficiency of these materials in pre-concentration of polycyclic aromatic hydrocarbons in water samples [23]. These successful studies have intrigued us to prepared C_{18}-functionalized magnetic silica NPs for pre-concentration of sudan dyes from large volume of water samples.

In this study, C_{18}-functionalized ultrafine magnetic silica nanoparticles (C_{18}-UMS NPs) were synthesized by coating ultrafine Fe_3O_4 NPs with silica and subsequently modified with dimethyl octadecyl chlorosilane (OCS). Ultrafine magnetic NPs, Fe_3O_4 NPs, prepared by chemical coprecipitation method in this study have smaller diameter, larger surface area and can be more easily dispersed in aqueous samples compared with those prepared by solvent-thermal method. These magnetic adsorbents were used to extract four kinds of sudan dyes (sudan I, II, III and IV) in water samples based on MSPE. The sudan dyes were analyzed by the ultra fast liquid chromatography (UFLC). To our best knowledge, the application of C_{18}-UMS NPs to separation and concentration of sudan dyes from large volume water samples was reported first time.

2. Experimental

2.1. Chemicals and water samples

The standards of sudan I (content 90%), sudan II (content 88%), sudan III (content 96%) and sudan IV (content 92%), were obtained