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Separation and concentration of natural products by fast forced adsorption using well-dispersed velvet-like graphitic carbon nitride with response surface methodology optimisation

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ABSTRACT

Well-dispersed velvet-like graphitic carbon nitride nanoparticles with a large surface area were prepared and utilized for separation and concentration of bioactive compounds from fruit extracts by fast (20 s) forced adsorption. The large surface area, enhanced non-covalent interactions of this nanoparticle with bioactive compounds and good dispersity in different solvents benefited its application as a good sorbent. To evaluate their adsorption capabilities, these carbon nitride nanoparticles were used for separation and concentration of flavonoids from fruit extracts by a forced-adsorption dispersive solid phase extraction method. The combined use of this nanoparticle and our experimental conditions showed excellent precision (3.6–4.7%) and sensitivity (limits of detection (S/N=3): 0.6–3.75 ng/mL). This research provides an alternative strategy to prepare suitable sorbents for adsorption, separation and concentration of various compounds from different extracts.

1. Introduction

Recently, graphitic carbon nitride (g-C_3N_4), a two-dimensional (2D) material consisting of conjugated planes containing tri-s-triazine repeating units stacked through van der Waals interactions, has attracted a great deal of attention owing to its unique physicochemical properties [1–3]. The strong covalent bonds between the carbon and the nitrogen atoms in g-C_3N_4 impart great physicochemical stability to the material allowing it to withstand acids, alkalis and high temperatures [4,5]. Compared to the complex structure of some sorbents, the simple 2D structure of g-C_3N_4 is beneficial for fast adsorption and desorption of molecules with concurrent high recovery and low solvent consumption [6]. The g-C_3N_4 sheets have a double-sided polyaromatic scaffold structure with a large π-electron system which provides it with a strong affinity for aromatic compounds that are commonly present in drugs, pollutants and biomolecules [7–9]. Although, these unique properties of traditional g-C_3N_4 highlight its potential for use as a sorbent, wide application of this material is restricted by its small specific surface area. The surface area of bulk g-C_3N_4 synthesised by the traditional thermal condensation method is usually less than 5 $m^2\ g^{-1}$. To increase the specific surface area and produce more active sites, various nanoscale forms of g-C_3N_4, such as nanoparticles, nanosheets, nanotubes, nanofibers and nanoporous constructs of g-C_3N_4 have been synthesised [10–14]. However, these synthetic methods rely heavily on the use of hard or soft templates, complicated processes and special instruments. Therefore, the development of a simple and facile approach for the synthesis of g-C_3N_4 with a large specific surface area is of great importance for practical applications. Attempts towards this end have met with a success on the synthesis of a velvet-like g-C_3N_4 (V-g-C_3N_4) via a water-assisted, one-step thermal condensation of urea. The process was free of toxic solvents, templates and expensive chemicals. The large surface area and good dispersity (except in *n*-hexane) (Fig. 1) of V-g-C_3N_4 benefit its applications.

Although V-g-C_3N_4 was obtained with a large specific surface area, its direct use as a sorbent for traditional solid phase extraction (SPE) has several significant problems. This includes the possible escape of miniscule g-C_3N_4 sheets from the SPE cartridge/

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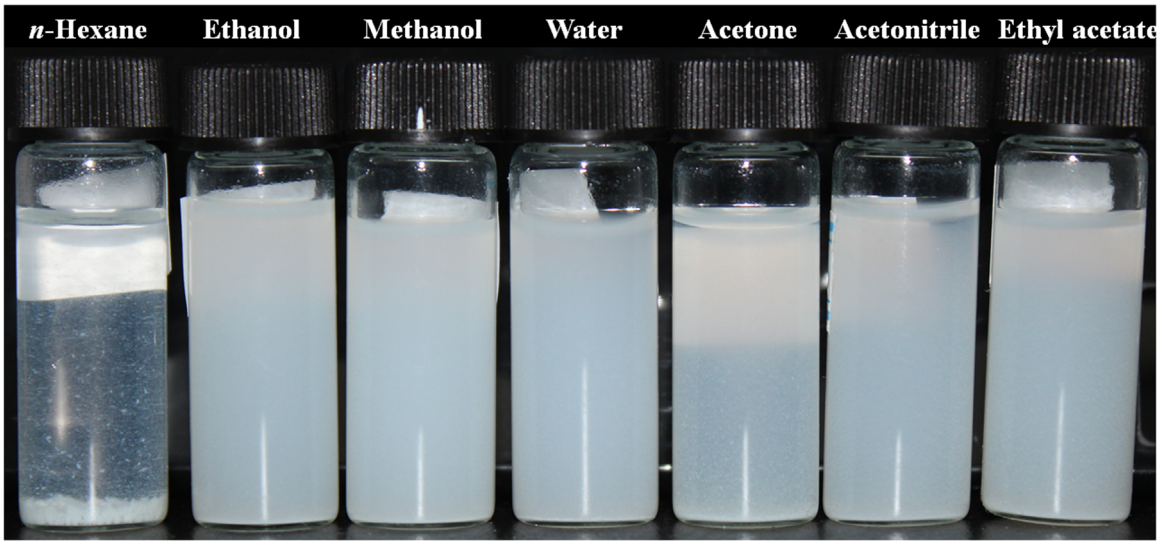

Fig. 1. Dispersity of V-g-C_3N_4 in different solvents.

column, especially under the high pressure conditions prevalent in online SPE systems [15]. On the other hand, dispersive solid phase extraction (DSPE) has many inherent advantages, such as no need to pass the extract through a SPE column, high sample throughput, and smaller utilized volume of organic solvent [16,17]. In DSPE, the sorbent material is added to the sample solution directly and then separated from the sample solution by a simple centrifugation or filtration. The analytes can be directly monitored on the sorbent surface using a spectroscopic technique [18], or they can be conveniently eluted/desorbed for a subsequent analysis of the eluted fraction [19]. In DSPE, besides the sorbent, the solvent used for the extraction of target compounds is also a crucial factor, because the adsorption capacities of sorbents are quite different in different solvents. Most of the research efforts in this area have focussed on the development of efficient sorbents for DSPE, but sadly, studies on examining different solvent polarities for analyte extraction in order to improve the adsorption capacities of sorbents are rare.

In this study, we used V-g-C_3N_4 as a sorbent to achieve fast and efficient DSPE of flavonoids with a special focus on the optimisation of the sorbent and solvent environment. This method was tested by extracting the slightly water-soluble flavonoids from different fruits extracts, which have been used to treat many diseases on account of their powerful antibacterial, anti-inflammatory and antioxidant properties [20–22]. This study exhibited the advantages of adding co-solvents such as water to improve DSPE efficiency by dramatically altering the solvent environment and forcing the analytes to move from the solvent to the sorbent (Fig. 2). Using this method, the flavonoids could be separated and concentrated very efficiently by DSPE with subsequent analysis by HPLC. All related process variables were studied, of which, significant variables were specifically investigated and optimised using the response surface methodology (RSM), which is a well-established statistical technique for optimising complex extraction procedures. This methodology can use quantitative data from appropriately designed experiments to evaluate multiple parameters and their interactions and thereby develop efficient mathematical models of the process [23]. As a result, a simple and efficient method was established for the separation and concentration of natural products. In more general terms, these results could contribute to the development of alternative strategies to improve the efficiency of DSPE processes.

2. Experimental

2.1. Chemicals

Melamine (> 99.0%), urea (99%), quercetin (≥ 98%), myricetin (≥ 98%), kaempferol (≥ 98%) and apigenin (≥ 98%) were obtained from Aladdin Industrial Inc. (Shanghai, China). Distilled water was filtered using a vacuum pump (Division of Millipore, USA) and a filter (HA-0.45, Division of Millipore, USA) prior to use. All the other solvents used were of HPLC or analytical grade.

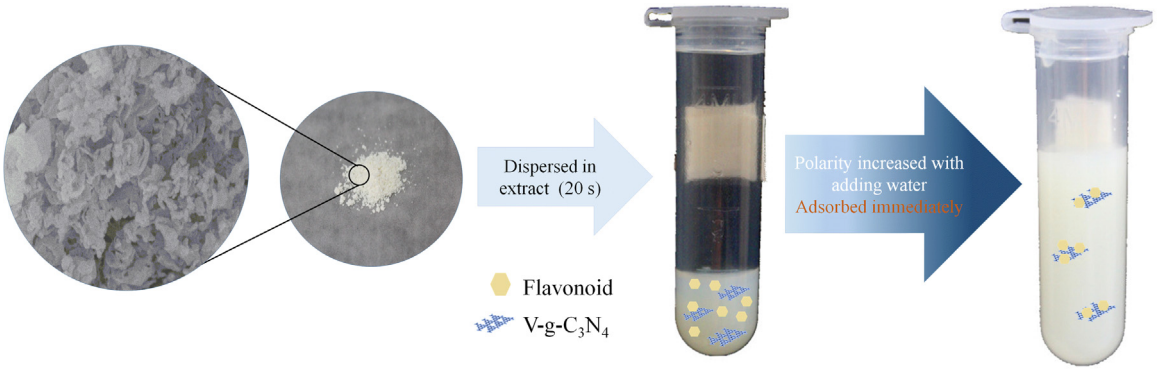

Fig. 2. Scheme of fast forced adsorption.