



# Immobilization of zeolitic imidazolate frameworks with assist of electrodeposited zinc oxide layer and application in online solid-phase microextraction of Sudan dyes

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## ABSTRACT

Herein a facile method for immobilization of zeolitic imidazolate frameworks (ZIFs) was developed. The ZIFs grew on electrochemically deposited zinc oxide (ZnO) layer while carbon fiber bundle served as substrate. The synthesized ZIFs-ZnO composite was packed into PEEK tube as sorbent for online solid phase microextraction (SPME)-HPLC-UV analysis of Sudan dyes. Good enrichment efficiency (200–461 fold), low limits of detection ( $0.002 \text{ ng mL}^{-1}$ ) and wide linear ranges ( $0.02\text{--}20 \text{ ng mL}^{-1}$ , correlation coefficient  $> 0.9996$ ) were achieved. The analytical method was demonstrated to be practical for analysis of Sudan dyes in environmental water samples with good recoveries (83.5%–95.0%).

## 1. Introduction

Zeolitic imidazolate frameworks (ZIFs) is a burgeoning porous polymer, which is early reported by O. M. Yaghi and coworkers [1]. The ZIFs is composed of two parts, namely the transition metal ion ( $\text{Zn}^{2+}$  or  $\text{Co}^{2+}$ ) in the center and organic ligands containing imidazole backbone around. The coordination effect between the transition metal ion and the organic ligands endows the ZIFs with three-dimensional network structure, similar to the tetrahedron crystal structure of  $\text{SiO}_4$ .

With unique structure, the ZIFs possess many properties, like good chemical stability, big surface area and numerous cages which can accommodate small molecules [2]. What's more, the side chain, size and species of the ligands are optional [3]. Thus researchers would design goal-directed structure towards particular application. As a result the ZIFs has been applied to gas adsorption and energy storage [4–6], catalyst [7,8] and sorbent for solid phase micro extraction (SPME) [9–11].

One disadvantageous factor for the application of ZIFs is lack of facile method to immobilize the material. In the aforementioned SPME cases, The ZIFs is immobilized by spin-coating [9] or other physical method. In our previous work we developed a polydopamine-assisted method for SPME of polycyclic aromatic hydrocarbons [12]. Though good enrichment factor was obtained, the method was complicated. More facile method is still urgent before ZIFs became universal online extraction sorbent.

Recently a report about construction of ZIF-8 on ZnO using ZnO colloidal spheres as template and zinc source within 8–60 min [13] evoked our interest. Meanwhile we found that ZnO can be electrodeposited on electrode by cathodic constant potential method [14]. We hypothesized that the ZnO be used as zinc source upon which ZIFs grew on the surface. By this way the ZIFs was immobilized to form ZnO-ZIFs composite and was used as sorbent.

To verify our hypothesis, the ZnO was electrodeposited on the surface of carbon fiber bundle. Then the ligand 2-mercaptobenzimidazole was added to form ZnO-ZIFs composite and an online SPME-HPLC method was developed based on the composite for the analysis of Sudan dyes. Parameters potential to affect the extraction were investigated and the application in environmental water sample was examined as well.

## 2. Materials and methods

### 2.1. Reagents and apparatus

Sudan I, Sudan II and Sudan III were purchased from Aladdin (Shanghai, China). Concentrated hydrochloric acid, sodium hydroxide, potassium bromide, ferric chloride, zinc nitrate, ammonium, potassium chloride, methylbenzene, N, N-dimethylformamide and hydrogen peroxide (30%, m/m) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). 2-mercaptobenzimidazole was purchased

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from TCI Development Co., Ltd (Shanghai, China). Methanol and acetonitrile were obtained from Sigma-Aldrich (Shanghai, China) and were used as received. Bare carbon fiber bundles were purchased from Cangzhou Lixin Material Science and Technology co., LTD (Hebei, China). PEEK tubes of 1/16 in. o.d. and 0.02 in.i.d. were got from VICI. A Milli-Q system ( $\geq 18 \text{ M}\Omega \text{ cm}$ ) (Millipore, MA, USA) was used to purify water for all solutions and mobile phases. All other reagents of analytical grade were used as received.

## 2.2. Instrumentation

The electropolymerization was operated with electrochemical analyzer CHI 842B (Chenhua Instrument Factory, Shanghai, China). The HPLC-UV system for separation and detection was from Shimadzu (Tokyo, Japan). The separation column was A Wondasil C-18 column (150 mm  $\times$  4.6 mm i.d.) with 5  $\mu\text{m}$  particle size from GL Science (Shimadzu, Japan), as well as a Shimadzu LC Solution software for data collection. A syringe pump from Baoding Longer Precision Pump Co., Ltd (Baoding, China) was used to loaded sample. The mobile phase was made of acetonitrile and water (90:10, v/v) flowed at  $0.8 \text{ mL min}^{-1}$  for isocratic elution. The UV detection wavelength was 510 nm and column temperature was set at 30 °C. The morphology image of the synthesized material was characterized by a field emission scanning microscope (Zeiss Ultra Plus, Germany). An IR spectrometer (Thermo Nexus, USA) was used to collect Fourier transform infrared (FTIR) spectra. The X-ray photoelectron spectrometer (KRATOS XSAM800) was from Manchester (Britain).

## 2.3. Preparation of sample solution

Three kinds of Sudan dyes were separately dissolved in acetonitrile at the concentration of  $200 \mu\text{g mL}^{-1}$  as stock solution and stocked in refrigerator at 4 °C. The standard sample solutions of lower concentration were prepared from stock solution by diluting with mobile phase before use every time. HCl and NaOH solution of  $0.1 \text{ mol L}^{-1}$  was used to adjust pH value.

## 2.4. Electro deposition of zinc oxide

The zinc oxide was deposited on carbon fiber bundle by according to Daniel Lincot's method [15]. The carbon fiber was cut into bundles of 13 cm in length and was washed with perchloric acid,  $0.1 \text{ mol L}^{-1}$  NaOH solution, double-distilled water and ultrasonicated in methanol separately before coating. Then the fiber bundle was dried and was nipped by one end (1 cm in length) on the three electrode system by a clamp, while the remaining part was immersed in solution as work electrode. Platinum wire as counter electrode and saturated calomel was used as reference electrode. Before electro deposition, the fiber bundle was applied potential between -0.2–0.8 V in potassium ferricyanide solution until symmetric redox peaks appeared. Accompanied with sparging of oxygen,  $0.5 \text{ mol L}^{-1}$  zinc nitrate solution (containing  $0.1 \text{ mol L}^{-1}$  kalium chloratum) served as supporting electrolyte. Voltage at -1.0 V was applied to the system and proper deposition time was chosen for the electro deposition of zinc oxide accompanied with constant magnetic stirring.

After electro deposition of zinc oxide, the carbon fiber bundle was washed with purified water and heated for 1 h at 100 °C to immobilize the zinc oxide crystal. Then the fiber bundle was turned over and the same procedures were applied to modify the fiber bundle again.

## 2.5. Growth of zeolitic imidazolate framework on zinc oxide modified carbon fiber

The growth of zeolitic imidazolate framework was operated by solvothermal method. Firstly the ligand 2-mercaptobenzimidazole (5 mM) was mingled with ammonia, methanol and methylbenzene

(molar ratio 1:1:45:45) to form crystalline solution. The carbon fiber bundle with zinc oxide layer was immersed in the solution and was transferred to the water bath at 60 °C for 30 min to establish the nucleating site of ZIFs crystal, accompanied by constant magnetic stir. Then the carbon fiber was took out for growth of the crystal in ligand solution (0.01 g/mL 2-mercaptobenzimidazole solution, N, N-dimethylformamide as solvent) at 120 °C for 48 h. After reaction, the modified carbon fiber bundle was washed with methanol and purified water to remove unreacted reagents and was dried at 60 °C for further use.

## 2.6. Online analysis of Sudan dyes

A PEEK tube (15 cm) was manually packed with the modified carbon fiber bundle and was directly connected to the six-port valve as online extraction column. Methanol of certain volume was pushed through by a syringe pump to remove the air and impurities in the tube before sample loading. 20 mL sample solution was prepared by diluting 20  $\mu\text{L}$  stock solution with purified water. There are two steps for online SPME-HPLC-UV analysis of Sudan dyes, sample loading and sample elution. In the sample loading step, sample solution was loaded into the packed PEEK tube for extraction while the six-port valve was set at load position to let the mobile phase flow directly into the separation column. For the eluting and separation step, the mobile phase went through the packed PEEK tube and eluted extracted analytes into the column for separation and detection by switching the six-port valve to injection position. Thus the elution and separation were combined into one step [16,17].

For method validation, standard samples of Sudan dyes were prepared by diluting stock solution to a series of concentrations with acetonitrile. Then 20  $\mu\text{L}$  standard samples were diluted to 20 mL by purified water of certain pH value, respectively. The obtained solutions were loaded onto the extraction tubes for analysis.

## 2.7. Online analysis of spiked water sample

The water samples were respectively collected from the East Lake and tap water in our lab. Firstly the water samples were filtered through a 0.22  $\mu\text{m}$  membrane to obtain the filtrates, which were collected to be loaded for online analysis by above procedure and to prepare spiked water sample separately. Fig. 1

## 2.8. Evaluation of enrichment factor

The samples for online extraction were prepared by diluting the concentrated sample solution to 1000 folds so that the final sample concentration was as low as that in real sample. If the analytes in dilute solutions were extracted efficiently (close to total extraction), the peak area of analytes in elution we got were equal to that of the directly injected concentrated standard sample (without dilution to 1000 folds). In this work the enrichment factor was assessed the same way with our previous work [17].

## 3. Results and discussion

### 3.1. Characterization of modified carbon fiber bundles

The morphologies of zinc oxide and ZnO-ZIFs modified carbon fiber bundles were characterized with scanning electron micrographs (Fig. 2). After modification, a layer of cubic columnar crystal formed on the carbon fiber (Fig. 2A and Fig. 2B), with size between  $200 \times 200 \times 400 \text{ nm}^3$ . The morphology was noticeable different from that of bare carbon fiber bundle. After further growth of ZnO-ZIFs, microsphere of ZIFs was obvious on the ZnO crystal (Fig. 2C and Fig. 2D), with size diameter among 30–80 nm. The scanning electron micrographs proved success of ZnO-ZIFs modification.

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