Modified magnetite nanoparticles for colorimetric sensing of anionic surfactants in water

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Determination of anionic surfactants in water is classically based on the ion pairing of anionic surfactants with the methylene blue dye. As the optical absorption peaks of the dye and the ion pair overlap each other at 662 nm, it is required that the ion pair should be separated from the dye by chloroform extraction. In this reported work, it was found that the magnetite nanoparticles coated with poly(acrylic acid) could rapidly adsorb the methyl blue dyes in water and result in an obvious shift in optical absorption from 662 to 590 nm, which realises the spectral separation of the dye and the ion pair. Accordingly, using methyl blue dyes and the modified magnetite nanoparticles, anionic surfactants in water can be directly determined without extraction and/or separation. The lower limit of detection was 0.10 mg/l, and improved to 30 μg/l by magnetic removal of the nanoparticles. The functionalised magnetite nanoparticles allowed the development of a simple procedure for colorimetric sensing of anionic surfactants without the use of hazardous chlorinated organic solvents.

1. Introduction: Anionic surfactants (AS) are widely applied in industry and in household products such as detergents, paints and petroleum products. As a group that give rise to critical environmental concern, it has become imperative to monitor their levels in surface water and wastewater [1]. The well-known methylene blue (MB) colorimetric assay uses MB to form ion pairs with AS in water, which are then extracted by chloroform and determined by colorimetry [2]. The method was limited by the tedious isolation procedure and the use of relatively large amounts of harmful solvents. Moreover, it cannot usually be used for in situ screening. Hence, it is necessary to develop new strategies for AS sensing that require little or no sample preparation and have high sensitivity.

Nowadays, magnetic nanoparticles are attracting great interest in various fields [3–5]. The unique properties of magnetic nanoparticles, including superparamagnetism and high adsorption capacity, make them an efficient alternative to materials conventionally used in sample preparation and pollutant removal. For the determination of AS in particular, magnetic nanoparticles deposited onto carbon nanotubes [6], or modified with cationic surfactants [7], were used for solid-phase extraction of AS prior to high-performance liquid chromatography. However, they involve time-consuming sample preparation and complicated instruments that cannot usually be used for in situ screening.

Here, for the first time we utilise the magnetic nanoparticles for colorimetric sensing of AS in water, based on the strong adsorption of the MB dye by poly(acrylic acid)-coated magnetite (PAA@Fe_3O_4) particles [8, 9]. More importantly, it is found that adsorption of MB on PAA@Fe_3O_4 nanoparticles results in an obvious shift in optical adsorption of MB, that is, a 'spectral separation' of MB from the ion pair MB–AS. Thereby, we have developed a colorimetric sensing method of AS without solvent extraction of MB–AS (see Fig. 1). Furthermore, magnetic removal of the complex MB-PAA@Fe_3O_4 in a solution could eliminate the colour/spectral background of the complex and improve the sensitivity of the assay. This simple and fast method holds potential for environmental monitoring such as onsite screening of AS contamination in water.

2. Materials and methods: PAA@Fe_3O_4 nanoparticles were synthesised by alkaline co-precipitation and in situ polymerisation. Typically, a 5 ml solution of 0.1 M Fe^{2+} and 0.2 M Fe^{3+} was added dropwise into 50 ml of a 0.1 M NaOH solution under vigorous mechanical stirring and a flow of nitrogen gas. The colour of the suspension turned black immediately. After stirring for 30 min, the precipitated powders were collected by applying a magnet, and washed four times with deoxygenated water, and then were stirred to disperse in 50 ml of a 1.0 M acrylic acid solution for 30 min. Subsequently, 1.5 ml of a 30% H_2O_2 solution was added into the Fe_3O_4 colloid solution. After stirring for 10 min, the colour of the suspension turned dark yellow, and the powders were washed four times with water with the aid of a magnet, and finally were dried in a vacuum drying oven or stored in a 0.01 mM NaOH solution.

The magnetic properties of the prepared particles were measured with a vibrating sample magnetometer (EV-11, ADE Technologies). Transmission electron microscopy (TEM, TECRAI20, Philips), X-ray diffraction (XRD, D/MAX-1200, Rigaku) with nickel-filtered CuKα radiation and a thermal analyser (DTG-60, Shimadzu) were used for characterisation of the prepared nanoparticles. An UV–Vis spectrophotometer (UV-2450, Shimadzu) and a Fourier transform infrared (FTIR) spectrometer (Nicolet 5700, ThermoElectron) were used to carry out spectral measurements.

Assay of AS in water is performed as follows. A 10 ml solution of 20 mM phosphate buffer (PB, pH 7.5), 20 μM MB and 5.0 mg/l PAA@Fe_3O_4 was added into a 10 ml water sample. After mixing for 10 min, the absorbance at 662 nm was measured, and the change in absorbance of the sample relative to the blank (ΔA) was used to determine the concentration of AS in the sample water. Alternatively, after mixing, the particles were removed from the solution by applying a magnet, and then the ΔA was measured to determine the concentration of AS in the sample water. All the tests were repeated five times. According to the standard MB colorimetric assay of AS [2], sodium dodecylbenzene sulfonate (LAS) was used as the reference material, and the content of AS in the sample was expressed as the concentration of LAS.
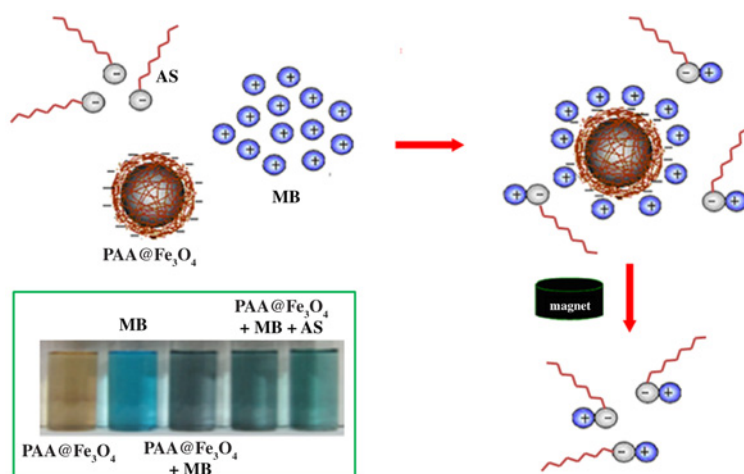
Figure 1 *AS sensing based on PAA@Fe₃O₄ nanoparticles*
Inset (from left to right): PAA@Fe$_3$O$_4$ nanoparticles (2.5 mg/l), MB (10 μM), their mixture and adding AS (0.5, 1.0 mg/l) into the mixture

All reagents were of analytical grade and used as received without further purification. Deionised doubly distilled water was used throughout.

3. Results and discussion: The synthesised PAA@Fe$_3$O$_4$ particles have a good dispersibility and an average size of 9 ± 2 nm, as determined by TEM (Fig. 2a). The XRD pattern of the particles (Fig. 2b) confirmed the crystallinity of the product. The broadening of the XRD peaks was possibly caused by the coated PAA or small particle size. The prominent peaks correspond to the (311) and (440) reflections of Fe$_3$O$_4$, respectively, and the medium is assigned to (220), (400) and (511) reflections, respectively. It is indicated that the reaction process does not result in a phase change of the Fe$_3$O$_4$. The thermogravimetric analysis (TGA) (Fig. 2c) shows that the weight loss of the uncoated Fe$_3$O$_4$ particles was 6% in the range of 100–600°C because of the removal of adsorbed water. The weight of the

PAA@Fe$_3$O$_4$ particles has a small loss until 180°C and a significant loss during 180–450°C, indicating that the decomposition of PAA was taking place in this temperature range. The amount of PAA coated on the magnetite surface was estimated to be 35 ± 5 wt% on the basis of TGA data. From the FTIR spectra of uncoated and surface-modified magnetite nanoparticles (Fig. 2d), the IR band at around 590 cm^{-1} is characteristic of the Fe–O vibrations. The three new peaks at 1715, 1568 and 1405 cm^{-1} appear because of the binding of the carboxyl groups (COO−) to the surface of the particles to form carboxylate groups. All of those results reveal that the surface of Fe$_3$O$_4$ was successfully modified with PAA through chemical bonding. The very rich carboxyl groups on the surface of the PAA@Fe$_3$O$_4$ nanoparticles make them to be easily and steadily dispersed in water, especially in a basic solution. Less than 10% changes in absorbance (400–800 nm) were observed for solutions of 100 mg/l PAA@Fe$_3$O$_4$ dispersed in 0.01 mM NaOH during
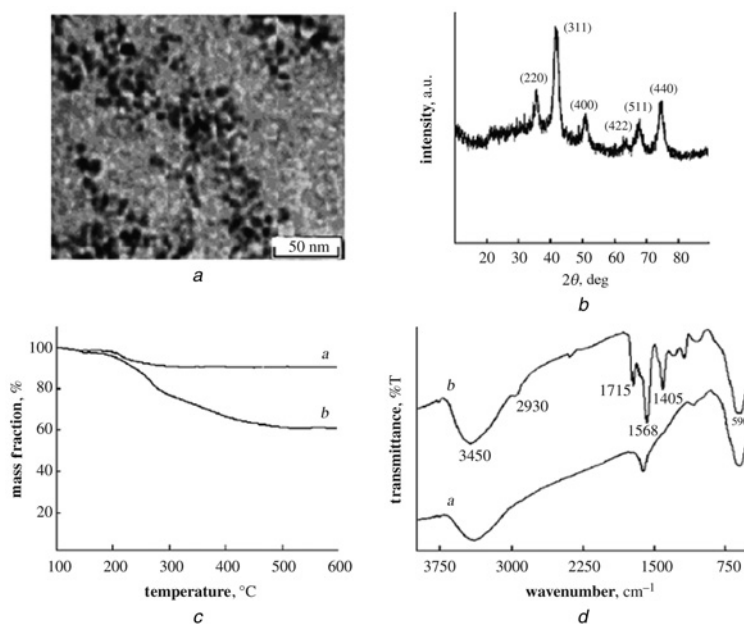

Figure 2
a TEM
b XRD pattern of PAA@Fe$_3$O$_4$ nanoparticles
c TGA curves
d FTIR spectra of the prepared Fe$_3$O$_4$ (*a*) and PAA@Fe$_3$O$_4$ (*b*) nanoparticles
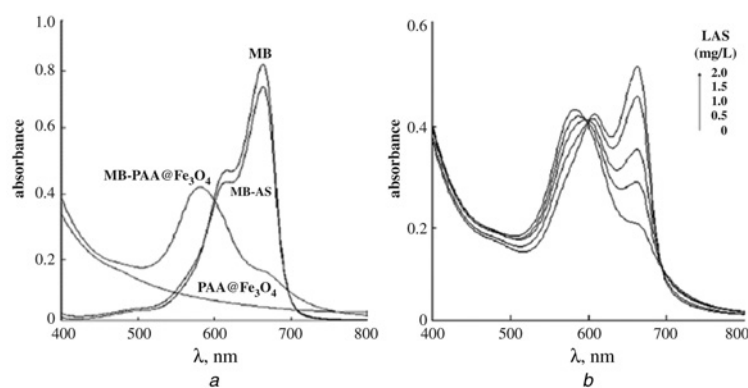
Figure 3
a Spectra of PAA@Fe$_3$O$_4$ nanoparticles (2.5 mg/l), MB (10 μM), MB-PAA@Fe$_3$O$_4$ and MB-AS (10 μM MB + 0.5 mg/l LAS)
b Spectra of addition of LAS into the mixture of MB-PAA@Fe$_3$O$_4$

1–30 days at room temperature. The magnetic coercive force and the residual magnetisation of the synthesised PAA@Fe$_3$O$_4$ nanoparticles were zero at room temperature. The saturation magnetisation of the particles was determined to be ca. 41 emu/g, slightly lower than that of the uncoated Fe$_3$O$_4$ nanoparticles (43 emu/g) because of the presence of PAA. These results indicate that the PAA@Fe$_3$O$_4$ nanoparticles synthesised were superparamagnetic.

The optical absorption of solutions of the individuals (MB, PAA@Fe$_3$O$_4$), and the mixtures (MB-AS, MB-PAA@Fe$_3$O$_4$) are shown in Fig. 3*a*. In the visible region (400–800 nm), no peaks of the PAA@Fe$_3$O$_4$ nanoparticles appeared, although the absorbance was gradually increasing with the shorter wavelength. Both the MB and the ion pair MB–AS had absorption peaks at 662 nm, with a slightly lower absorbance for the ion pair. Importantly, the peak of MB disappeared almost completely and a new peak occurred at 590 nm for the mixture of MB and PAA@Fe$_3$O$_4$ nanoparticles. In the mixture, most MB cations were strongly bound to the anionic carboxyl groups on the particle surface and resulted in the formation of the complex MB-PAA@Fe$_3$O$_4$, which should be the source of the blue-shift of the MB peak. As shown in Fig. 3*b*, addition of AS to the complex led to the recovery of the peak at 662 nm and the reduction and red-shift of the peak at 590 nm. The former should be contributed from the formation of the ion pairs of MB–AS, and the latter from the release of the MB on the particle surface. From the solution colour, it was also observed that the blue content of the mixture was greater with the increase in the AS concentration (see the inset in Fig. 1). In addition, the absorbance or colour of the solution became stable within 10 min since the mixing of the water sample with MB and PAA@Fe$_3$O$_4$ nanoparticles. Consequently, the concentration of AS in a water sample can be directly and rapidly determined with the change in absorbance of the MB–AS formed in the solution.

The concentrations of MB and PAA@Fe$_3$O$_4$ nanoparticles were selected for their use to determine AS in water. The change in absorbance in response to a fixed LAS amount (0.5 mg/l) with different contents of PAA@Fe$_3$O$_4$ nanoparticles are shown in Fig. 4*a*. The concentration of MB was defined at three levels (5, 10 and 20 μM) to facilitate precise measurements of absorbance. It can be seen that, at a lower level of MB (or PAA@Fe$_3$O$_4$ particles in excess), the absorbance change was decreased with higher particle contents because of the scattering background of particles (see curve a). At higher levels of MB (curves b and c), the change was also down deviated with smaller particle amounts because of the presence of free MB in solution. In an appropriate amount range of PAA@Fe$_3$O$_4$ nanoparticles (2.5–3.5 mg/l), the absorbance change responding to LAS was slightly disturbed because of the absence of free MB. Therefore, 10 μM of MB and 2.5 mg/l of the magnetite particles were used.

The effect of solution pH on the responded change in absorbance was also investigated, as demonstrated in Fig. 4*b*. Protonation of the carboxyl groups on particle surface and deprotonation of the MB cations in solution, respectively, would be promoted at lower and higher levels of pH (<6.0 and >8.0). The former hinders the adsorption of MB from solution, and the latter impedes the formation of MB–AS ion pairs. Thus, both lower the response to AS in water. In addition, the absorbance change was also significantly decreased with a more concentrated buffer, because of a stronger shielding effect applied on the electrostatic interaction of MB cations and AS anions. Rationally, a weak basic and low salt medium (pH 7.5, 1.0 mM PB) was beneficial for the usage of MB and PAA@Fe$_3$O$_4$ nanoparticles to determine AS in water.

The proposed method was calibrated using LAS standard solutions under the above conditions optimised. The optical response (Δ*A*) was in good linear relation to the concentration of LAS in
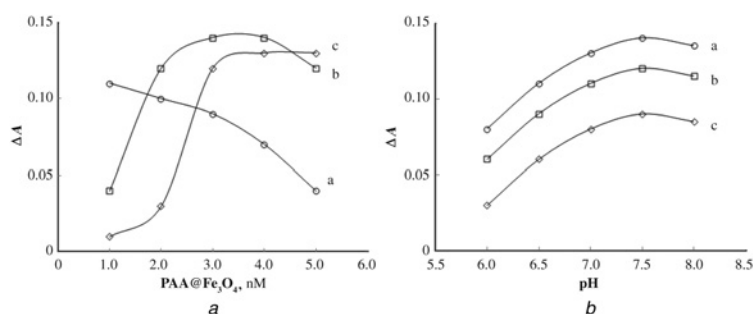

Figure 4
a Effect of PAA@Fe$_3$O$_4$ concentration on the absorbance change (Δ*A*) in response to LAS (0.50 mg/l) at various levels of MB (a: 5.0, b: 10 and c: 20 μM)
b Effect of the buffer pH on Δ*A* at various buffer concentrations (a: 1.0, b: 5.0 and c: 10 mM)
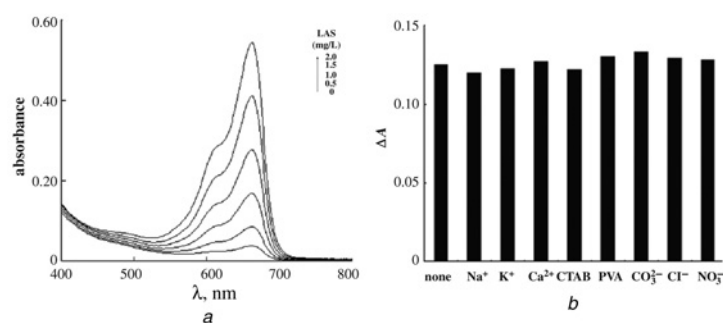
Figure 5
a Spectra of AS determination with magnetic separation
b Effect of coexistent substances on the absorbance change (ΔA) in response to LAS (2.0 µM)
Concentrations of Na^+, K^+ and $Ca^{2+} = 0.50$ mM, CTAB and PVA = 0.20 mM and CO_3^{2-}, Cl^- and $NO_3^- = 0.20$ mM

Table 1 AS detection in real water samples using MB and PAA@Fe$_3$O$_4$ nanoparticles without magnetic separation ($n = 5$)

Sample	Added, mg/l	Determined, mg/l	RSD, %	Recovery, %
1	–	0.19	5.1	–
	0.50	0.51	4.8	102
	1.00	0.99	3.7	99.0
	2.00	1.98	2.5	99.0
2	–	0.00	–	–
	0.50	0.49	4.5	98.0
	1.00	0.98	3.3	98.0
	2.00	1.97	2.3	98.5
3	–	0.00	–	–
	0.50	0.48	4.9	96.0
	1.00	1.02	2.9	102
	2.00	2.13	3.1	107

the range of 0.20–5.0 mg/l. Based on the three times of the signal-to-noise ratio, the lower limit of detection was estimated to be 0.10 mg/l. This method could be improved by removing the background of the magnetite particles. Through a simple magnetic aggregation of the particles, the absorbances of the blank and the LAS solutions were greatly reduced and enhanced, respectively (see Fig. 5*a*). The detection limit was achieved at 30 µg/l, which is better than the traditional MB assay with solvent extraction. In addition, the response to LAS was checked in the coexistence of substances usually found in aqueous solutions, including inorganic cations (Na^+, K^+ and Ca^{2+}) of 250 times and anions (Cl^-, NO_3^- and CO_3^{2-}) of 100 times, cationic surfactant (cetyltri-methylammonium bromide, CTAB) and non-ionic surfactant (poly-vinyl alcohol, PVA) of 100 times. The results are shown in Fig. 5*b*; in all cases, nearly the same change in absorbance of the MB–AS was observed (the relative deviation <5%), indicating that no remarkable interference to the AS determination was found in the presence of these chemical species. Finally, the protocol without magnetic separation was applied in the determination of AS in three real samples taken from the river water in Chongqing. Good results were obtained, that is, in all cases the RSD was <5% and the recovery was in the range of 95–110% (see Table 1). The precision and accuracy of the proposed method were suitable for the environmental monitoring of ASs in water.

4. Conclusion: In summary, poly(acrylic acid)-modified magnetite nanoparticles were synthesised and used for colorimetric sensing of ASs in water. The sensing is based on that the colour or the absorption wavelength of MB bound to the carboxyl-conjugated nanoparticles is obviously shifted. It allows us to directly detect the absorption of the ion pair of MB and ASs in water, without the need of solvent extraction of the ion pair from the residual dye. Alternatively, the background aroused from the nanoparticles could be easily removed away by magnetic separation, which improved the sensitivity and precision. Not requiring the harmful and tedious solvent extraction used in traditional MB assay, the proposed method is very simple and green, and holds potential application in environmental monitoring.

6 References

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