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Electrostatically in situ binding of zwitterionic glycine on the surface of MGO for determination of nitrite in various real samples

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ABSTRACT

Zwitterionic dispersive magnetic solid phase extraction (ZI-DMSPE) was developed through in situ binding of glycine on the magnetic graphene oxide, electrostatically. This highly selective sorbent was applied for the determination and preconcentration of trace levels of nitrite in soil, sausage, water samples (tap, mineral, and rain), and vegetables (potato, onion, spinach, radish, and lettuce) prior to its determination by UV–Vis spectrophotometry. The major advantage of the method is the analyte adsorption in both acidic and basic media. The sorbent was characterized by SEM, XRD, EDS, and FT-IR. Several parameters affecting ZI-DMSPE were optimized. Under the optimal conditions, LOD and RSD were obtained 17 ng L^{-1} and 1.3% respectively. Preconcentration factor and sorption capacity of the proposed method were 666 and 238 mg g^{-1} respectively. Accuracy was assessed by comparing results with those obtained by direct determination using ion chromatography and spiked real samples.

1. Introduction

Nitrate and nitrite are the Oxo anion forms of nitrogen that exists widely in the environmental and food products. Nitrate is the more stable form of oxidized nitrogen and not dangerous for human health, but by the chemical and microbial reaction can be reduced to nitrite that is an extremely reactive form of nitrogen (Pandurangappa & Venkataramanappa, 2011). The high concentration of nitrite in food should be strictly controlled because it can react with secondary amines and amides to form carcinogenic N-nitrosamine in the stomach within high toxicity. Moreover, nitrite in the bloodstream combines with hemoglobin to produce methemoglobin (Li et al., 2016). Vegetables and fresh water are the major sources of nitrate, whereas processed meat and animal food products are the main nitrite-containing foods. According to the US EPA and WHO, the maximum contamination levels of nitrite in the drinking water are 1 ppm and 3 ppm, respectively (Xue et al., 2018).

Up to now, many methods have been reported for the monitoring and determination of nitrite including chemiluminescent (Wu, Wang, Lin, Zheng, & Lin, 2016), electrochemical (Zhang et al., 2018), chromatographic (Zhang, Peng, Jiang, Chai, & Barnes, 2018), capillary electrophoresis (Erol, Erdogan, & Onar, 2017) and spectrofluorimetric (Wang, Yu, & Yu, 2012). Each method has advantages and disadvantages. The spectrophotometric methods are the utmost greatly used methods for the determination of nitrate and nitrite due to its inexpensive analytical practicality and simplicity. The spectrophotometric method used for the determination of nitrite originally is the Griess assay. Nitrite is determined by diazotizing with sulfanilic acid under acidic condition and subsequently couples with N-(1-naphthyl) ethylenediamine (NED) to produce a red-violet colored, water-soluble azo dye. After the reaction, the absorbance of the products is proportional to the nitrite concentration (Wang et al., 2017).

Due to the low concentrations of NO_2^- in environmental samples and the matrix interferences, separation and preconcentration step is usually recommended prior to determination. Some sample preparation methods, including liquid-liquid extraction (LLE), liquid-liquid microextraction (LLME), solid phase extraction (SPE) and solid phase microextraction (SPME) have been employed (Hou, Zhu, Ding, & Lv, 2008; Li et al., 2015; Wells, Laplaze, Bennett, & Vernoux, 2013). Most of the traditional sample preparation techniques with less or more limitations in practical applications, that were associated with labor-intensive, operation-tedious, time-consuming and analyte loss, led to undesirable recovery and accuracy. Dispersive solid phase extraction (DSPE) is a kind of SPE that the adsorbent is mixed in a solvent and dispersed into the sample solution containing the analyte. In spite of the low cost and simplicity of DSPE, this method needs filtration or centrifugation that increase the extraction time. Nowadays, dispersive magnetic solid phase extraction (DMSPE), based on the magnetic adsorbent, has

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attracted increasing attention due to its easy operation, time saving and high sorption capacity (Chen et al., 2018). In this method, the analyte is adhered to the magnetic adsorbent by physical or chemical interactions. The solution is exposed onto the strong magnet to separate the magnetic adsorbent from solvent without filtration and centrifugation that resolves the traditional SPE problems (Musa, Wan Ibrahim, Mohd Marsin, Abdul Keyon, & Rashidi Nodeh, 2018). Magnetic Nanoparticles (MNPs) can provide abundant suitability owing to their properties and unique size. MNPs are synthesized by the magnetic material, such as cobalt, nickel, and iron. Fe_3O_4 nanoparticles and other magnetic materials played a serious role in the DMSPE procedure (Yavuz, Tokalıoğlu, & Patat, 2018). Different types of magnetic nanoparticles such as magnetic core-shell composites, Fe_3O_4@SiO_2/Au nanoparticles, silica coated magnetic nanoparticles, etc. have been used as magnetic adsorbent for nitrite determination (Monaco et al., 2017; Rho et al., 2014). Considering the advantages of the DMSPE, the adsorbent used in this method must possess properties such as chemical stability, multiple binding sites, and high specific surface area.

Various adsorbents have been used in DMSPE. Recently, graphene oxide (GO) and carbon nanotube (CNT), has attracted considerable attention as a potential sorbent for separation of trace pollutant in environmental samples. Nitrite measurement has already been done with magnetic multi-wall CNT (MMWCNT) in our research group (Daneshvar Tarigh & Shemirani, 2014). GO is the single layer and special two-dimensional structure that has a specific surface area about two times larger than MWCNT. The main advantage of GO is the variety of oxygen-containing groups (e.g. hydroxyl, carboxyl, and epoxy) that makes it easily modified with suitable functional groups. The major disadvantage of the CNT is the high toxicity of this adsorbent. However, it is difficult to separate GO from aqueous solutions, because of its good water dispersibility and high hydrophilicity (Molaei, Bagheri, Asgharinezhad, Ebrahimzadeh, & Shamsipur, 2017).

Since the GO surface is unselective, competitive adsorption blocking determination of analytes can happen. To improve the sorption capacity and selectivity, a variety of functional groups onto the GO surface is usually accomplished. Modification of the GO surface can be done in two ways, namely non-covalent and covalent. In non-covalent functionalization, The GO surface is modified by hydrogen bonding, Vander Waals forces, and π-π stacking interactions. In the covalent mode, chemical bonding is formed (Pytlakowska et al., 2016). For example, Limei Cui et al. reports EDTA-functionalized magnetic GO for removal of Pb(II), Hg(II) and Cu(II) in water (Cui et al., 2015). Fe_3O_4@GO@ polyamides were designed as the sorbent for determination of lead ions in fish mollusk tissue (Mehdinia, Ramezani, & Jabbari, 2017). Another effective way has coated the surface of the adsorbent with zwitterion (ZI). ZI materials are super hydrophilic materials that contain both cationic and anionic groups. ZI has received major attention today because of the presence of oppositely charged ionic groups on the surface simultaneously. As well as, ZI, in which negative and positive charges are located in near proximity show alternative ion selectivity contrasted to standard cation and anion ion-exchangers (Asiabi, Yamini, & Shamsayei, 2017; Chu et al., 2015).

Amino acids are the best example of zwitterions. Glycine (Gly) is the simplest possible and the only non-chiral amino acid that exists in different forms: cationic fully protonated, natural zwitterion and anionic deprotonated (Ghasemi, Rezvani, Ghasemi, & Graiff, 2018). Gly modified GO (GO-Gly) have been successfully explored as sorbent for highly efficient and selective preconcentration of heavy metal cations and oxyanions i.e. Cu(II), Zn(II), Se(VI), Cr(III) and Cr(VI) (Pytlakowska et al., 2016). In the aqueous solution, Gly is amphoteric. Amphoteric molecules defined as molecules which can either donate or accept a proton (Li, Holmberg, & Bordes, 2013). In this work, Gly was attached on the surface of MGO electrostatically. Due to the amphoteric properties of Gly, nitrite can be adsorbed on the MGO surface in both acidic and basic solutions. So, the proposed method has a simplest synthesis method, which also shows a good performance for nitrite sorption.

Considering the properties of MGO and the simplicity of spectrophotometry, zwitterionic dispersive magnetic solid phase extraction (ZI-DMSPE) was subscribed to develop a specific and valid analytical technique that could be applied to a variety of samples such as vegetables, sausage, soil, and water samples. For this aim, the nitrite ions were adsorbed on the MGO-Gly surface and then washed from the adsorbent's surface with methanol. The sorbent was collected using an external magnetic field. Sulfanilic acid and hydrochloric acid were added to the supernatant solution to form a diazonium salt. Until the azo dye agent (NED) was added, a red-violet color appeared. The main factors affecting extraction efficiency, including pH, amount of the adsorbent, adsorption/desorption time, eluent type and its volume were studied. After DMSPE process, analyte was detected by UV/Vis spectrophotometry and showed good recovery.

2. Materials and methods

2.1. Reagents and chemicals

All chemicals used were of analytical reagent grade, and doubly distilled water was used in the preparation of all solutions in this experiment. Ammonium ferrous sulfate, ammonium ferric sulfate, ammonium hydroxide, hydrochloric acid, methanol, sodium hydroxide, and hydrogen peroxide 30%, sulfanilic acid, NED, and Gly were purchased from Merck (Darmstadt, Germany). Nitrite solution ($1000\,mg\,L^{-1}$) was prepared by dissolving 0.1500 g sodium nitrite in water and diluting to 100 mL. Working standard solutions were prepared by appropriate dilution. Sulfanilic acid (1 g in 100 mL phosphoric acid 5%) and NED (0.1 g in 100 mL water) were used and stored in the darkness at 4 °C. The pH of sample solutions was adjusted by $0.5\,mol\,L^{-1}$ HCl and NaOH solution.

2.2. Apparatus

A UV–Vis spectrophotometer (Perkin Elmer, Lambda 25) was used to measure the absorbance of azo dye. The pH of the aqueous solutions were measured by a digital pH meter (Metrohm, model 781, Herisau, Switzerland) equipped with a glass combination electrode. Magnetic separation was done by a strong magnet with 1.31 magnetic field. A Eurostar20 mechanical stirrer equipped with glassware stirrer (Ika, USA) was applied for stirring of solutions. X-ray diffraction (XRD) measurements were performed using a Philips (Netherland) with monochromatized Cu-K_α radiation. The FT-IR spectra ($400–4000\,cm^{-1}$) were recorded using KBr pellets by Thermo (USA). The MGOs were characterized by scanning electronic microscope (SEM) (TESCAN, MIRA III, Czech Republic). Energy dispersive x-ray spectrometry (EDS) was performed by Oxford ED-2000 (England).

2.3. Synthesis of the materials

GO was prepared according to the modified Hummers method (Han et al., 2012). The MGO was then prepared by the in-situ chemical coprecipitation of Fe^{+3} and Fe^{+2} in the alkaline solution in the presence of GO (Qu, Wang, Kong, Yang, & Chen, 2007). Modification of MGO surface can be performed in two ways, namely non-covalent and covalent. In this study, synthesis of MGO-Gly is based on electrostatic attraction between MGO and Gly. In the first step, the pH of the solution was adjusted at 4 by HCl ($0.5\,mol\,L^{-1}$), after that, 2 mL of MGO suspension (containing 10 mg of the adsorbent in ultra-pure water) was dispersed into the solution. Later on, 1 mL of Gly ($0.1\,mol\,L^{-1}$) was added and the solution agitation for 2 min using a mechanical stirrer equipped with glassware stirrer (1000 rpm). The synthesis procedure is shown in Fig. S1.