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Fluorescence enhancement effect of Eu(III)–thenoyltrifluoroacetone–cetyltrimethyl ammonium bromide in water-dissolved organic matter extracted from wheat straw

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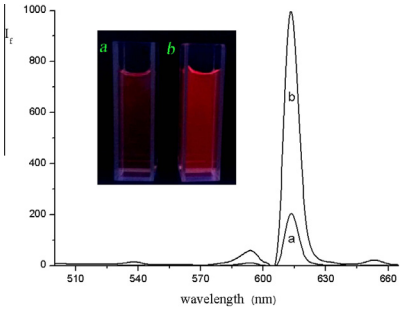
HIGHLIGHTS

- 3D-EEM of water-dissolved organic matter extracted from wheat straw is studied.
- DOM-WS can significantly enhance the fluorescence of Eu(III)–TTA–CTAB.
- Adding DOM-WS can reduce TTA dosage for the detection of Eu(III).

GRAPHICAL ABSTRACT

DOM from wheat straw can dramatically increase the fluorescence of Eu(III)–TTA–CTAB. The strong red fluorescence of Eu(III)–TTA–CTAB–DOM-WS can even be observed by naked eyes under a common UV lamp irradiation. Four emission peaks located at 537 nm, 592 nm, 614 nm and 653 nm, corresponding to $^5D_1 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_3$ of Eu(III) characteristic transition, respectively.



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ABSTRACT

The fluorescence spectral characteristics of water-dissolved organic matter extracted from wheat straw (DOM-WS) were studied using three-dimensional excitation–emission matrix (3D-EEM) fluorescence spectroscopy. The results indicated that 3D-EEM spectra of DOM-WS showed four different fluorophores: humic-like, visible fulvic-like, UV fulvic-like and protein-like substances. It is interesting that DOM-WS can obviously enhance the fluorescence intensity of Eu(III)–thenoyltrifluoroacetone–cetyltrimethyl ammonium bromide system. On the basis of this study, a new fluorescence method for the determination of trace amounts of Eu(III) was developed. Under the optimal conditions, the enhanced fluorescence intensity was in proportion to the concentration of Eu(III) in the range of 8.0×10^{-8}–8.0×10^{-7} mol/L. The detection limit ($S/N = 3$) was 1.1×10^{-9} mol/L. This method was applied to the analysis of Eu(III) concentration in standard sample and obtained satisfactory results. It may be a new way to use wheat straw effectively.

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1. Introduction

Dissolved organic matter (DOM) is a heterogeneous mixture of various organic compounds with different molecular sizes, structures, and functional properties [1]. DOM widely distributed in nature, which has a great influence on the activation, migration and eco-toxicity of heavy metals, nutrients and organic pollutants [2–6]. The composition of DOM usually includes low molecular weight substances, such as organic acids, sugars, and amino acids, as well as complex molecules of high molecular weight, such as humic substances, enzymes and polyphenol [7,8].

Rare earth elements have electric, magnetic, optical, biological and other properties, and play an important role in the agricultural, chemical, and biological fields [9–11]. High sensitivity and high selectivity of fluorescence methods based on the luminescence of rare earth elements (especially Eu^{3+}, Tb^{3+}) have attracted considerable concern [12,13]. Organic reagents, such as β-diketone, aromatic carboxylic acid, phenanthroline and its derivatives often serve as a ligand with rare earth ions in order to improve fluorescence properties. Surfactant, organic solvent and other co-ligand can further enhance the rare-earth ions' luminescence intensity. However, water-dissolved organic matter extracted from wheat straw (DOM-WS) as the rare earth ion fluorescence enhancement reagent has not been reported.

Due to its simplicity, high sensitivity, non destruction of sample and detailed information, three-dimensional excitation–emission matrix (3D-EEM) is frequently employed to characterize fluorescence properties of DOM [14–16], such as preservation [17], source [18] and dynamic [19]. DOM is usually quantified by dissolved organic carbon and/or dissolved organic nitrogen [20–22]. But DOM is non-homogeneous compound, and its C/N ratio varies greatly [23–25]. So far few works have been reported in the literature on the spectral changes accompanied with concentration changing. In this work we reported 3D-EEM fluorescence spectral changes of DOM-WS in water at different dilution rates. Besides, we found that DOM-WS can obviously enhance the fluorescence intensity of Eu(III)–thenoyltrifluoroacetone–cetyltrimethyl ammonium bromide system. It is a promising utilization of DOM-WS.

2. Materials and methods

2.1. Materials and reagents

Wheat straw was collected from Heze city, Shandong province, China, in summer. Straw was dried naturally, and wiped up with a soft cloth, then cut into about 1 cm. The DOM was extracted from straw with ultrapure water (18.25 MΩ cm) using a straw-to-water ratio of 1:50 (w/v, dry weight) soaked 6 d. Straw-water mixture were shaken on the rotary shaker at 200 rpm for 24 h. After that, the suspensions were centrifuged at 12500 rpm for 30 min and filtered through three layers of medium-speed qualitative filter paper and a piece of 0.45 μm sterilized membrane, respectively. The filtrate was stored at 0–4 °C in a refrigerator before being used.

Stock standard solution of Eu^{3+} (1.0×10^{-2} mol/L) was prepared by dissolving 0.1760 g Eu_2O_3 (99.99%, Shanghai Yuelong chemical plant) in amount of hydrochloric acid (1:1, v/v), evaporating the solution nearly to dryness and diluting to 100 mL with water. Stock solution of thenoyltrifluoroacetone (TTA, 1.0×10^{-2} mol/L) was prepared by dissolving 0.2222 g TTA (Shanghai, Sinopharm Chemical Reagent Co., Ltd) in 30 mL ethanol and then diluting to 100 mL with ethanol. Stock solution of cetyltrimethyl ammonium bromide (CTAB, 1.0×10^{-2} mol/L) was prepared by dissolving 1.8222 g CTAB (Shanghai, Sinopharm Chemical Reagent Co., Ltd) in water and diluting to 500 mL with water. NaAc (0.2 mol/L) was prepared by dissolving 4.1015 g NaAc (Tianjin, Kermel Chemical Reagent plant) in 250 mL flask, then diluting 10-fold, and adjusting the pH to 5.60 with 0.02 mol/L HAc. All the reagents employed in this work were of analytical grade without further purification. Water used throughout was distilled water.

2.2. Apparatus and instruments

Three-dimensional excitation–emission matrix fluorescence spectra were recorded on a Hitachi model F-4500 fluorescence spectrophotometer, equipped with an F-4500 system program for data processing. The full-scan fluorescence landscape with excitation ranging from 200 to 450 nm and emission ranging from 250 to 650 nm was determined. The slits were set to 10 nm for both excitation and emission, and scan speed was set at 30,000 nm/min. The two-dimensional fluorescence spectra were performed using a Perkin-Elmer LS-55 spectrofluorimeter. The excitation wavelength was 350 nm, and excitation slit was 10 nm and emission slit 3.5 nm, and scan speed was set at 200 nm/min. The fluorescence intensity was measured at $\lambda = 614$ nm in a 1 cm quartz cell. The pH was measured on a Delta 320-S pH meter (Mettler-Toledo, Shanghai). The UV photo was taken under ZF-20D black-box type UV analyzer (Gongyi Yuhua, Zhengzhou) irradiation.

3. Results and discussion

3.1. 3D-EEM spectra of DOM-WS

Fluorescence properties of various dilutions of DOM-WS were monitored by three-dimensional fluorescence spectrometry. The 3D-EEM contour plots of DOM-WS are shown in Fig. 1.

From Fig. 1, it can be seen that the fluorescence spectra of various dilutions of DOM-WS have obviously difference. The main parameters and analyses of fluorescence spectra of various diluted times DOM-WS are given in Table 1. DOM-WS has four main fluorescence peaks: humic-like, visible fulvic-like, UV fulvic-like and protein-1ike [26]. And the fluorescence peaks of humic-like and visible fulvic-like appear in 5-fold diluted DOM-WS solution (Fig. 1a). Visible fulvic-like fluorescence peak exhibits in the four diluted DOM-WS solutions. Compared with 5-fold diluted DOM-WS, humic-like fluorescence peak of 10-fold diluted DOM-WS blue shifts to $\lambda ex/\lambda em = 375/480$ nm (Fig. 1b) and its intensity strongly reduces. In addition, a new UV fulvic-like peak appears. The 3D-EEM spectra of diluted 50 times are similar to those of diluted 100 times sample except fluorescence intensity (Fig. 1c, d and Table 1). Mainly fluorescence peaks are protein-1ike and UV fulvic-like peaks. The former's fluorescence excitation and emission wavelength are about 280 nm and 360 nm, the latter are about 230 nm and 363 nm, respectively. And the visible fulvic-like peak shifts to short wavelength ($\lambda ex/\lambda em = 310/460$ nm) and its intensity is lower than that of 5 times and 10 times diluted DOM-WS solution. These results show that DOM-WS is a mixture containing a variety of compounds. The protein-1ike fluorescence is predominated in low concentration DOM-WS. The fluorescence of high concentration DOM-WS is attributed to humic-like. We think that the inner filter effect may be one of the reasons that the 3D fluorescence spectra of DOM-WS of various concentrations differ from one another. Some light absorption species, such as lignin or phenolic acids in DOM-WS, can absorb excitation and emission light, leading to the decrease of fluorescence intensity in short wavelength, especially at higher concentration.

It was found that the pH of DOM-WS was dependent on its solution diluted extent. The pH value of 5 times, 10 times, 50 times and 100 times DOM-WS dilutions are 7.47, 6.71, 6.52 and 6.12, respectively. Thus, the effect of pH change on 3D-EEM spectra of