



Contents lists available at ScienceDirect

Journal of Hazardous Materials

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



Determination of phthalate esters in airborne particulates by heterogeneous photo-Fenton catalyzed aromatic hydroxylation fluorimetry

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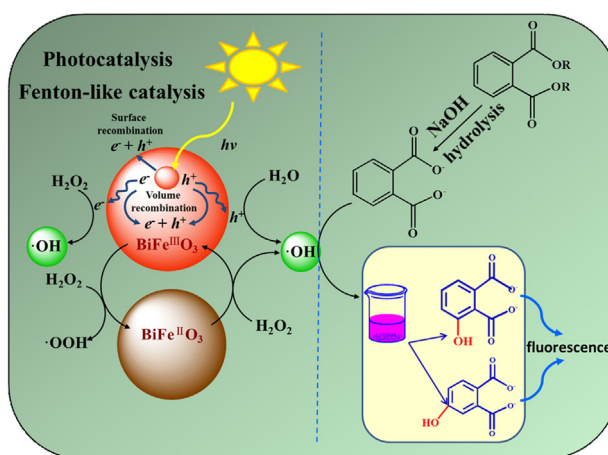
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HIGHLIGHTS

- Phthalic acid esters (PAEs) were determined by aromatic hydroxylation fluorimetry.
- PAEs can react with $\bullet\text{OH}$ in VMT-BiFeO₃/H₂O₂ to form fluorescent hydroxyl phthalates.
- Fluorescence intensity is proportional to PAEs concentration.
- A good linear relationship was obtained in range of 3.8×10^{-7} to $4.8 \times 10^{-5} \text{ mol L}^{-1}$.
- PAEs in airborne particulates were determined with satisfactory results.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 28 June 2016
Received in revised form
30 September 2016
Accepted 24 October 2016
Available online xxx

Keywords:

Fluorimetry
Heterogeneous photo-Fenton
Vermiculite supported BiFeO₃
Phthalate esters
Airborne particulates

ABSTRACT

The environmental contaminants phthalic acid esters (PAEs) were determined by aromatic hydroxylation fluorimetry combined with heterogeneous photo-Fenton process in the presence of vermiculite supported BiFeO₃ (VMT-BiFeO₃). In strong alkaline solution, PAEs were hydrolyzed into phthalates with no fluorescence, which then reacted with hydroxyl free radicals produced in photo-Fenton process catalyzed by VMT-BiFeO₃ to form the fluorescent hydroxyl phthalates. The fluorescence intensity was proportional to the concentration of PAEs with the maximum excitation and emission wavelength of 300 nm and 417 nm, respectively. A good linear relationship can be obtained in the range of 3.8×10^{-7} to $4.8 \times 10^{-5} \text{ mol L}^{-1}$ for DEP with correlation coefficient of 0.9997, and the sensitivity of the method was high with detection limit of $5.43 \times 10^{-8} \text{ mol L}^{-1}$. The method has been successfully applied to determine total PAEs in airborne particulates with satisfactory results.

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1. Introduction

As the plasticizers to make plastics more flexible, phthalic acid esters (PAEs) are widely used in variety of industrial, agricultural and domestic applications, such as various medicines, automobiles, packings, households and building materials [1]. PAEs are teratogenic, carcinogenic and mutagenic compounds with endocrine disrupting effects [2]. With the development of the plastics industry and the large-scale usage of phthalates, PAEs have been becoming global environmental contaminants, which attracted huge attentions by the whole world. Most of the present analytical methods for the determination of PAEs are based on gas chromatography (GC) [3], liquid chromatography (LC) [4], gas chromatography/mass spectrometry (GC/MS) [5] and liquid chromatography/mass spectrometry (LC/MS) [6]. Both of them have low detection limits and quantitation limits, but require expensive apparatus.

In numerous studies, the fluorescence analysis has been widely used in foodstuff, environment and biological analysis due to its simple instrument and high sensitivity. But so far there have been few reports on fluorescence detection for PAEs, because PAEs cannot generate fluorescence by themselves. Previous research indicates that some aromatic compounds with no or weak fluorescence could generate strong fluorescence by aromatic hydroxylation. Based on it, coumarin [7], terephthalic acid [8] and some other aromatic compounds [9] has been employed as fluorescence probes for detection of hydroxyl free radical ($\cdot\text{OH}$) in aqueous system. As a successful treatment for advanced oxidation process (AOP), Fenton reagent can rapidly convert hydrogen peroxide (H_2O_2) to hydroxyl free radical with high oxidative activity in acidic medium, which is known for more than a century [10,11]. Thus, an indirect and high-precision fluorescence analysis of PAEs has been realized since generated hydroxyl free radical in the Fenton system could oxidize phthalates formed by hydrolysis of PAEs to generate hydroxyl phthalates with high fluorescence intensity [12].

Heterogeneous Fenton-like photocatalytic system, which could provide a promising alternative for producing a large amount of hydroxyl free radical under light irradiation, can be available over a wide pH range and prevent ferric hydroxide sludge effectively [13–15]. Among all Fenton-like reagents studied, perovskite-type BiFeO_3 has been known for high hydroxyl free radicals yield and significant responsivity to visible light due to possessing Fe(III) and narrow band gap, and therefore attracts much research interest and becomes an important family for heterogeneous Fenton oxidation of contaminants [16–18].

Vermiculite (VMT) is a natural clay mineral and possesses a layered structure, high mechanical strength, good thermal stability and low cost [19]. The adsorptive capacity and porosity properties, which are important to the application of separation [20], adsorbent [21] and catalyst [22], can be improved by modifications with metals or metal oxides. In this work, VMT loading BiFeO_3 nanoparticles was prepared from immobilization of BiFeO_3 nanoparticles onto VMT by sol-gel method, and used for the simple, rapid and sensitive determination of PAEs firstly. The effect of initial parameters on the fluorescence emission has been fully investigated, and the catalytic mechanism was also preliminarily studied.

2. Materials and methods

2.1. Reagents

Dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP) were purchased from Acros Organics (NJ, USA). Iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) were provided by Sinopharm

Chemical Reagent Beijing Co., Ltd. Ethylene glycol monomethyl ether, dodecylamine, tetraethyl orthosilicate (TEOS), tartaric acid, acrylamide, H_2O_2 (30 wt.%) were supplied by Beijing Chemical Factory. NaOH, HCl, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ and KH_2PO_4 were provided by Shanghai Zhanyun Chemical Co., Ltd. Raw VMT was purchased from Xinjiang Yuli Xinlong Vermiculite Co., Ltd., Xinjiang, China. The VMT is composed of 38.76% SiO_2 , 24.05% MgO , 20.04% Al_2O_3 , 6.22% K_2O , 4.93% Fe_2O_3 , 3.03% CaO , 2.02% Na_2O and 0.94% TiO_2 with a cation exchange capacity (CEC) value of 98.64 mmol/100 g. The other reagents were analytically pure and used without further purification. Distilled water was used throughout the study.

2.2. Preparation and characterization of catalysts

The handpicked VMT was mixed with distilled water and stirred for 24 h strongly. Later, the flaky (plate like) VMT was filtered and washed with distilled water multiple times, then dried in an oven at 100 °C. Modified VMT was prepared as follows: firstly, 3.64 g dodecylamine and 2.0 mL tetraethyl orthosilicate were dissolved in mixed solution of ethanol and water with the volume ratio of 1:1, then 10 g purified VMT (300 mesh) was added. The mixture was heated at 80 °C for 4 h by stirring quickly. The precipitate was washed with absolute ethanol and distilled water for three times, respectively, then dried at 80 °C overnight.

The VMT- BiFeO_3 was synthesized by sol-gel process. Iron nitrate (0.008 mol) and bismuth nitrate (0.008 mol) were dissolved in ethylene glycol monomethyl ether (20 mL), 0.3304 g modified VMT was dispersed into precursor solution, followed by adding 0.008 mol tartaric acid, 0.02 mol acrylamide. After that, the mixture was stirred for 1 h at 40 °C to form a sol. The sol was heated for 6 h at 80 °C to form a black brown viscous gel, which was then calcined at 600 °C for 2 h in muffle furnace. After cooled to room temperature and grinded to powder in agate mortar, the product was obtained and denoted as VMT- BiFeO_3 . In the meantime, BiFeO_3 and expanded VMT were also prepared in the same way.

Thermogravimetry (TG, SeikoTG/DTA6300), Fourier transform infrared spectrometry (FT-IR, Shimadzu IRAffinity-1), UV-vis diffuse reflection spectrometry (UV-vis DRS, Shimadzu UV-2550), X-ray diffraction (XRD, XD-2, $\text{Cu K}\alpha$ radiation), and field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) were performed to characterize the resultant catalysts.

2.3. Fluorimetry process

RF-5301 fluorescence spectrophotometer from Shimadzu equipped with a Xenon lamp was employed to measure the fluorescence using the following conditions: quartz cuvette 1.00 cm, slit widths 5 nm, wavelength excitation range from 270 to 330 nm (each 2 nm) and wavelength emission range from 390 to 500 nm (each 2 nm), scan rate 12000 nm/min.

Aromatic hydroxylation was conducted in VMT- $\text{BiFeO}_3/\text{H}_2\text{O}_2$ system under either the dark or irradiation conditions. A 400 W high pressure mercury lamp ($\lambda_{\text{max}} = 365 \text{ nm}$) was used as the source for irradiation, and the light flux at the liquid level was measured to be $450 \mu\text{W cm}^{-2}$ approximately. All experiments were carried out in a 200 mL batch quartz reactor with a reflux device for temperature control. In a typical procedure, individual PAE or mixture of PAEs solution were firstly hydrolyzed under strong alkaline condition, and then a proper volume of HCl (1:1) was added to adjust the previous solution to be neutral, followed by diluting with distilled water to 100 mL. Then a certain amount of VMT- BiFeO_3 was dispersed into the above-prepared solution, and the suspension was stirred in the dark for 30 min to reach the adsorption-desorption equilibrium. The initial pH of the suspension was adjusted to a certain value using dilute aqueous HCl or NaOH solution, followed by adding H_2O_2 solution. Samples were taken at regular time

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