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Preparation of size-controlled magnetite nanoparticles with a graphene and polymeric ionic liquid coating for the quick, easy, cheap, effective, rugged and safe extraction of preservatives from vegetables

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ABSTRACT

Size-controlled magnetite nanoparticles (Fe_3O_4) with 200–1000 nm were synthesized by co-precipitation method. Then Fe_3O_4@SiO_2@G@PIL was synthesized and used as modified QuEChERS adsorbent for the determination of preservatives in vegetables. The size of about 200 nm of Fe_3O_4 in Fe_3O_4@SiO_2@G@PIL was selected as optimum size to clean-up. It not only exerted the nanometer features of magnetic nanoparticles, but also displayed the large specific surface area of graphene (G) and the solvent effects of polymeric ionic liquids (PILs). Various experimental parameters have been investigated. Under the optimized conditions, a simple, rapid and effective method for the determination of 20 preservatives residues in vegetables was established by modified QuEChERS to gas chromatography/mass spectrometry (GC–MS) analysis. The good linearity with correlation coefficients (R^2) of 0.9972–0.9999 was obtained over the range of 0.02–2.00 mg/L for 20 preservatives. The detection limits of the proposed method for 20 preservatives ranged from 0.82 to 6.64 μg/kg. The adsorbent was successfully applied for extraction and determination of preservatives in vegetable samples, which thus was time-saving with keeping good clean-up performance.

1. Introduction

Synthetic magnetite nanoparticles (Fe_3O_4) have been widely studied in the last decades. The synthetic methods of Fe_3O_4 included hydrothermal synthesis method [1], sol gel [2], chemical co-precipitation method [3–6], ultrasonic chemical reduction method [7], solvothermal and reverse microemulsion [8] and so on. The co-precipitation method was the well known method with its simplicity and productivity. On the other hand, Fe_3O_4 is an attractive material for essential applications such as catalysts, chemical sensors, biological assays, ferrofluids and electrophotographic developers [9] owing to its high coercivity, superparamagnetism, large specific surface area and low toxicity. The unique properties of Fe_3O_4 can be tuned with the help of variation of size and structure. The particle sizes of magnetic nanoparticles can be regulated by systematically adjusting the reaction parameters [10], such as time, speed, temperature, pH and the concentrations of reagents. Therefore the different sizes of magnetic nanoparticles can be fabricated. For example, an average particle size of 8, 12 and 35 nm [11], 11.4 nm [12] and 30–100 nm [13] were successfully synthesized, which were applied for waste water purification, targeted-drug carriers and biomedicine, respectively. Specifically, when Fe_3O_4 particles were used as adsorbent material for purification, their sizes were controlled with small nanometers to provide large specific surface area and favorable dispersibility. When Fe_3O_4 particles were made into drug in vivo, the small particles were better able to circulate in the blood due to very small volumes and the large particles were more easily captured and degraded by the liver and spleen in virtue of strong immunogenic. All these indicated that different sizes of the magnetic nanoparticles had an important effect on their properties. In this study, the effects of different sizes of Fe_3O_4 as magnetic adsorbent on the purification of 20 preservatives were particularly discussed. Graphene (G) is a new allotropic member of carbon with a unique two-dimensional and one-atom-thick sheet structure [14]. It has shown many unusual useful physicochemical properties, including large surface area, fast

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Table 1
The retention times, target ions, calibration curves, LOD, and R^2 for the GC/MS analysis of the compounds.

No.	Compounds	Retention time (min)	Selected ions (*m/z*)	LOD (μg/kg)	Equations of standard curves	R^2
1	Phenyl ether	10.525	170[a], 141, 77	4.30	$Y = 9.4 \times 10^5X + 3963.4$	0.9998
2	Methyl-4-hydroxybenzoate	11.858	152[a], 121, 93	2.34	$Y = 1.6 \times 10^5X - 8859.5$	0.9972
3	Isoprocarb	12.297	121[a], 91, 136	2.56	$Y = 8.1 \times 10^5X - 2704.9$	0.9995
4	2-Naphthol	12.373	144[a], 115, 116	1.06	$Y = 7.5 \times 10^5X - 34508$	0.9982
5	Ethyl-4-hydroxybenzoate	12.518	166[a], 121, 138	6.64	$Y = 9.3 \times 10^4X - 3483.6$	0.9992
6	Propyl-4-hydroxybenzoate	13.620	121[a], 138, 180	2.72	$Y = 7.8 \times 10^5X - 31077.0$	0.9990
7	4-Phenylphenol	14.571	170[a], 141, 115	4.40	$Y = 1.0 \times 10^6X$-22809.0	0.9994
8	Butyl paraben	14.723	121[a], 138, 194	2.25	$Y = 6.8 \times 10^5X - 21512$	0.9994
9	Pentachloronitrobenzene	14.967	295[a], 142, 214	2.29	$Y = 8.5 \times 10^4X + 353.9$	0.9996
10	Pyrimethanil	15.194	198[a], 199, 200	6.23	$Y = 7.0 \times 10^6X + 112782.8$	0.9995
11	Metalaxyl	16.437	206[a], 132, 249	0.82	$Y = 2.8 \times 10^5X - 1010.8$	0.9999
12	Chlorpyrifos	17.140	314[a], 258, 286	1.21	$Y = 1.5 \times 10^5X + 2019.2$	0.9996
13	Triadimefon	17.237	208[a], 210, 181	5.06	$Y = 5.6 \times 10^4X + 359.19$	0.9995
14	Procymidone	18.145	283[a], 285, 255	1.73	$Y = 2.5 \times 10^5X + 4031.9$	0.9996
15	Enilconazole	18.837	215[a], 173, 175	4.60	$Y = 9.2 \times 10^4X - 5439.9$	0.9984
16	Myclobutanil	19.129	179[a], 150, 206	4.37	$Y = 4.6 \times 10^5X + 9825.3$	0.9985
17	Flusilazole	19.161	233[a], 206, 315	2.15	$Y = 9.7 \times 10^5X + 12125$	0.9995
18	Propiconazole	20.458	259[a], 173, 261	1.90	$Y = 1.3 \times 10^5X - 4113.6$	0.9982
19	Tebuconazole	20.717	125[a], 163, 250	1.12	$Y = 3.4 \times 10^5X + 2598.8$	0.9990
20	Prochloraz	23.398	180[a], 308, 310	0.94	$Y = 8.3 \times 10^4X - 4716.0$	0.9988

[a] Quantitative ion, the order of the compound in paper was consistent with the table.

carrier mobility, excellent optical transparency, fracture strength, and thermal conductivity [15]. So it has been widely applied as sorbent. Wen et al. [16] used graphene oxide-based microspheres as the adsorbent of QuEChERS method to extract non-steroidal estrogens from water samples. Shi et al. [17] utilized graphene as the adsorbent of solid-phase extraction (SPE) to analysis the carbamate pesticides in environmental water samples. Li et al. [18] adopted magnetic graphene as the adsorbent of magnetic solid-phase extraction (MSPE) to extract carbamate pesticides in tomato samples. Moreover, G is suitable as an adsorbent for sample preparation because G has a very large specific surface area [19] and can produce a strong π-π electron interactions with organic molecules to reflect a high adsorption capacity [20]. Amine modified G can adsorb pigment and long chain fatty acids [21,22].

Room temperature ionic liquids (RTILs), which are inorganic and organic salts with melting points below 100 °C have attracted increasing attention in the analytical chemistry community, mainly due to its high ionic conductivities, high densities, high polarities, high heat capacities, high thermal and chemical stabilities [23–27]. Specifically, ILs have been widely used for sample pre-treatment including solid-phase extraction [28], magnetic solid-phase extraction [29], liquid–liquid microextraction [30,31] and so on. Traditionally, ILs bonded Fe_3O_4 can be as an adsorbent for extraction and enrichment target compound [32,33]. But, the polymeric ionic liquids (PILs)-bonded Fe_3O_4 combines the properties of ILs, polymers and magnetic to increase their adsorption capacity, which have been applied to analysis and detection. For example, Zheng et al. [34] used PIL-modified magnetic nanoparticles for extraction and enrichment of organophosphorus pesticides from tea drinks. Bi et al. [35] utilized poly(ionic liquid)-bonded magnetic nanospheres as a high-performance sorbent for the pretreatment and determination of phenolic compounds in water samples. Furthermore, the hydrophilic and dispersible of G will be enhanced when the G was coated with PIL. Ding et al. [36] made use of magnetic chitosan and graphene oxide-functional guanidinium ionic liquid composite for the solid-phase extraction of protein.

Quick, easy, cheap, effective, rugged and safe (QuEChERS) is a type of sample preparation method, which was first developed in 2003 to determine preservatives in complex samples [37]. The method has the advantages of high recoveries in preservatives with a wide scope of polarity and volatility, high throughput, low cost and smaller use of organic solvent [38]. The traditional adsorbents of this method are graphitized carbon black (GCB), primary secondary amine (PSA) and C_{18}. In order to find a better adsorbent, magnetic nanoparticles have been used as adsorbent in QuEChERS to save time, G has been used as adsorbent to adsorb pigment and long chain fatty acids, PIL with many advantages also can be attempted to be as adsorbent. When the composite adsorbent of Fe_3O_4@SiO_2@G@PIL was used for the QuEChERS, it could bring more superiority. The first merit of Fe_3O_4@SiO_2@G@PIL was that the complex microspheres could effectively adsorb impurity owing to a strong π-π electron interactions of G and polymer properties of PIL. The second merit of Fe_3O_4@SiO_2@G@PIL was that PIL could improve hydrophilicity of graphene to combine with water soluble impurities and G could reduce the viscosity of IL to get better dispersion. The third merit of Fe_3O_4@SiO_2@G@PIL was that it improved the polymer properties and the possibility of adsorption so that it could be applied more widely.

In this study, the effect of variation of temperature and rotating rate for the sizes of Fe_3O_4 were researched via coprecipitation method. And then the adsorbent of Fe_3O_4@SiO_2@G@PIL was fabricated by chemical synthesis. Next, experimental conditions had been reasonably optimized. The results attested that the proposed method for the analysis of preservatives residues in vegetables has the advantages of simplicity, rapidity and high-efficiency.

2. Experimental

2.1. Reagents and materials

Preservative standards (Table 1, analytic grade ≥99.0% purity) were bought from Dr. Ehrenstorfer GmbH. (Augsburg, Germany). 1-Vinyl-3-octylimidazolium bromide ([VOim]Br) was purchased from Shanghai Chengjie Chemical Co. (Shanghai, China). Graphene oxide powder (GO) was obtained from Jining Leadernano Technology Co., Ltd. (Shandong, China). Ammonium ferrous sulphate ($(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$) and Ammonium iron(III) sulfate dodecahydrate ($NH_4Fe(SO_4)_2{\cdot}12H_2O$) were purchased from Chongqing Beibei Chemical Reagent (Chongqing, China) and Shanghai Chemical Reagent Co., Ltd. (Shanghai, China), respectively. 1-vinyltriethoxysilane (VTES) was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 2,2′-Azobisisobutyronitrile (AIBN) was brought from Chengdu Kelong Chemical Reagent Co., Ltd. (Sichuan, China). Polyvinylpyrrolidone (PVP) was purchased from BSQ Chemistry Technique Co., Ltd. (Shanghai, China).

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