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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

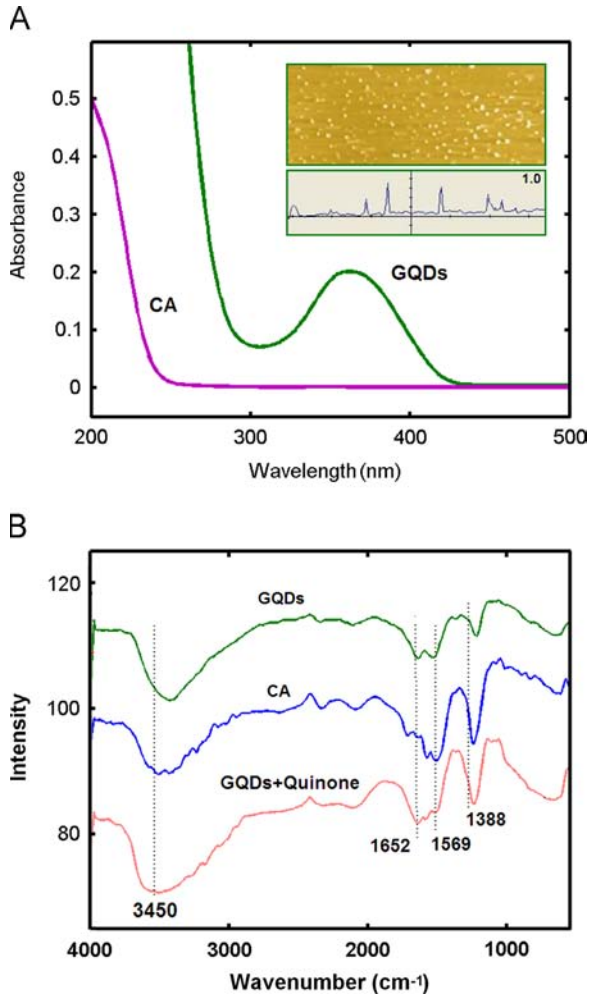

Fig. 1. AFM image of the deposited GQDs from aqueous solutions on freshly cleaved mica substrates. (A) UV–vis spectra of GQDs and CA. Insert: the AFM image of GQDs nano-sheets with a thickness of ~1.0 nm and a particle size between 8 and 10 nm. (B) FT-IR spectra of the GQDs, CA and GQDs–phenol–enzyme reaction systems. BaF_2 pellets were used for FT-IR measurements.

a possible C–H stretching vibration at about 1380 cm^{-1} [33]. This suggested the presence of the carbonyl and C–H groups. Bands present at 1569 cm^{-1} and 3450 cm^{-1} corresponded to the COO^- and OH stretching vibrations. In general, the GQDs and CA spectra were similar, and this indicated that the functional groups remained unchanged during the carbonizing process of the GQDs. Finally, the FT-IR spectrum from the reaction mixture, which included the GQDs–phenol–HRP grouping, showed significant bands at 3450 cm^{-1} (hydroxyl group), as well as a new band at 1652 cm^{-1} (stretching vibration C=O) [33]. These results further confirmed that there was no new substance produced during the reaction process.

3.3. RLS analysis of the GQDs and the phenol–HRP–H_2O_2 systems

The effect of phenol and quinone intermediates on RLS spectral intensity was investigated qualitatively by mixing these compounds with GQDs. The following reactions summarise the associated interactions:

$$\text{Phenol} + H_2O_2 + \text{HRP} \rightarrow \text{Quinone} + H_2O \quad (1)$$

$$\text{Quinone} + \text{GQDs} \rightarrow \text{products(RLS spectrum observed)} \quad (2)$$

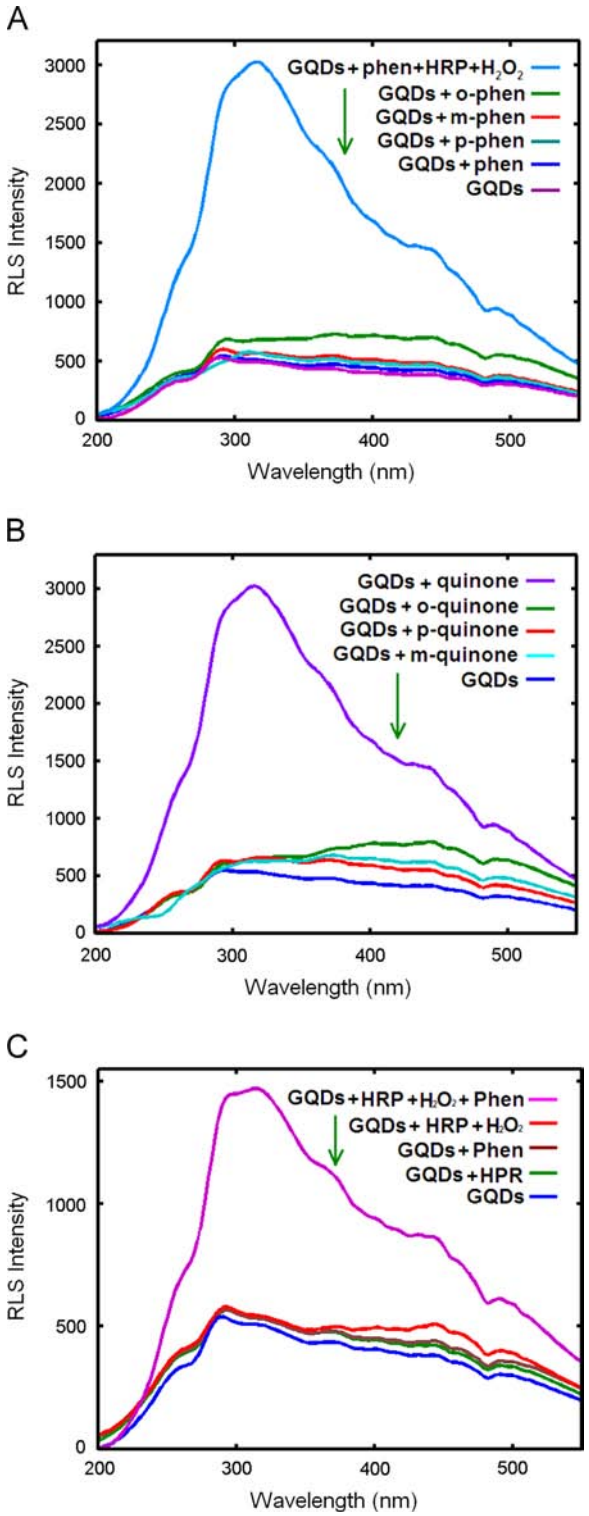

Fig. 2. (A) RLS spectra of GQDs (8 mg mL^{-1}); GQDs with the addition of, *o*-, *m*-, and *p*-phenol isomers (all at 3×10^{-5} M) and benzoquinone intermediates (7.2×10^{-6} M) in pH 7.4 Tris–HCl buffer. (B) RLS spectra of GQDs and phenol (7.2×10^{-6} M), *o*-, *m*-, and *p*-phenol isomers (all at 3×10^{-5} M) respectively in the presence of HRP (6 mg L^{-1}) and H_2O_2 (8.6×10^{-3} M) in pH 7.4 Tris–HCl buffer. (**C**) RLS spectra of GQDs upon the addition of H_2O_2; HPR; H_2O_2–HPR; phenol–H_2O_2–HPR (experimental conditions as (B)).

$$(o, m \text{ or } p)\ \text{Dihydroxybenzene} + \text{GQDs} \rightarrow \text{products}(\textbf{no}\ \text{RLS spectrum}) \quad (3)$$

$$(o, m \text{ or } p)\ \text{Benzoquinone} + \text{GQDs} \rightarrow \textbf{no}\ \text{RLS spectrum} \quad (4)$$

$$HRP/H_2O_2(\text{or } HRP+H_2O_2)+GQDs \rightarrow \textbf{no}\ RLS\ spectrum \quad (5)$$

Thus, RLS spectra were obtained from the first three reactions (Eqs. (1)–(3)) in the 200–550 nm range. Spectra were also obtained with the quinone derivatives: pyrocatechol, resorcinol, and hydroquinone, respectively. First, it was demonstrated that in the presence of the phenol–HRP–H_2O_2 mixture (Fig. 2A), the spectrum was considerably enhanced relative to the spectrum from the GQDs alone. Also, for solutions of just the phenol derivatives, i.e. in the absence of the HRP–H_2O_2, the spectra were not strongly affected. Thus, the sharp increase in the absorption at 310 nm may be attributed to the formation of the quinone intermediates via the enzyme-catalyzed oxidation of the phenol [35]. In general, the intensity of light scattering effects is closely related to the size of the particle formed during a reaction, and is proportional to the square of the molecular volume of the aggregated molecules [36,37]. Thus, in the present work, the formation of the molecular aggregates may result from the electrostatic interactions [31] between the GQDs and benzoquinone – the latter molecule is a well known electron acceptor [35], and the GQDs are electron donors [38]. The zeta potentials of the GQDs and the benzoquinone were −22.2 mV and −14.3 mV, respectively. It is well known that the higher the absolute value of zeta potential, the better is the dispersion of the molecules. The zeta potential of GQDs increased (see Fig. S1, Supplementary Material) from −22.2 to −17.4 mV as 7.2×10^{-6} M benzoquinone was added to an 8 mg mL^{-1} GQDs solution. This indicated that the dispersion of the molecules in the reaction decreased, and the charge of benzoquinone was partly neutralized by the charge of the GQDs. Based on the FT-IR and zeta potential results in this work, and also, the conclusions from the references mentioned above [35–37], the reaction mechanism involved was the result of the electrostatic interaction of GQDs with benzoquinone.

Thus, to investigate the effects of the GQDs and quinone intermediates on the RLS spectral response, three different quinones (Eq. (4)), which could be formed in the presence of enzymes, i.e. pyrocatechol, resorcinol and hydroquinone, were added to the reaction mixture. It should be noted that the concentrations of the quinones were the same as that of phenol, i.e. 1.2×10^{-5} M. The RLS spectral intensity in the presence of these quinones was not significantly enhanced (Fig. 2B). Thus, only the quinone in the presence of phenol appeared to react with the GQDs and induce the light scattering effects. Consequently, a strong RLS band developed in the vicinity of the original absorption [39].

Because the RLS intensity was directly correlated with quinone intermediates, which are related to phenol, the effects of HPR and H_2O_2 on GQDs were investigated separately. First, HPR (6 mg L^{-1}) was added to the GQDs aqueous solution without phenol, and it was noted that the spectral intensity did not increase significantly (Eq. (5)). Similarly, no significant change of spectral intensity was observed with just the 8.6×10^{-3} M H_2O_2 (Fig. 2C). However, when phenol (3×10^{-4} M) and the HRP–H_2O_2 reactants were added to the GQDs, a strong absorption peak was detected. It should be noted that in the case of phenol/quinone interactions only quinone in the presence of GQDs could enhance the light scattering effects.

The above reaction studies suggested that the GQDs-enzyme system is appropriate for the analysis of phenol with the use of the absorption peak at 310 nm.

3.4. Optimization of the experimental conditions

Interactions of GQDs with different molecules [33] indicated that pH was an important factor in determining the optimum RLS spectrum, and hence, the influence of pH was investigated in this work. The synthesized GQDs are stable at neutral pH, but at low or high pH, they may be denatured. Thus, the Tris–HCl buffer in the pH 6.0–8.0 range was investigated, and the results indicated that the intensity of the RLS spectra of the GQDs solution measured over this pH range, was effectively constant. Consequently, a pH 7.4 buffer was chosen as the working medium.

The kinetic effects of HPR and H_2O_2 on the catalytic reaction of phenol were also investigated as a function of their concentrations in the ranges of 3.0–12 mg L^{-1} HPR and 2.8×10^{-3}–1.44×10^{-2} M H_2O_2, respectively. The results indicated that the absorbance spectra increased with increasing HPR and H_2O_2 concentrations, and reached maximum values at 6.0 mg L^{-1} and 8.6×10^{-3} M, respectively. Consequently, 6.0 mg L^{-1} and 8.6×10^{-3} M concentration values were selected for HPR and H_2O_2.

3.5. Phenol analysis with the use of the GQDs and the RLS technique

A series of solutions with different concentrations of phenol was analysed with the use of the RLS technique in the 200–550 nm spectral range and in the presence of HRP and H_2O_2. The results from the calibration curves (at 310 nm) clearly indicated that phenol could be satisfactorily analysed in the 0.60×10^{-7}–2.16×10^{-6} M (Fig. 3A) and 2.40×10^{-6}–2.88×10^{-5} M concentration ranges, respectively (Fig. 3B). The results also showed (Table 1) that

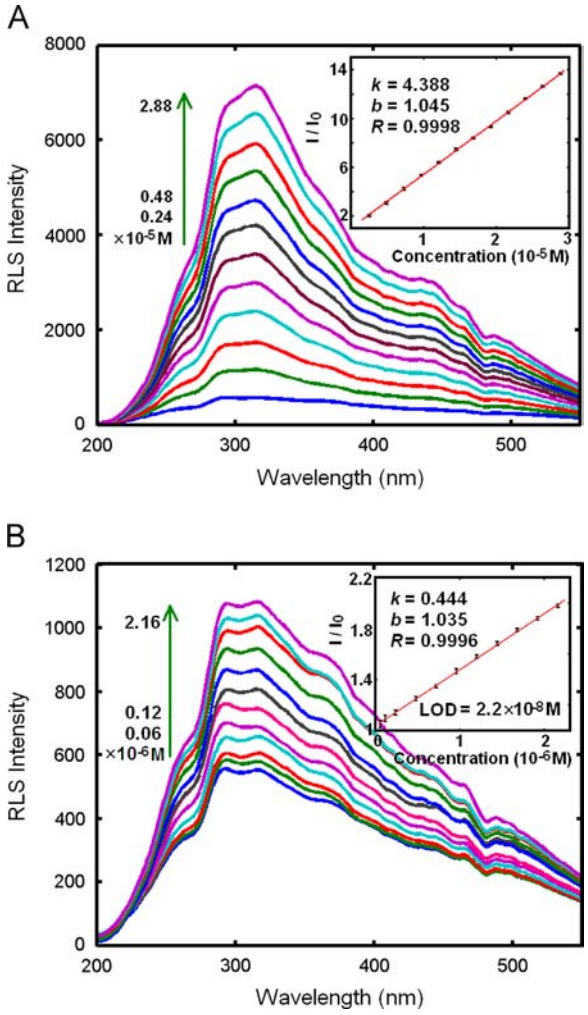

Fig. 3. (A and B) RLS spectra of phenol at different concentrations in the presence of GQDs and the enzyme mixture and recorded at 310 nm. The inserts of (A) and (B) demonstrate the linear relationship between (I/I_0) and the concentration of phenol–enzyme system. Figures of merit (see inserts): *k*, *b* and *R* are the slope, intercept and the correlation coefficient for the two linear plots, respectively; experimental conditions are as described in Fig. 2B).

Table 1
Performance of the novel method for the analysis of phenol in comparison with that from other studies.

Methods	Linear range (mol L^{-1})	LOD (mol L^{-1})	Response time (min)	Refs.
UV–vis	1.6×10^{-5}–2.1×10^{-4}	6.4×10^{-6}	5.0	[9]
Colormetry	1.06×10^{-8}–4.25×10^{-6}	8.93×10^{-9}	6.0	[2]
Electrochemistry	1.0×10^{-7}–1.1×10^{-5}	7.0×10^{-8}	<1.0	[10]
HPLC	1.06×10^{-7}–1.06×10^{-5}	3.19×10^{-8}	<21	[5]
CdTe QDs	5.0×10^{-7}–1.0×10^{-3}	5.0×10^{-7}	1.0	[35]
RLS	6.0×10^{-8}–2.88×10^{-5}	2.20×10^{-8}	< 1.0	This work

the novel analytical method described in this work has a significantly improved method sensitivity in comparison with a previously published spectrophotometric procedure for phenol – linear range: (1.52–17.96 μg mL^{-1}, i.e. $0.16–1.9\times10^{-5}$ M) [9]. The detection limit was found to be 2.20×10^{-8} M with the use of the Miller and Millers' method [40] (insert: Fig. 3B). This detection limit was better than those reported for the electrochemical method coupled with multivariate calibration (7.0×10^{-8} M) [10], and the fluorescence quenching method, which involved the CdTe quantum dots (LOD = 5.0×10^{-7} M) [35]. In addition, it was noted that the LOD of the novel RLS method was better than that reported for the HPLC analysis for the determination of phenol (3.0 ng mL^{-1}) [5]. The calibration set of samples was analysed separately three times and the analytical precision was ±5% (see error bars in insert, Fig. 3). These results together with the ones discussed earlier, indicated that the novel RLS method is particularly useful for the analysis of trace amounts of phenol in water.

3.6. Phenol analysis with the use of the GQDs and the RLS technique – method selectivity

To investigate the effects of common interfering substances on the determination of phenol in waste waters with the use of the novel RLS method, various controlled amounts of the interfering substances were added individually to a standard water sample containing 5.8×10^{-6} M phenol. Thus, different amounts of amino acids, glucose, ascorbic acid, common metal cations including Na^+, K^+, Al^{3+}, Zn^{2+}, NH_4^+, Pb^{3+} and Fe^{3+}, and some common anions, such as SO_4^{2-}, NO^{3-}, Cl^-, Br^- and Ac^-, as well as phenol homologues such as benzodiazepines, aminophenol and nitrophenol, were used for the interference study. The concentration of interfering substances was gradually increased and the criterion for interference was calculated at a relative error of less than ±5%. The results were represented as normalized spectral intensities ($R - R_0/R$; Fig. 4), and they indicated that, in general, the metals ions, did not show any interfering effects even at 100 fold concentration level. The exceptions were Fe^{3+} and Pb^{3+} ions, which may have formed complexes with the unmodified CA molecules in the reaction. There was also no interference effect observed with the common anions, phenol homologues and some benzoquinone compounds. Thus, the novel method for the analysis of phenol in water with the use of the RLS technique and the GQDs–quinone system, demonstrated an improved selectivity when compared with other methods found in the literature [8–10,35].

3.7. Analysis of phenol in different water samples

As described in Section 2.6, three kinds of water sample containing trace quantities of phenol were prepared with compositions,

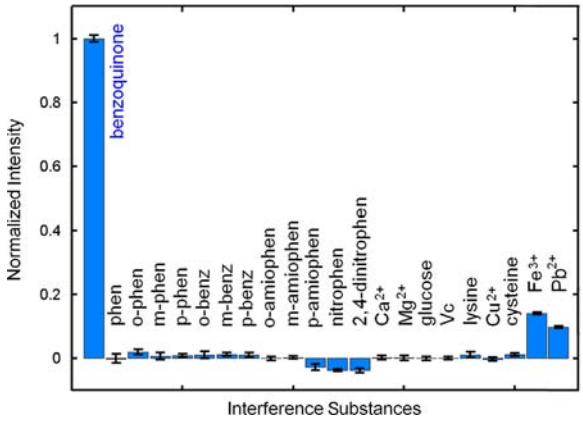

Fig. 4. Normalized spectral intensity ratios at 310 nm representing the effect of various interfering substances (all at 5×10^{-4} M; [phenol]: 5.85×10^{-6} M) on the GQDs in pH 7.4 Tris–HCl buffer. Here normalized intensity = $(R-R_0)/R$, where R and R_0 represent the measured and original RLS intensity, respectively.

Table 2
Analysis of phenol in spiked waste water samples.

Samples (mg L^{-1})[a]	Phenols		
	Added	Found[b]	Recovery (%)
Papermaking water			
Sample 1	0.30	0.30 ± 0.01	98.7
Sample 2	0.30	0.29 ± 0.01	98.0
Sample 3	0.30	0.28 ± 0.02	94.6
Industrial waste water			
Sample 1	0.70	0.68 ± 0.02	97.1
Sample 2	0.70	0.65 ± 0.04	93.2
Sample 3	0.70	0.60 ± 0.04	86.0
Pharmaceutical waste water			
Sample 1	0.60	0.60 ± 0.01	100.6
Sample 2	0.60	0.58 ± 0.02	97.3
Sample 3	0.60	0.56 ± 0.03	93.8

[a] Three waste water samples were spiked. The ratios of interferent: phenol in samples 1, 2 and 3 were 1:10, 1:50 and 1:100, respectively.
[b] The final value was the mean of three determinations ± standard deviation.

which represented industrial, pharmaceutical and papermaking waste waters. These were prepared by adding potentially interfering reagents, which were typical of a particular waste water. The % Recoveries of the phenol analyte in the different water samples indicated the accuracies of the method (Table 2). In general, the analyses of pharmaceutical and papermaking waste water samples produced %Recoveries of the phenol analyte in the range of 93.8–98.7%, suggesting that the novel method produced quite satisfactory results for practical application. On the other hand, for industrial waste waters, the %Recoveries were less encouraging being in the range of 86.0–97.1%. It would appear that the presence of inorganic acids in these samples affected the HRP and GQDs in the reaction mixture. Thus, it is clear that the novel method for analysis of trace amounts of phenol in waste waters may be susceptible to strongly acidic backgrounds of the phenol containing samples. In addition, the performance of the method with pharmaceutical and papermaking waste waters was quite satisfactory. However, the RLS intensity of the three spiked waters was clearly influenced by the concentrations of the interferences, which were more than 100 times than that of the phenol analyte. Thus, when the interference concentrations were high then the catalytic ability of HRP would be significantly inhibited, and almost no changes of the RLS intensity would be observed. Consequently, the performance of this novel method for the determination of phenol was rather better than that of the well

Table 3
Phenol analysis of water samples from two lakes with the use of the novel method.

Samples[a]	Phenol (mg L^{-1})			
	Detected	Added	Found	Recovery (%)
Qingshanhu lake	–[b]	0.70	0.70 ± 0.02[c]	99.4
	–	0.20	0.19 ± 0.04	98.3
Qianhu lake	–	0.70	0.71 ± 0.02	101.2
	–	0.20	0.20 ± 0.05	99.5

[a] Qingshanhu lake water was collected from the eastern part of Nanchang city, and Qianhu lake water was sampled from the Nanchang University campus.
[b] Not detected.
[c] Mean value of three determinations ± standard deviation.

established phenol analytical methods in water with the use of the HPLC techniques [5].

Furthermore, the applicability of the novel method for phenol analysis in water samples was investigated. The results obtained by the standard addition method (Table 3) indicated that the accuracy of the novel method was rather better than that reported for several of the previous, different methods. Also, the LOD value was very low and the average Recoveries of phenol in these two water samples were in the range of 98.3–101.2%.

4. Conclusions

A novel, sensitive and rapid RLS method for analysis of trace amounts of phenol in different kinds of waste water was successfully researched and developed. It involved a solution containing synthesized GQDs, the HRP enzyme and H_2O_2, which in the presence of phenol formed GQDs–quinone species. This then produced a strong RLS band at 310 nm, which was suitable for analysis. The detection limit for phenol in water was 2.20×10^{-8} M. The literature suggests that this is the lowest reported detection limit for phenol in waste waters. Furthermore, this is a phenol selective method even in the presence of several phenolic compounds and heavy metal ions.

Acknowledgements

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.03.007.

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