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# Detection and quantification of phenol in liquid and gas phases using a clay/dye composite

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ABSTRACT

In this study, an organic dye lucigenin (BNMA) was successfully intercalated into the interlayer of montmorillonite (MMT) to prevent fluorescence quenching. With its enhanced fluorescent property, the composite was fabricated into solid strips for it fast and sensitive phenol detection in both liquid and gas phases. Under proper optimizations it is anticipated that the composite would show great potential for phenol determination in real world environment such as wastewater treatment industry.
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## Introduction

Phenol is one of the oldest antiseptic agents and was used as disinfectant, chemical intermediate and mail cauterizer [1]. Discharging from chemical plants, pharmaceuticals, and petroleum refineries resulted in its wide existence in the environment [2]. Its identification and quantification are critical to environment monitoring perspective [3]. With a relative high Henry's law constant, its concentration in gas phases would also affect indoor air quality. As such, considerable efforts were taken to develop various techniques for its detection, such as chromatographic [4], spectrophotometric [5], photocatalytic [6], adsorptive [7], and electrochemical [8]. However, their practical application may be limited due to extensive sample pretreatments, low sensitivities, or complicated manipulations [9,10]. Furthermore, high instrumentation costs and energy consumption would add additional limits [11,12]. With the well-established toxic effects of phenol on health, the USFDA set the phenol concentration of bottled drinking water to 1 mg/L [13], while the 29 CFR 1910 of OSHA of USA currently has the phenol limit in gas phase of 5 ppm or 19 mg/m$^3$ [14]. Thus, there is a growing need to detect phenol at extremely low concentrations. In addition, a simple, yet super sensitive, method to be able to analyze phenol concentrations in both liquid and gas phases, particularly at the household scale, will be of great importance.

To analyze phenols in aqueous phase with low concentrations, extraction is almost inevitable. With SPME extraction, 13 chlorophenols and phenol in landfill leachates could be analyzed by GC–MS in 90 min with a detection limit (DL) ranges from 0.005 μg/L for pentachlorophenol to 2.5 μg/L for phenol [15]. Similarly, detection and determination at the μg/L to ng/L levels for water samples could be achieved using a polydimethyl siloxane stir bar as an extraction medium followed by thermal desorption [16]. GC-FID and GC–MS were able to achieve a DL as low as 0.01 and 0.05 ng/L, but the method involved in using dichloromethane for extraction and cleanup of the extractants by silica gel column chromatography [17]. For rapid phenol identification and quantification with UV–vis, the phenol determination was in the range of 0.5–50 mg/L [18].

For gas phase phenol detection and quantification, OSHA developed Method 32 in 1981 [19]. In this method, 24 L of air sample need to be collected at a sampling rate of 0.1 L/min. The target for this method was 5 ppm or 19 mg/m$^3$. For lower concentrations, the air samples need to be desorbed with

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methanol and analyzed with HPLC-UV to improve the DL to 0.01 ppm. Later in 2008, the Agency for Toxic Substances and Disease Registry (ATSDR) of the U.S. Department of Health and Human Services developed the toxicological profile for phenol to summarize all accredited methods for phenol analyses in biological and environmental samples [20]. Using cyclodextrin–silica hybrid microporous composite as the sampler, air samples were collected at flow rate of 0.11 L/min for 3 h followed by desorption using acetonitrile for 30 min at 70 °C, by which phenol DL was reduced to 1 and 5 ppb by an HPLC fluorescence detection and GC–MS analysis [21]. An HPLC-UV method could lower the detection limit to 0.05 ppb for a gas sample of 150 L, but the method is time consuming. It needs to bubble the gas through a sampling solution of 0.06% sodium hydroxide at a rate of 1–2 L/min and then a buffer solution made of 0.51% of sodium bicarbonate and 0.21% of sodium carbonate and a derivatizing solution containing 0.1% *p*-nitrobenzenediazonium tetrafluoroborate need to be added to the sampling solution followed by 15 min reaction time [22]. Thus, there is still a growing need to develop methods for biological and environmental samples [20]. Furthermore, there has been no report on a simple method that can detection phenol in both liquid and gas phases at the sub ppb level.

Fluorescence spectroscopy becomes one of the increasingly used techniques, due in part to its sensitivity compared to other techniques [23]. As such, organic and inorganic semiconducting luminescent materials showed great prospective in Ref. [24]. Compared with traditional fluorescence materials, their advantages include effective in energy cost and minimal in environmental contamination. Furthermore, organic light-active materials with conjugated structures may have higher light quantum efficiency, are flexible and color tunable, and can be mass-produced [25]. Using a highly fluorescent ionic complex made of 3,4,9,10-perylene tetracarboxylic acid and 6-deoxy-6-amino-β-CD, the phenol DL was reduced to 0.03 μM, the lowest value reported in the literature [26].

Rarely clay minerals were used as substrates for the fabrication of organic-inorganic complexes for luminescence and fluorescence applications. Intercalation of terbium picolinate complexes via covalent interactions into the interlayer of kaolinite resulted in a luminescent hybrid material exhibiting a stronger characteristic emission of $Tb^{3+}$ with a broad band at 277 nm on its excitation spectra [27]. Separately, kaolinite, montmorillonite (MMT), and layered double hydroxide were used as fillers for the fabrication of nonflammable alginate nanocomposite aerogels via a freeze-drying process [28].

In this study, we prepared a fluorescence composite material for its supersensitive phenol detection and quantification in both liquid and gas phases. Due to quenching effect, the photoactive molecules lucigenin (BNMA) was first intercalated into the interlayer of MMT to reach maximum separation and minimal aggregation. A monolayer intercalation was optimized at the nanometer scale. Fluorescence quenching was assessed using variety of solutions. The BNMA/MMT composite was fabricated into solid test strips with activated microcrystalline cellulose, which resulted in an excellent response in phenol detection with a DL of 0.01 mM level by instruments, in comparison to a DL of 0.05 mM for a biosensor system [29,30], and 0.1 mM for a fluorescence detection [31]. Gas phase phenol could be detected at the ppm levels by naked eyes and ppb level by instruments with a detection limit as low as 0.35 ppb.

## Experiment and methods

### *Materials*

The MMT was purchased from the Clay Mineral Repositories in Purdue University and was used as received. Its exchange capacity (CEC) was 85 ± 3 $mmol_c$/100 g [32,33], the external surface area was 23 $m^2$/g [34], and the average particle size was 3.2 μm with a $d_{25}$ to $d_{75}$ in the range of 3–10 μm. The BNMA was purchased from J&K technology Co., Ltd. Its $pKa_1$ and $pKa_2$ values are 3.3 and 5.1.

### *Preparation of BNMA intercalated MMT*

To test the effect of initial BNMA concentrations on its florescence performance, 10 mL of BNMA aqueous solution with initial concentrations of 0.002, 0.004, 0.01, 0.04, 0.1, 0.2, 0.4, 1, and 2 mM were mixed with 0.2 g of MMT in each 50 mL centrifuge tube and shaken at 150 rpm at room temperature for 4 h. To test the contact time of BNMA on its intercalation into MMT, the mixing time was set at 1, 3, 5, 10, 10, 30, 40, 60, and 120 min with an initial BNMA concentration of 0.2 mM, while other experimental conditions were the same. The mixtures were centrifuged at 10,000 rpm for 20 min. After removal of the supernatant, the solids were then dried at 60 °C and ground to powder for material characterization. The product was denoted as BNMA/MMT.

### *Preparation of the activated microcrystalline cellulose (AMC)*

To make the product more practical for phenol detection and quantification, the BNMA/MMT needs to have additives to increase its mechanical strength, flexibility, and permeability for fast equilibrium attainment. Thus, AMC was used as one of the additives. The AMC was prepared by adding 10 g of microcrystalline cellulose and 250 mL of distilled (DI) water into a 500-mL Erlenmeyer flask and mixed for 48 h under magnetic stir. The mixture was then centrifuged and supernatant removed followed by addition of 250 mL of acetone and mixed for 24 h. After removal of the supernatant by centrifugation, 250 mL of N-N dimethyl ethylamine was added and mixed for another 24 h. After being centrifuged and washed with DI water, the product was freeze-dried for 48 h.

### *Preparation of the composite aerogel test strips (CATS) for phenol detection in liquid and gas phases*

The optimal condition tested in the BNMA concentration (0.1 mM) and time series (2 h) was utilized for the fabrication of the CATS. To each 50-mL Erlenmeyer flask, 1 g of AMC and varying amounts of BNMA/MMT at the AMC to BNMA/MMT ratios of 1:0.5, 1:1, 1:1.2, 1:1.6, and 1:2 were added together with 20 mL of 8% LiCl in N-N dimethyl ethylamine solution. The mixture was stirred to increase its viscosity and gelling effect. Periodically, more DI water (in a fraction of 15 mL) was added followed by 5 min stirring and 12 h settling. The viscous suspension was then protruded into a mold and freeze-dried for 48 h, similar to a freeze-drying process to fabricate nonflammable alginate nanocomposite aerogels [28]. This final product would have good mechanical strength and flexibility with high porosity.

### *Phenol detection and quantification in liquid and gas phases*

The following solutions at a concentration of 0.5 M were initially screened for fluorescence quenching of BNMA: $CO_3^{2-}$, $NO_3^{-}$, $SO_4^{2-}$, $Br^-$, $Cl^-$, $PO_4^{-}$, phenol, *o*-chlorophenol, *m*-chlorophenol, *p*-chlorophenol, toluene, cetrimethyl ammonium bromide (CTAB), $C_{16}$mimCl, $CrO_4^{2-}$, $Cd^{2+}$, $Pb^{2+}$, and $Hg^{2+}$. They were dropped onto the CATS. Then, the fluorescence intensities were determined using a fluorescence spectrophotometer.

To evaluate the phenol DL and linear response range (LRR) in liquid, drops of phenol solutions at concentrations of 0.01 μM to

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