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Graphene quantum dots and the resonance light scattering technique for trace analysis of phenol in different water samples

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ABSTRACT

A novel, highly selective resonance light scattering (RLS) method was researched and developed for the analysis of phenol in different types of industrial water. An important aspect of the method involved the use of graphene quantum dots (GQDs), which were initially obtained from the pyrolysis of citric acid dissolved in aqueous solutions. The GQDs in the presence of horseradish peroxidase (HRP) and H_2O_2 were found to react quantitatively with phenol such that the RLS spectral band (310 nm) was quantitatively enhanced as a consequence of the interaction between the GQDs and the quinone formed in the above reaction. It was demonstrated that the novel analytical method had better selectivity and sensitivity for the determination of phenol in water as compared to other analytical methods found in the literature. Thus, trace amounts of phenol were detected over the linear ranges of 6.00×10^{-8}–2.16×10^{-6} M and 2.40×10^{-6}–2.88×10^{-5} M with a detection limit of 2.20×10^{-8} M. In addition, three different spiked waste water samples and two untreated lake water samples were analysed for phenol. Satisfactory results were obtained with the use of the novel, sensitive and rapid RLS method.

1. Introduction

In general, phenol is an important chemical in industry and agriculture but traces of its toxic residuals are widespread in the environment [1–3], particularly in waters of some developing countries [4]. The current, common methods for trace analysis of phenol, benzodiazepines, aminophenol and similar compounds in different waters include high performance liquid chromatography (HPLC) [5,6], gas chromatography–mass spectrometry (GC–MS) [7], chemiluminesence [8], UV–vis spectrophotometric [9], and electrovoltammetry [10,11], but the associated instruments are relatively expensive to purchase and maintain. The methods can be rather complicated, time-consuming and sometimes require the use of toxic solvents. Consequently, inexpensive and relatively simple methods of analysis for trace amounts of phenols in different waters would be useful. Recently, fluorescent carbon nanomaterials [12], such as fullerene [13], nanodiamonds [14], carbon nanotubes [15] and carbon quantum dots [12], have been noted for their strong fluorescence, chemical and photo-stability as well as low toxicity [12,16]. In particular, graphene quantum dots (GQDs) have been developed from these types of nanomaterial. GQDs are graphene sheets with dimensions less than 100 nm [17]. Their band gap and optical properties can be manipulated by reducing their size to nano-level [18]. Thus, GQDs have strong quantum confinement and edge effects, and their potential applications have been investigated for sensors, bioimaging and electronic devices [19,20]. Analyses in aqueous media using such sensors or devices, have relied on fluorescent GQDs, which have been commonly prepared in two different ways, i.e. "top-down" or "bottom-up" methods. Thus, generally, the "top-down" methods involve: reoxidation [21], electrochemistry [22], hydrothermal graphene oxide [18] and chemical oxidation of carbon fibres [23], while the "bottom-up" methods are mainly concerned with condensation reactions, which proceed via carbonization of a selected organic precursor such as the hexa-peri-hexabenzocoronene (HCB) [24] and dendritic arene [25]. Resonance light scattering (RLS) technique, which is associated with the UV region [26], generally involves the measurement of the light scattered from aggregated analytes or from particles/oligomers of nanometre dimensions. The RLS signal can be readily recorded by coupling and synchronously scanning both the excitation and emission monochromators on a conventional spectrofluorimeter [27–30]. Recently, novel materials, such as nanoparticles and quantum dots (QDs) in association with the RLS technique, have been successfully utilised for analysis of: proteins [27,31], antibiotics [28], viruses [32] and metal ions [26]. However, in all of these studies, some significant interfering substances were found, and these, to some extent, compromised the analytical methodology.

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The aims of this work were (1) to use GQDs and the RLS technique for the analysis of phenol; (2) to investigate the selectivity of this method in order to ascertain if the RLS technique has improved this important quality assurance property for trace analysis of phenol in water, and (3) to apply the developed novel method for quantitative analysis of phenol in spiked waste water samples, which were prepared so as to simulate industrial, pharmaceutical and papermaking waters, respectively.

2. Experimental

2.1. Materials and reagents

Citric acid (CA, 99%, w/w) was obtained from Sigma-Aldrich Co. Shanghai, China. H_2O_2 (30%, w/w), horseradish peroxidase (HPR, more than 300 units/mg) and sodium hydroxide (96%, w/w) were purchased from Aladdin Industrial Corporation Co., Shanghai, China. Phenol was obtained from Shanghai Chemical Co. Ltd., China and was used as the Certified Reference Material (CRM). All the aqueous solutions were prepared with double distilled water. Tris–HCl buffer (0.05 M, pH 7.4), was prepared by mixing 10 mL 0.2 M 2-amino-2-(hydroxymethyl)-1,3-propanediol with 17 mL 0.2 M HCl, and diluted to 50 mL with water. All the reagents were Analytical Grade and were not purified further.

2.2. Instrumentation

The atomic force microscope (AFM) images were made with the use of an AJ-III instrument (Shanghai Aijian Nanotechnology, China) in the tapping mode. Fourier transform infrared spectra (FT-IR) were collected with the use of a Thermo Nicolet 380 FT-IR spectrometer (Thermo Nicolet Co., USA). UV–vis absorption spectra were obtained with the use of an Aglient 8453 spectrophotometer supplied with a 1 cm quartz cell (Aglient instruments, USA). The RLS scattering spectra were collected at room temperature (25.0 ± 0.5 °C) with the use of a Hitachi fluorescence spectrophotometer F–7000 (Hitachi Ltd., Tokyo, Japan) equipped with a 1 cm quartz cell. The slit widths were set at 10.0 nm and 5.0 nm, respectively. All pH measurements were made with an Orion SA 720 digital pH-metre. Zeta potential data were measured on a Zetasizer analyzer (Nano ZS90, Malvern Instruments, UK).

2.3. Preparation of graphene quantum dots

The GQDs were produced with the use of a simple "bottom-up" method in which citric acid was incompletely pyrolyzed [33]. An accurately weighed aliquot (2.0 g) of CA was transferred to a 100 mL round bottom flask, which was then heated to 200 °C in an oil bath. After 30 min, the CA melted to produce an orange liquid. This liquid was then dissolved by dropwise addition of a sodium hydroxide solution (10 mg mL^{-1} NaOH) and vigorous stirring until the pH of the GQD solution was neutral (pH ~ 7.0). This solution was stored at 4 °C.

2.4. Analysis of phenol in the presence of HRP/H_2O_2

Firstly, a standard phenol–HPR–H_2O_2 solution was prepared: 200 μL 30 mM phenol, 300 μL 20 mg L^{-1} HPR and 60 μL 6% H_2O_2 solutions were mixed thoroughly and diluted with distilled water to 1.0 mL. Then, for each sample, a GQDs solution (10 μL) was transferred to a 1.0 cm quartz cell, and diluted with 0.05 M Tris–HCl buffer to give a total volume of 2.50 mL. Following this step, for each such sample, a phenol–HPR–H_2O_2 solution of different concentration was added to the cell. This solution was vigorously stirred, and the RLS spectrum was measured immediately. The RLS data were collected over the 200–550 nm every 2 nm with the use of a spectrofluorometer coupled and adjusted to scan excitation and emission monochromators ($\Delta\lambda = 0$ nm).

2.5. FT-IR spectroscopy of CA, GQDs and GQDs–quinone

The previously prepared GQDs were added to an equimolar quinone solution and allowed to react to form the GQDs–quinone mixture. Equimolar solutions of the CA, GQDs and GQDs–quinone were delivered dropwise with the use of a glass capillary, onto a dry BaF_2 pellet, and allowed to dry. FT-IR spectra of CA, GQDs and GQDs–quinone were recorded in the range of 500–4000 cm^{-1}. The FT-IR spectra were corrected by subtraction of the blank BaF_2 spectrum.

2.6. Analysis of water samples

The main difficulty with the common methods of water analyses has been the presence of interfering substances – they have serious effects on the selectivity of the methods [34].

To investigate this problem, three kinds of sample, including industrial, pharmaceutical and papermaking waste waters, were prepared by mixing standard solutions containing different interfering substances specific to each type of waste water. Thus, industrial waste water contained benzodiazepines, aminophenols, nitrophenols and metal ions as interfering substances, the pharmaceutical waste water samples were spiked with glucose, antibiotics and organic dyes, and the papermaking waste water contained glucose, acetic acid, methanol, sodium sulphite and sodium hypochlorite. In each of these samples, the ratio of phenol:interferent was set at 1:10, 1:50, 1:100 and 1:1000. Such samples were then diluted by double distilled water in a 25 mL flask and stored at room temperature for analysis.

2.7. Analysis of lake water samples

Two lake water samples were collected from different lakes in Nanchang city and their phenol content was determined. The water samples were allowed to stand for 24 h to precipitate any solid impurities. Then, the supernatant of each was filtered through a filter paper (#202, Wohua Co., Hangzhou, China) and collected. The filtrate samples were spiked by standard phenol solutions at different concentrations. Then the samples were diluted with pH 7.4 Tris–HCl buffer and submitted for analysis.

3. Results and discussion

3.1. Morphology of GQDs

The prepared GQDs solutions produced strong light emission when excited in the UV region at 365 nm. The AFM results (Fig. 1A) indicated that the morphology of the GQDs was characterized by nano-sheets with a thickness of ~1.0 nm and a particle size between 8 and 10 nm. These observations were consistent with similar previous GQDs studies [19,33].

3.2. Spectral characterization of GQDs

UV–vis absorption spectrum (200–900 nm) of the GQDs solution (Fig. 1A) has a strong peak at 362 nm, but there was no absorption peak in the case of the CA analyte in the same range. Thus, the presence of the band in the GQDs spectrum confirmed the formation of the quantum dots during the carbonization of CA.

FT-IR spectroscopy provided further evidence for the formation of GQDs (Fig. 1B). The spectrum of the GQDs and the CA solution indicated a C=O stretch vibration band at 1652 cm^{-1} as well as