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RESEARCH PAPER

Zeolite Imidazolate Framework 8 (ZIF-8) Decorated on ZnO Nanorods Resulting in Layered Double Hydroxide Layers for Determination of Phenolic Pollution in Water

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ABSTRACT

This study investigated the use of ZnO nanorods, made from layered double hydroxide layers and decorated with Zeolite imidazolate framework 8 (ZIF-8), as a new coating for solid-phase microextraction fiber (SPME). The effectiveness of the fabricated fiber in extracting phenolic compounds from the water sample was evaluated using gas chromatography-mass spectrometry. The effect of effective parameters, such as ionic strength, temperature, and extraction time, was examined to determine the ideal conditions. The calibration curves had a range of 0.01–300 ng mL^{-1} and acceptable linearity (R^2 > 0.995). The limits of detection were between 0.003 and 0.11 $ngmL^{-1}$, with a relative standard deviation of less than 8.4% under ideal conditions. The model was evaluated using river water and wastewater samples. The results showed that the proposed method is a straightforward, effective, and environmentally friendly approach for the quick and practical determination of phenolic compounds in real samples.

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INTRODUCTION

MOFs, which are coordination polymers with large, unique surface areas and based on metal nodes and multitopic organic linkers, possess a number of characteristics including high adsorption capacities, uniformly structured pore topologies at the nanoscale, and chemical tunability of both the pore environment and the outer surface. A low-cytotoxic and water-stable MOF can also be created. In analytical chemistry, MOFs have proven to be very appealing as highly efficient materials due to their inherent properties, and SPME is no exception given the range of applications they have.

The MOF-based fibers obtained with this procedure are commonly utilized in headspace SPME (HS-SPME) analysis. ZIFs are a new class of crystalline porous materials and a subset of MOFs with a topology similar to zeolites, which possess the characteristics of both zeolites and MOFs, including diversity in the lattice and pore structure, a modifiable structure, high specific surface area, and high thermal and chemical stability. These materials, therefore, can be used in various applications such as gas storage and separation, catalysts, chemical sensors, and other useful applications in nanotechnology. ZIFs are usually formed when cations of divalent metals, such as Zn and Co, and nitrogen atoms in imidazolate anions of binders bind together. ZIF-8 is a special type of ZIFs, with large pores (6.11 Å), a size twice of that of typical zeolites, and accessible tiny channels (4.3 Å)[1-5].

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ZnO nanoparticles (ZnO-NPs) have attracted considerable attention duez the separation process, a capillary column (HP-5) was employed with a length of 30 m and an inner diameter of 0.25 mm coated with a thickness of 0.25 µm. After the initial adjustment of the column temperature at 70 °C, the temperature at the next stages reached to 110 °C at a rate of 25 °C/min, 140 °C at a rate of 3 °C/min, and finally 180 °C at a rate of 20 °C/min and maintained at this temperature for 1 min. The injection valve, chromatograph interface to the detector, the quadrupole, and the ionization source were all set to temperatures of 275, 280, 230 and 150 °C, respectively. A flow rate of 1.1 mL.min^{-1} was adjusted for helium carrier gas. To investigate the morphology, a TESCAN scanning electron microscopy was employed. Additionally, an FT-IR instrument (Bruker Tensor) was used.

Synthesis of ZIF-8/ZnO/ZnAl-LDH

LDH precursors with Zn^{+2}/Al^{+3} molar ratio of 2 were prepared using the co-precipitation method. A mixed solution containing zinc nitrate hexahydrate and aluminum nitrate nonahydrate was added to a 500mL three-neck flask and 2M sodium hydroxide solution was added dropwise into the flask at 40°C while stirring vigorously. The resulting slurry was transferred to a Teflon-lined autoclave and heated at 100°C for 12 h. The suspension was filtered, washed multiple times with water, and finally dried at 80°C for 6 h. The synthesized ZnAl-LDH was placed in a solution of sodium hydroxide at 40 °C for 48 h to form ZnO nanorods on these composite layers. The ZIF-8/ZnO/ZnAl-LDH sample was synthesized by the in situ growth of ZIF-8 on ZnO/ZnAl-LDH. Typically, 0.36 g of pre-dried ZnO/ZnAl-LDH powder was mixed with 0.75 g of 2-methylimidazole and 0.405 g of HCOONa in 60 mL of methanol. The obtained slurry solution was added to 100 mL Teflon-lined stainless vessel and heated at 100 °C for 24 h in an oven. The white product was collected by centrifugation (3000 rpm, 3 min), washed three times by methanol, and dried at 50 °C for 24 h[3-4, 6-7].

Fabrication of SPME fiber

First, a piece of stainless steel wire with a radius of 200 µm was washed twice in a methanol solvent under ultrasound for 20 min and then dried at 70 °C. The wire (1 cm) inserted into a colorless twin glue, and any excess glue was wiped away with a clean tissue paper. The coated wire was then placed in a vessel containing the synthesized material powder and rotated on a table and then heated at 50 °C for 48 h to remove any unattached particles to the fiber. Finally, to clean the prepared fiber before being injected into the GC, it was heated at 260 °C at the injection inlet of the GC for 1 h.

RESULTS AND DISCUSSION

Structural morphology of the nanocomposites

Figs. 1 (a-c) display the SEM images of nanostructures obtained at each stage of the synthesis. Fig. 1a reveals the layered and plate-like morphology of the synthesized LDH obtained. Lamellar particles with hexagonal layer structure, which is a common structure for hydrotalcite-like material, is observed for LDH. Fig. 1b shows the growth of the nanorod structure ZnO particles on LDH sheets, and Fig. 1c illustrates the final nanocomposite (ZIF-8/ZnO/ZnAl-LDH). These images demonstrate the successful synthesis of ZIF-8 with polyhedral topologies, which is in agreement with previous literature[3-4].

The XRD patterns of LDH layers exhibited three distinct diffraction peaks at 2θ values of 11.7°, 23.5°, and 34.6°, which can be attributed to reflections of (003), (006) and (012) crystal planes of the ZnAl-LDH phase (Fig. 2). Unfortunately, a severe peak overlap between the LDH, ZIF-8, and ZnO phases rendered it impossible to detect all LDH phase-derived diffraction peaks and, consequently, its favored orientation could not be determined accurately. The pattern is well-matched with the published and simulated patterns. As shown in Fig. 3, FT-IR spectra depicted the typical vibrational frequencies of the LDH and ZIF-8 structures, which were consistent with those provided in the literature[3, 6, 8-10].

Optimization of head-space solid phase microextraction (HS-SPME) technique

To evaluate the efficacy and efficiency of ZIF-8/ZnO/ZnAl-LDH nanocomposite fibers, some phenolic compounds were extracted from aqueous samples. Before the optimization of parameters affecting the extraction, the complete desorption of the analyte adsorbed on the fiber was examined at the injection site of the GC and the corresponding separation was studied in the GC column. Different injection temperatures and various desorption times were tested for this purpose. The highest temperature that can be used for the desorption of

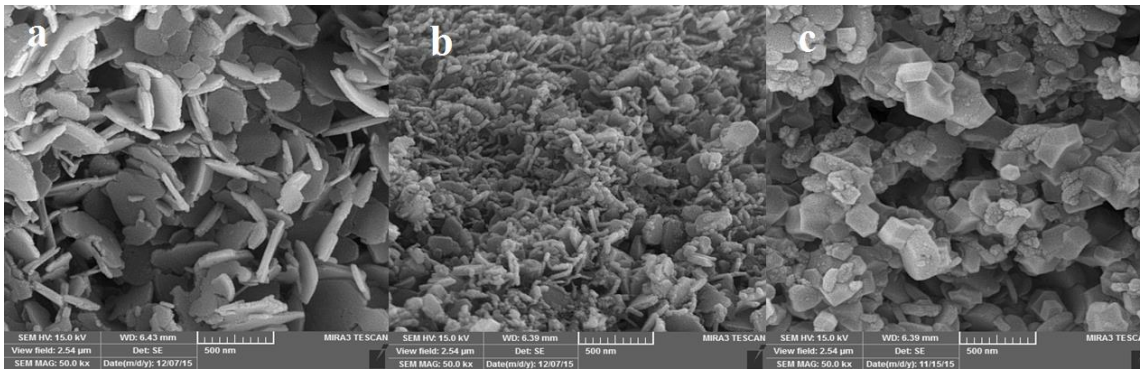

Fig.1: a: SEM images related to ZnAl-LDH, b: SEM images related to ZnAl-LDH/ZnO, and c: SEM images related to ZnAl-LDH/ZnO/ZIF-8 after 12 hours of synthesis.

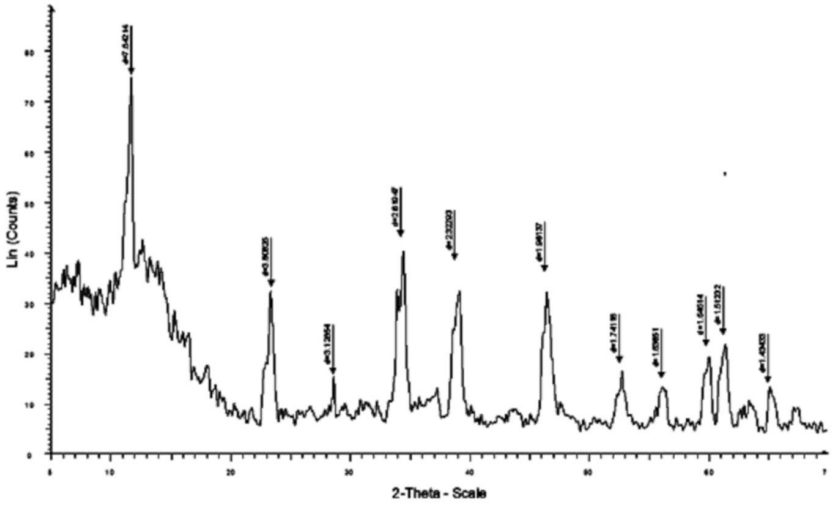

Fig. 2: XRD pattern of the synthesized ZnAl-LDH/ZnO/ZIF-8.

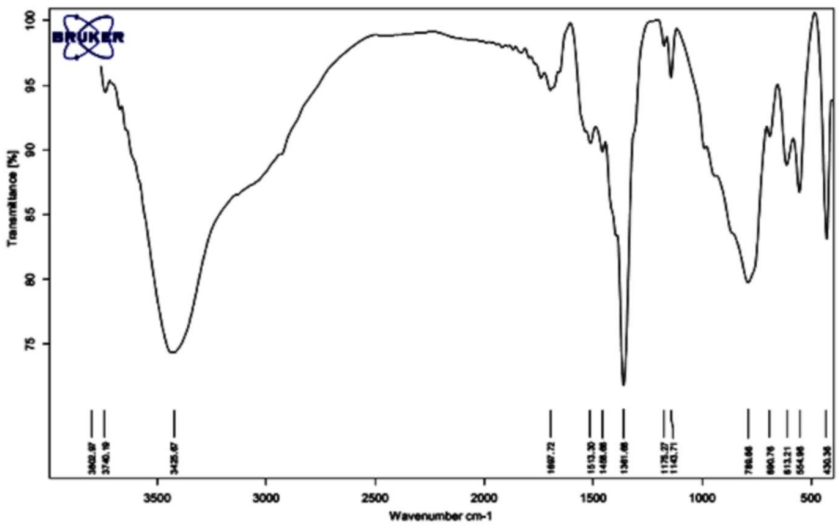

Fig. 3: FTIR spectra of the ZnAl-LDH/ZnO/ZIF-8 nanostructure.

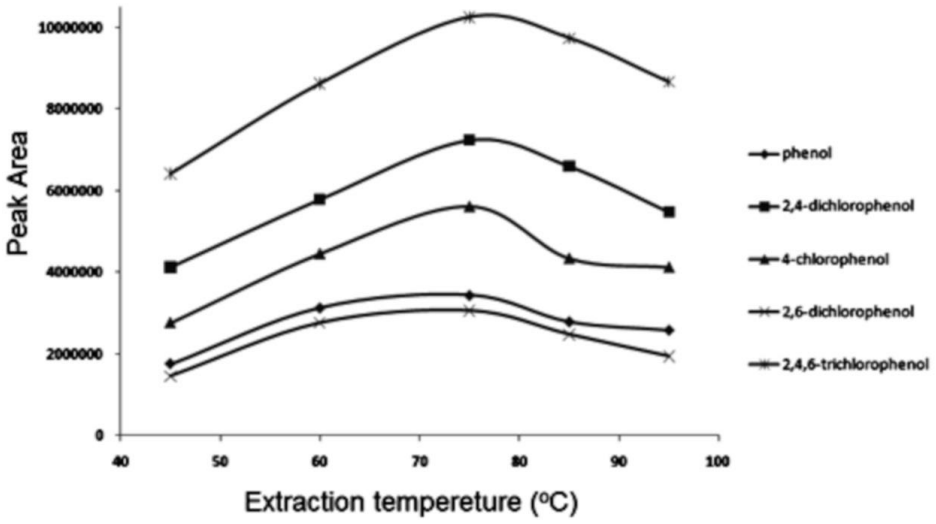

Fig. 4: Effect of time on microextraction

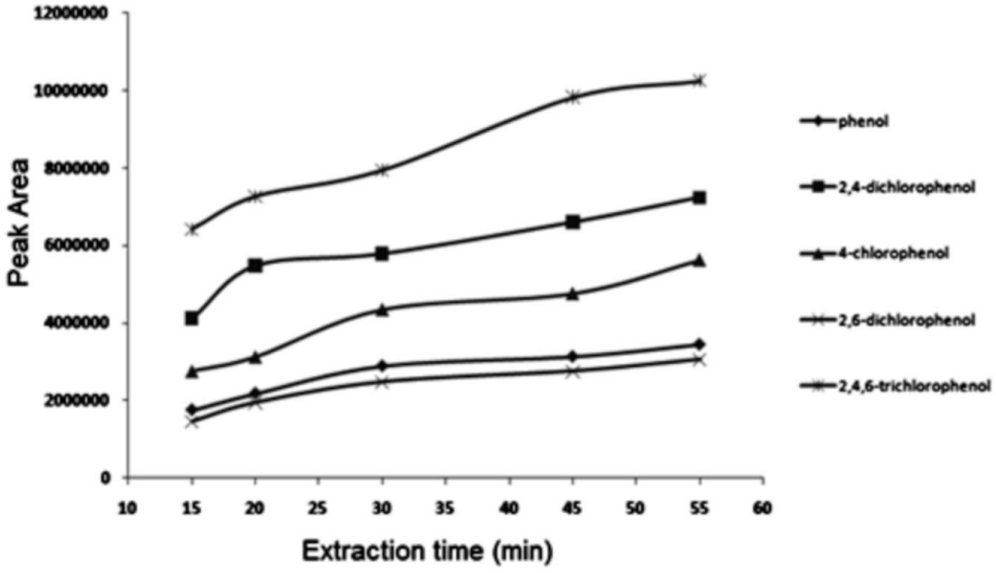

Fig. 5: Effect of temperature on microextraction

analyte from the fiber in GC was determined based on the thermostability of the fiber coating. Thus, a temperature range of 250-280 °C was tested and the best results were obtained at 270 °C, allowing for the desorption process to be performed without damaging the fiber. Desorption time was studied in the range of 1-5 min and a time of 2 min with the highest extraction was selected for complete desorption. After optimizing the desorption conditions, the parameters affecting the extraction efficiency (extraction time, extraction temperature, stirring speed, pH and ionic strength) were optimized.

Selection of microextraction temperature

Temperature has a significant effect on solid phase microextraction (SPME). Rising the temperature can increase the amount of analyte extracted by increasing the analyte distribution coefficients (K_d) between the headspace and the fiber. Thus, it is essential to optimize the extraction temperature. To do this, PCs were extracted from

Table 1: Some analytical data obtained for microextraction using the ZIF-8/ZnO/ZnAl-LDH nanocomposite fiber and comparison of the developed method with other methods

Compound	Current method				TMSPA/PDMS[d]		Polyacrilate[e]		PPy-DS[f]		MWCNTs-COOH[g]	
	DLR[a]	(R^2)	LOD[b]	%RSD[c]	LOD	%RSD	LOD	%RSD	LOD	%RSD	LOD	%RSDz
Phenol	1-300	0.998	0.22	7.2	0.05	9.2	2.5	5.2	-	-	3.67	2.47
4-Chlorophenol	0.1-100	0.995	0.05	6.9	0.05	6.8	-	-	-	-	-	-
2, 4-Dichlorophenol	0.01-100	0.994	0.004	8.3	0.02	9.2	0.05	3.6	-	-	5.27	6.38
2, 6-Dichlorophenol	0.01-100	0.997	0.005	6.5	-	-	0.05	4.9	0.63	4.7	-	-
2, 4, 6-Trichlorophenol	0.01-100	0.995	0.004	9.1	0.02	8.7	-	-	-	-	4.76	5.65

[a] Dynamic Linear Range. [b] Limit of detection calculated as three times the baseline noise (ngmL^{-1}). [c] Relative Standard Deviation. [d] 3-(trimethoxysilyl) propyl amine/PDMS (TMSPA/PDMS) [22] [e] Ppolyacrilate [23]. [f] Dodecyl sulfate-doped polypyrrole (PPy-DS) [24]. [g] Oxidized multiwalled carbon nanotubes (MWCNTs-COOH) [25].

the headspace of the sample solution at different temperatures (45-95 °C). The peak area of the analyte against the applied temperature (Fig. 4) demonstrates that the uppermost extraction efficiency is achieved at 75 °C.

The effect of extraction time

Extraction time is a critical factor in solid phase microextraction, as it influences the analyte distribution between the solution and the fiber. The sensitivity and reproducibility are maximized when a balanced distribution of the analyte is established between the fiber and the sample. To examine the effect of time on the amount of analyte extracted, this study investigated the extraction process within a period of 15-55 min. It was found that the amount of extracted analyte reached a constant value after 45 min (Fig. 5).

The effect of ionic strength of solution and stirring speed of the solution

The addition of salts such as NaCl and Na_2SO_4 to the aqueous phase typically enhances the transport of organic compounds to the headspace, thereby improving the extraction efficiency of the organic analyte in most conventional extraction techniques. In the current study, NaCl with concentrations ranging from 0 to 30 % (w/v) was added to the samples and it was observed that the extraction efficiency rose by salting up to 15 % (w/v). Stirring the solution increases the mass transfer rate in the solution, reducing both the time necessary to reach equilibrium and the extraction time. In this work, the results from different stirring rates (0-700 rpm) revealed that the extraction of PCs increased by increasing the stirring rate, with 500 rpm being selected as the optimal speed.

Quantitative assessment and analysis of real samples

The analytical performance of the method was examined (Table 1). Correlation coefficients (R2) ranging from 0.985 to 0.998 were found, with a linear range of 0.01-300 ngmL^{-1}. To assess the repeatability and reproducibility of the method, four fibers were also examined by extracting water samples containing 10 ngmL^{-1} analytes. The results demonstrate that the method has good repeatability and reproducibility (Table 1). LODs ranged from 0.003 to 0.28 ngmL^{-1} based on signal-to-noise (S/N) ratios of three.

Table 2: The results obtained for the analysis of the spiked water samples (10 $ngmL^{-1}$) by the proposed method, under the optimized conditions.

Compound	Polsangi bridge	Chichih river
Phenol	10.5(0.4)	10.8(0.8)
4-Chlorophenol	10.7(0.3)	10.9(0.5)
2, 4-Dichlorophenol	10.3(0.2)	10.5(0.7)
2, 6-Dichlorophenol	10.5(0.8)	10.6(0.8)
2, 4, 6-Trichlorophenol	10.8(0.3)	10.7(0.6)

The performance of the ZIF-8/ZnO/ZnAl-LDH SPME fiber was compared to other published microextraction methods for the extraction and determination of the selected pesticides in order to assess its performance. Table 1 displays the findings of the comparison. The data indicate that the proposed method has linear ranges, RSDs, and extraction times are comparable to those of other reported methods. In addition, the sensitivity of the current fiber is either superior or comparable to that of reported methods.

The ZIF-8/ZnO/ZnAl-LDH SPME fiber was employed for the enrichment and analysis of pesticides in river water samples and to demonstrate the viability of this approach. The analytical process followed the steps outlined above, and the experimental results are presented in Table 2. The river water samples did not contain any phenolic compounds. The data in Table 2 demonstrate the successful application of this method for the real samples.

After more than 50 analyses, the lifespan of the homemade SPME instrument was evaluated using a spiked sample of 10 $ngmL^{-1}$ as the performance test model. The extracted phenol was used to assess the durability of the ZIF-8/ZnO/ZnAl-LDH SPME fiber after repeated sampling/desorption cycles. After 50 cycles, the extractability of phenol remained almost unchanged. The current data clearly demonstrate that the designed fiber has a moderately high level of durability (RSD% < 8.4). Thus, this lack of significant variation in the findings is an indication of the instrument's stability.

CONCLUSION

This study is the first to utilize a highly sensitive solid-phase microextraction method based on the nanocomposite ZIF-8/ZnO/ZnAl-LDH to determine PCs in an aqueous sample. The technique is repeatable, highly sensitive, and has a wide linear range. The suggested approach can be applied to further research on aromatic compounds present in soil and water at low concentrations. The results indicate that the prepared fiber has a high level of extractability. Moreover, the proposed method has the distinct advantages including high sensitivity, no requirement for organic solvents, high selectivity, and low LODs.

CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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