Chinese Chemical Letters xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Original article

Determination of methylene blue by resonance light scattering method using silica nanoparticles as probe

Jin Fan, Zhi-Hai Xie*, Xiao-Xiao Teng, Yu Zhang

Key Laboratory of Synthetic & Natural Functional Molecular Chemistry of The Ministry of Education, College of Chemistry & Material Science, Northwest University, Xi'an 710127, China

ARTICLE INFO

Article history:
Received 6 October 2016
Received in revised form 2 November 2016
Accepted 14 November 2016
Available online xxx

Keywords:
Methylene blue
Silica nanoparticles
Aggregation
Resonance light scattering
Determination

ABSTRACT

A simple and novel method was developed to determine methylene blue (MB) by resonance light scattering (RLS) using silica nanoparticles (SiO_2NPs) as the probe. It was found that MB could enhance the RLS intensity of SiO_2NPs. Moreover, the increase in RLS intensity was linear with the concentration of MB over the range of 0.01–3.0 μg mL^{-1}. The limit of detection (LOD) was as low as 4.36 ng mL^{-1} (3σ) and the relative standard deviation (RSD) was 2.4% (n = 6). Under the optimum experimental conditions, this proposed method was successfully applied for the determination of MB in aquaculture samples with recoveries between 96.3% and 107%. Possible mechanisms for the RLS enhancement of SiO_2NPs in the presence of MB were also discussed.

1. Introduction

Methylene blue (MB) is one of the most common cationic dyes that is widely used as a chemical indicator, biological stain and aquaculture fungicide [1,2]. In spite of its extensive applications in various fields, it has been reported that exposure to large doses of MB can cause some harmful effects [3]. Therefore, the quantitative determination of MB has become increasingly important. Several methods have been reported for the determination of MB including high performance liquid chromatography (HPLC) [4,5], electrochemistry [6], capillary electrophoresis [7], chemiluminescence [8] and spectrophotometry [9]. Another analytical method gaining importance is RLS, which is characterized by its high sensitivity, simple setup and convenient operation. Thus, RLS has been widely applied for the determination of different analytes including inorganic ions, organic compounds, biomacromolecules and pharmaceuticals [10–15].

In recent years, RLS methods using gold/silver nanoparticles as probes for the determination of organic compounds have been reported [16–19], where the RLS is increased by the analytes through either aggregation of existing nanoparticles or formation of new nanoparticles. Some recent examples include the RLS determination of salmeterol xinafoate [20], ethion [21], thiamazole [22] and raloxifene [23]. In addition, Li *et al.* [24] investigated the interaction between MB/TiO_2 nanocomposites and bovine serum albumin by RLS. SiO_2NPs are an interesting class of inorganic nonmetallic materials which exhibit many special physicochemical properties and have been extensively explored for a variety of applications [25–27]. The use of SiO_2NPs as probe for the determination of MB by RLS technique has not been reported so far.

In this paper, a simple and novel method for the determination of MB using SiO_2NPs as probe was established. The proposed method was based on that the added MB could enhance the RLS intensity of the SiO_2NPs in aqueous solutions. Optimum conditions for the determination of MB were investigated and the related mechanisms were also considered. The proposed method has been used for the analysis of MB in aquaculture and water samples with satisfactory results.

2. Results and discussion

2.1. Absorption spectra

The absorption spectra of SiO_2NPs, MB and SiO_2NPs–MB are displayed in Fig. 1. Four absorption peaks at 664 nm, 611 nm, 291 nm and 246 nm were observed for MB (Fig. 1a), while there was no absorption peak for the SiO_2NPs dispersion (Fig. 1b). The absorption of MB was decreased when SiO_2NPs was added (Fig. 1c). In particular, the presence of SiO_2NPs causes a significant reduction

* Corresponding author.
E-mail address: xiezhihai8@163.com (Z.-H. Xie).

http://dx.doi.org/10.1016/j.cclet.2016.11.025

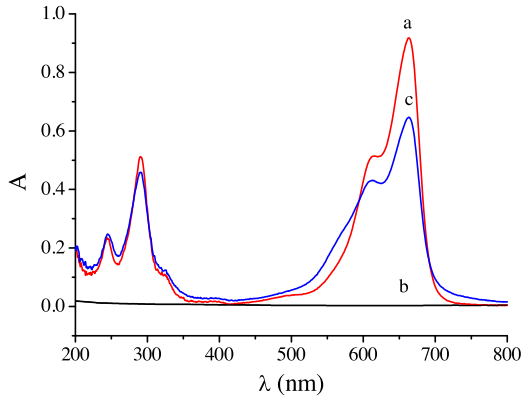

Fig. 1. Absorption spectra of (a) MB; (b) SiO_2NPs; and (c) SiO_2NPs + MB. Conditions: MB, 5.0 μg mL^{-1}; SiO_2NPs, 0.002%; pH 10.0.

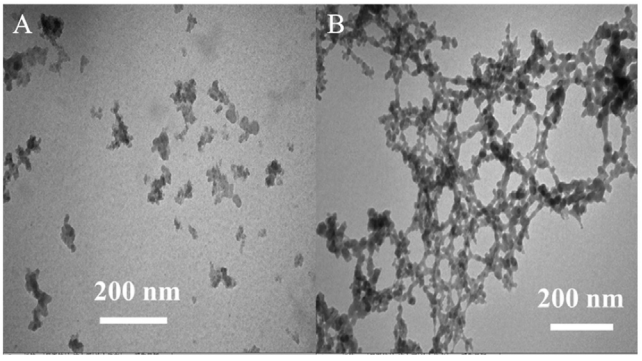

Fig. 3. Transmission electron microscope images of SiO_2NPs dispersion (A) and SiO_2NPs–MB system (B). Conditions: SiO_2NPs, 0.002%; MB, 3.0 μg mL^{-1}; pH 10.0.

in the absorption intensity (A) at 664 nm (A decreases from 0.918 to 0.647). This phenomenon might be due to the fact that MB gets adsorbed on the surface of SiO_2NPs to form SiO_2NPs–MB aggregates, which lowers the concentration of MB in the solution.

2.2. RLS spectra

Fig. 2 illustrates the RLS spectra of SiO_2NPs, MB and SiO_2NPs–MB at pH 10. The RLS intensity of MB was relatively weak in the wavelength range of 250–700 nm, as well as that of the SiO_2NPs. However, with the addition of MB to SiO_2NPs, the RLS intensity, characterized by a maximum peak signal at 370.0 nm, was enhanced significantly. Moreover, the RLS intensity increased linearly with increase in the MB amount. Therefore, the concentration of MB could be determined by RLS technique using SiO_2NPs as probe.

2.3. TEM images of SiO_2NPs and SiO_2NPs–MB

The TEM images of SiO_2NPs and SiO_2NPs–MB are shown in Fig. 3. The average diameters of the SiO_2NPs in the dispersion were found to be about 100 nm (Fig. 3A). When the SiO_2NPs reacted with MB under the optimal conditions, the aggregation of MB with the SiO_2NPs not only increased the size of the nanoparticles, but also changed their shape. The SiO_2NPs–MB aggregates exhibit the network structure as shown in Fig. 3B.

2.4. Effects of pH and buffer

The pH value played a very important role in the interaction between SiO_2NPs and MB. Therefore, the influence of pH on ΔI_{RLS} was investigated with two common buffer solutions in the pH range 9.0–11.0, and the results are shown in Fig. 4. It can be seen that the BR buffer solution was better than NH_3–NH_4Cl, and the ΔI_{RLS} of the solution depended greatly on the pH value. ΔI_{RLS} increased sharply when the pH increased from 9.0 to 10.0, and then it remained constant with the further increase in pH above 10.0.

Zeta potential of the SiO_2NPs dispersion was measured to detect the changes in the SiO_2NPs surface charges and the results are shown in Fig. 5. Zeta potential decreased remarkably with the increase in pH value and it remained constant at pH above 10.0, which was in accordance with the results of pH studies. Therefore, pH 10.0 with BR buffer solution was chosen for further research.

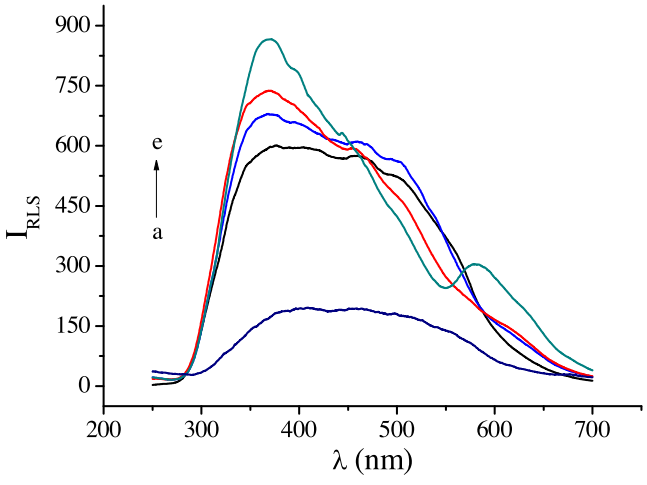

Fig. 2. RLS spectra of (a) MB, 3.0 μg mL^{-1}; (b–e) SiO_2NPs + MB. Conditions: SiO_2NPs, 0.002%; MB (b–e) (μg mL^{-1}), 0, 0.5, 1.0 and 2.0; pH 10.0.

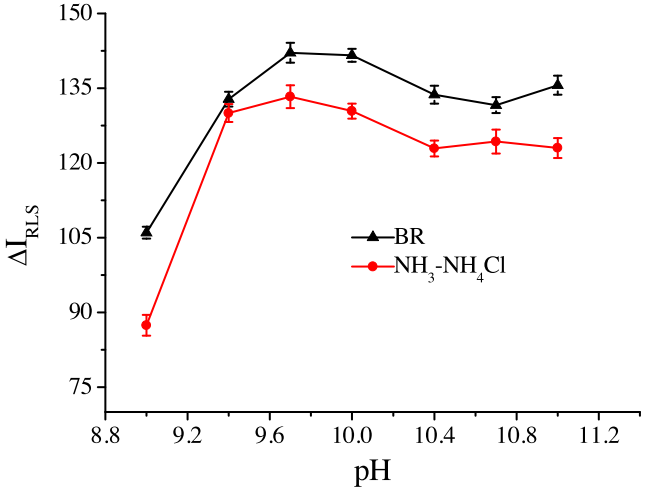

Fig. 4. Effects of pH and buffer solutions on ΔI_{RLS}. Conditions: SiO_2NPs, 0.002%; MB, 1.0 μg mL^{-1}.

Please cite this article in press as: J. Fan, et al., Determination of methylene blue by resonance light scattering method using silica nanoparticles as probe, Chin. Chem. Lett. (2016), http://dx.doi.org/10.1016/j.cclet.2016.11.025