

RESEARCH PAPER

## Application of LDH/Halloysite Nanocomposite as Solid-Phase Microextraction Fiber Adsorbent for Determination of Phenolic and Chlorophenols Compounds

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### ABSTRACT

In this research, layered double hydroxide/halloysite (LDH/Halloysite) nanocomposite was synthesized as a coating for solid-phase microextraction fiber for extraction of phenolic compounds (PCs) in the plasma and water samples. The size, morphology, composition, and properties of the prepared nanocomposite were also characterized using scanning electron microscopy (SEM), Fourier transform- infrared spectroscopy (FT-IR), energy-dispersive X-ray spectrometry (EDX), and thermogravimetric analysis (TGA). After solid-phase microextraction, the phenolic compounds were quantified via gas chromatography-mass spectrometry. Analytical merits of the method, under optimum conditions (extraction temperature: 80°C, extraction time: 30 min, pH: 6.5, stirring rate: 500 rpm, and salt concentration: 15%  $wv^{-1}$ ), are 0.01–200  $ng mL^{-1}$  for the linear dynamic range and 0.2-4  $pgmL^{-1}$  for the limit of detection. In optimum conditions, the repeatabilities for one fiber ( $n = 3$ ), expressed as relative standard deviation, was between 4.1 and 7.6% for the phenolic compounds. Ultimately, for the analysis of the river water and plasma samples, the SPME technique was successfully applied.

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### INTRODUCTION

Halloysite is a type of aluminosilicate mineral clay ( $Al_2Si_2O_5(OH)_4.nH_2O$ ) with micro or nano structure and is found in nature in three forms of tubular, spherical, and planar. The outer and inner diameters of halloysite nanotubes (HNTs) are usually 30-50 nm and 1-30 nm, respectively, and often have multilayer walls. [1] Each wall is composed of 1:1 layers of alumina and silica, which form the inner and outer layers, respectively. This difference in inner and outer layer chemistry results in different charges at the inner and outer surfaces of HNT layers at various pHs. [2] This type of halloysite is frequently applied in the controlled release of materials, nanoreactors, nanotemples,

and pollutant adsorption, and is expected to be able to adsorb certain materials due to its nanotube structure. Recently, the applications of halloysite nanotubes have been extensively studied in the adsorption of pollutants and other substances. For example, the aqueous adsorption of methylene or malachite green has been extensively investigated by HNTs. [3-5]

During the past decade, several methods have been used for preconcentration and determination of trace levels of organic pollutants in aqueous solutions including solid phase extraction (SPE), solid phase micro extraction (SPME), liquid phase microextraction (LPME), liquid-liquid extraction (LLE), floatation separation, precipitation, membrane filtration

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etc. SPME is a preconcentration technique that possesses favorable properties including solvent free, fast diffusion rate, portable, easy-to-use, and high enrichment factor.[6-8] Moreover, SPME can integrate sampling, extraction, and sample introduction into a single step and become an attractive alternative to most of the conventional sampling techniques. SPME was initially introduced for the analysis and determination of volatile organic pollutants at trace levels in different matrices. In this field, the development of new materials is mainly aimed at the achievement of superior selectivity with regard to target analytes or specific classes of compounds as well as at the development of less breakable and more stable supports. [9-23]

In this paper, ZnAl-LDH nanosheets were grown via a simple, facile and inexpensive precipitation method on halloysite nanotube (HNT). The potential use of the ZnAl-LDH/HNT was assessed as an extraction phase for head space solid phase microextraction (HS-SPME). Phenolic compounds as an organic pollutants were utilized as model compounds for SPME. The investigated compounds were defined via gas chromatography-mass spectrometry detection.[24-29] The ZnAl-LDH/HNT fiber' extraction ability was investigated and a comparison was made. The effects of various experimental parameters like sample ionic strength, pH, extraction time, and desorption condition on the method's extraction efficiency were investigated. Ultimately, for the analysis of the river water and plasma samples, the SPME technique was employed in a successful manner.

## EXPERIMENTAL

### Materials and methods

Halloysite nanotubes (HNT), Phenolic compounds including Phenol, 4-Chlorophenol, 2, 4-Dichlorophenol, 2, 6-Dichlorophenol, 2, 4, 6-Trichlorophenol, 3-Nitrophenol, 4-Nitrophenol, 3-Nitroaniline, 4-Nitroaniline with a purity of >98% were obtained from the Merck Company (Darmstadt, Germany). Structures and some physicochemical properties of phenol and the four chlorophenols under investigation are listed in Table 1. Sodium hydroxide and aluminum nitrate, zinc nitrate, hydrochloric acid, sodium chloride, methanol and all chemical solvents (analytical-reagent grade) were supplied from Merck or Fluka companies. Deionized water was

prepared with a Milli-Q water system (Millipore, Billerica, MA, USA). A mixture stock solution of the selected phenols (100 mg L<sup>-1</sup> of each analyte) in methanol was prepared and stored at 4 °C in a refrigerator. By appropriate dilutions of the stock solution with deionized water fresh working standard solutions were daily prepared.

Water samples were collected (on June 2019) from polluted parts of a river at Polsangi bridge (Aji river, Tabriz, Iran) and Sofy river at Dejhban bridge in Maragheh city. The water samples were collected into glass bottles (200 mL) without a concave bottom. The samples were stored at 4 °C in darkness and were analyzed within 24 h of collection. To eliminate the suspended particles, the samples were centrifuged at 7000 rpm for 6 min before they were subjected to the proposed procedure. The pH values of studied water samples were in the range of 6.5–7.4. The pH value of samples was adjusted to 4.5 using HCl solution (1 M) prior to their analysis. Plasma samples collected from the blood transfusion center (East Azerbaijan) were obtained from the local pathobiology laboratory.

### Instrumentation

A gas chromatography device (Model 7890A, Agilent, USA), equipped with a mass spectrometer detector (5975C) and bifurcated/non-bifurcated injection valve was utilized in this experiment. Recording of chromatograms and processing of data were conducted using the Chemstation and Wiley 7N computer library software. For the separation process, a capillary column (MS HP-5, W&J Company, USA) was applied with a length of 30 m and an inner diameter of 0.25 mm coated with stationary phase with a thickness of 0.25 μm.

After initial tuning of the column temperature at 70 °C, the temperature at the next steps reached 110 °C at a rate of 25 °C.min<sup>-1</sup>, 140 °C at a rate of 3 °C.min<sup>-1</sup>, and finally 180 °C at a rate of 20 °C.min<sup>-1</sup> and maintained at this temperature for 1 min. Temperatures of the injection valve, chromatograph interface to the detector, the quadrupole, and the ionization source were set at 275, 280, 230, and 150 °C, respectively. The flow rate of helium carrier gas was adjusted to 1.1 mL.min<sup>-1</sup>. In this research, the morphology of the prepared nanocomposite was examined by a TESCAN MIRA3-FEG-SEM electron microscope (University of Tabriz). A FT-IR device (Bruker

Table 1: Calibration curve, correlation coefficient, detection limit, linear range of the calibration curve and relative standard deviation values for PCs analysis.

Compound	DLR (ng mL <sup>-1</sup> )	Regression coefficient	LOD (pg mL <sup>-1</sup> )	Repeatability R.S.D. %	Reproducibility R.S.D. %
Phenol	0.01-200	0.998	0.4	5.9	9.2
4-Chlorophenol	0.01-200	0.988	0.3	6.7	8.3
2, 4-Dichlorophenol	0.01-150	0.999	0.4	4.1	6.9
2, 6-Dichlorophenol	0.01-150	0.998	0.2	4.3	8.6
2, 4, 6-Trichlorophenol	0.01-150	0.997	0.2	3.9	7.3
3-Nitrophenol	0.1-200	0.997	4	7.3	11.9
4- Nitrophenol	0.1-200	0.996	3	7.6	12.1
3-Nitroaniline	0.1-200	0.997	2	4.9	10.2
4- Nitroaniline	0.1-200	0.995	2	5.3	11.2

Tensor 27) was used to further confirm the synthesis and examine the chemical structure of the synthesized substance. The working conditions of the gas chromatograph are presented below.

#### Synthesis of ZnAL-LDH/HNT

To synthesize this composite, 0.1 g of HNT was dispersed into a 10 mL water under ultrasonically agitating for 5 minutes to obtain a uniform suspension. Then, another 100 mL solution containing Zn (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Al (NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (the molar ratio of Zn to Al was set to 2:1) and 0.04 M of urea were added drop-wise into the above suspension under vigorous stirring at a constant pH=10 maintained by simultaneous addition of alkaline solution. The mixture was agitated and heated (80 °C) simultaneously for 24 h, and the product was separated using a centrifuge. The residue was washed several times in distilled water and finally in ethanol and allowed to dry in a vacuum oven at 60°C for 6h.

#### Preparation of the SPME fiber

In general, employing high mechanical stable metal wires as fiber supports in SPME enhanced the robustness of this method for routine analysis. For this purpose, a piece of stainless steel wire (4 cm-long with a 0.2 mm diameter) was cleaned twice by introducing into the methanol and with the assistance of sonicating for 20 min in an ultrasonic bath and then dried at 70 °C. Afterward, the wire (1 cm) with epoxy glue was limed and the synthesized LDH/HNT powder

was immobilized onto the wire. In the following, the resulting coated wire was heated for 48 h in an oven to 50 °C, gently polished to eliminate non-bonded particles, and then connected to the laboratory-made SPME holder device. In the end, the prepared SPME fiber was conditioned in the injection port of gas chromatograph at 275 °C under helium gas for 2 hours. The fabricated fiber, assembled to its SPME holder device, was applied to the proposed HS-SPME method.

#### HS-SPME process

Five mL of deionized water or samples (see Section 2.2), spiked with the interested analytes (10 µg L<sup>-1</sup>, each analyte) with pre-established pH 4.5 (using 1 M HCl solution) and ionic strength (10%, w/v, NaCl), was placed into a 15-mL clear glass vial (59 mm × 18 mm i.d.). The vial was immediately sealed with a PTFE/silicone septum screw cap after introducing the magnetic stir bar. In the following, the vial was placed into a water bath thermostated at 80 °C. Then, the SPME device needle was passed through the septum and the fiber was pushed out from the needle and for 30 min exposed to the headspace over the aqueous solution, which was continuously stirred by a magnetic stirrer at 500 rpm. Subsequently, the fiber containing the retained analytes was retracted into the needle and transferred immediately to the GC injector in the splitless mode where the compounds were thermally desorbed by applying a temperature of 275 °C for 2 min. To remove the possible residues

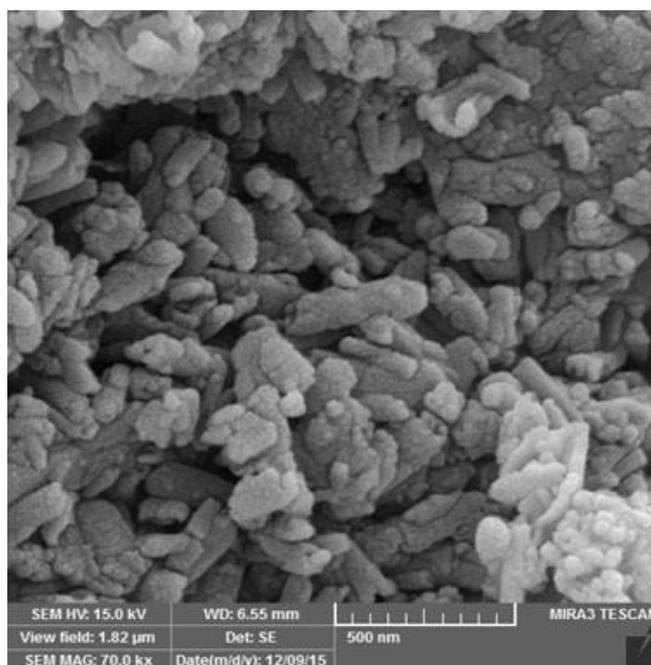


Fig.1: The SEM images of the LDH/HNT.

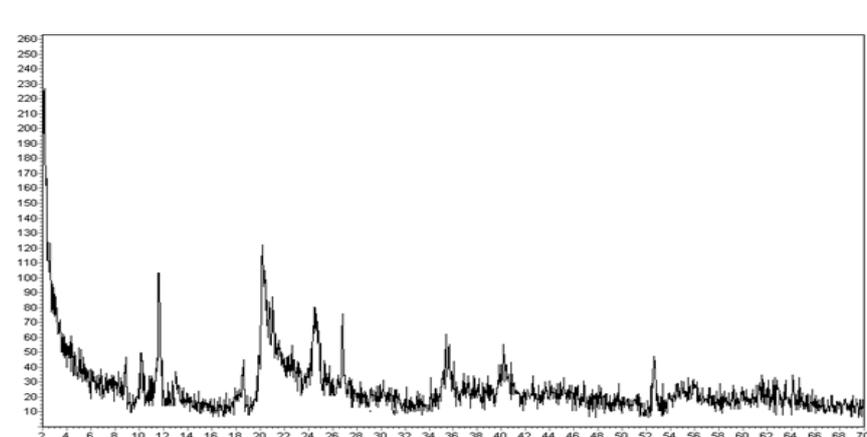


Fig.2: The XRD pattern of LDH/HNT.

on the fiber, it remained in the GC injection port until 2 min after opening the split valve.

## RESULTS AND DISCUSSION

### *Structural morphology of the synthesized structure*

The SEM image of the LDH/HNT is presented in Fig. 1. As it is seen, the prepared LDH/HNT nanocomposite possesses a homogeneous structure, which should considerably enhance the available surface area on the coating for adsorption.

The XRD pattern of LDH/HNT is shown in Fig. 2, which reveals that it is in agreement with

the related pattern in previously reported work. The characteristic diffraction peaks of a LDH phase with the

indexes (003) and (006) were identified at low  $2\theta$  angle, while the non-basal peaks were associated with the indexes (101), (015), (018), (110) and (113) at higher  $2\theta$  angles. The XRD pattern of LDH/HNT sample also had peaks corresponding to the metahalloysite or aluminum silicate hydroxide. The diffraction peaks at  $2\theta = 12, 20.1, 24.6, 35.0, 37.9, 54.5$  and  $62.6$  corresponded to (001), (100), (002), (110), (003), (210) and (300) planes, respectively

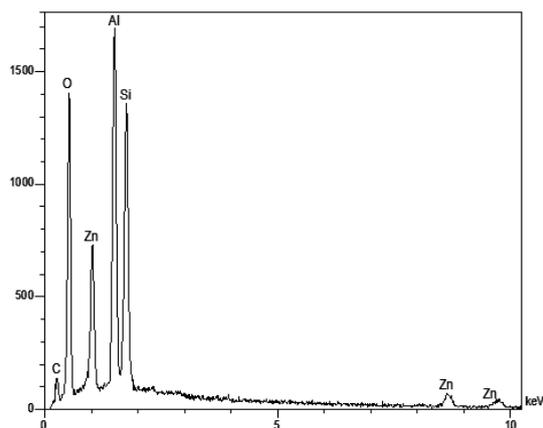


Fig.3: The elemental composition was also investigated via EDX (energy-dispersive X-ray spectroscopy).

[45, 46].

To further confirm the formation of the hybrid, elemental composition was performed. The elemental composition was also investigated via EDX (energy-dispersive X-ray spectroscopy). According to Fig. 3, the only elements observed at the LDH/HNT were the Al, Zn, O and Si elements.

The thermal stability of the fabricated fiber is an essential parameter that must be regarded because the desorption of analytes in SPME fiber is performed in the hot injector port. TGA curve of LDH/HNT is illustrated in Fig. 4. LDH/HNT is stable up to 400 °C. The first weight loss at 50-100 °C corresponds to the loss of surface water. The second weight loss step of at 180-250 °C corresponds to the loss interlayer water of LDH, and the third weight loss step at 400-550 °C corresponds to the dehydroxylation of the HNT structure.

#### *Optimization of the head space solid phase microextraction (SPME) technique*

To assess the capability and efficiency of ZnAl- LDH/HNT nanocomposite fibers, some of PCs were extracted from the aqueous samples in the head space SPME. The use of head space SPME technique is usually preferred because it significantly excludes damage to fibers caused by the sample matrix and prevents the extraction of annoying agents, thereby extending the lifespan of SPME fibers.

Before the optimization of parameters influencing the extraction, the complete desorption of the analyte adsorbed on the fiber was examined at the injection site of the GC device, and the corresponding separation was studied in the GC

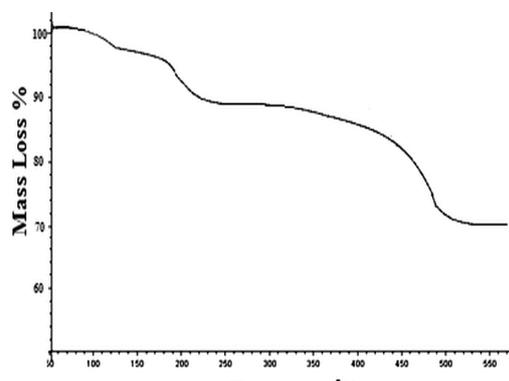


Fig.4: TGA curve of LDH/HNT.

column. The different injection site temperatures and various desorption times were tested for this purpose. The maximum temperature that can be applied for the desorption of the analyte from the fiber in GC is determined based on the thermostability of the fiber coating. Accordingly, a temperature range of 220-280 °C was examined and a temperature of 280 °C yielded the best results for the analyte desorption, allowing the implementation of analyte desorption process without damaging the fiber. Desorption time was investigated in the range of 1-5 min, and finally, a time of 2 min with the upmost extraction was selected for complete desorption. The parameters influencing the extraction efficiency (extraction time, extraction temperature, stirring speed, pH, and ionic strength) were optimized after optimizing the desorption conditions.

#### *pH effect*

The impact of pH was investigated here as phenolic compounds have acid-base characteristics and their extractability is significantly affected by pH. The solution pH level makes a major contribution to the extraction procedure. Moreover, transferring analytes from the sample solution to the headspace is accelerated by the sample solution pH as the main factor. Accordingly, the impact of pH ranging from 2 to 10 was surveyed with the addition of suitable hydrochloric acid or sodium hydroxide solution to the aqueous phase. The maximal efficiency was achieved at pH 6.5. At low and high pH, there is a significant shift of the acid-base equilibrium for the phenols towards the neutral types that

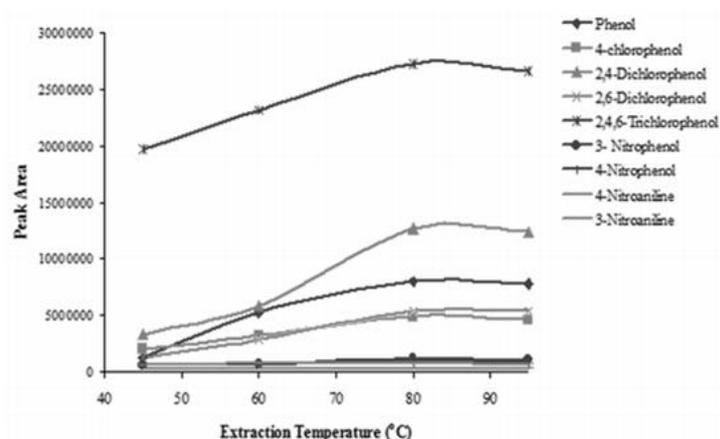


Fig. 5: Effect of temperature on microextraction.

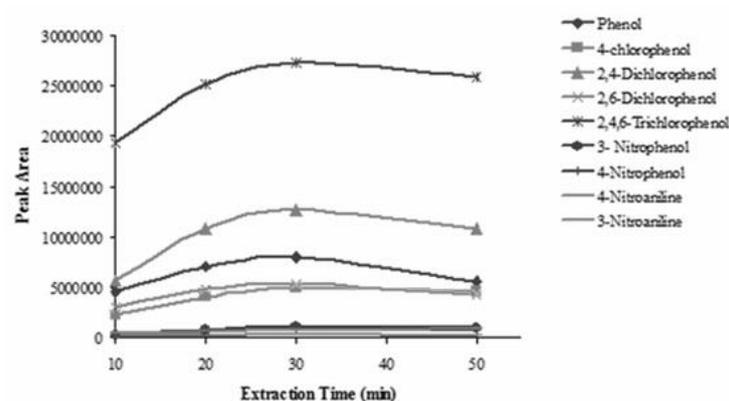


Fig. 6: Effect of time on microextraction.

possess elevated vapor pressure and higher affinities towards the fiber, thereby increasing the extraction efficacies. The pH of 6 was selected for future experiments.

#### Selection of microextraction temperature

In solid-phase microextraction, the temperature has a dual impact. This means that as an increase in the temperature can augment the amount of analyte extracted by increasing the analyte distribution coefficients ( $K_d$ ) between the headspace and the fiber, it also increases desorption between the two at very high temperatures. Therefore, it is an absolute necessity to optimize the extraction temperature. For this purpose, PCs were extracted from the headspace of the sample solution at a temperature range of 45–95 °C. Fig. 5 shows the peak area of the analyte against the applied temperatures, indicating that the uppermost extraction efficiency occurs at 80 °C.

#### The effect of extraction time

In solid-phase microextraction, the extraction time is an important factor, as it affects the analyte distribution between the solution and the fiber. The sensitivity and reproducibility are maximum when there is a balance in the analyte distribution between the fiber and the sample. To test the impact of time on the amount of analyte extracted in this research, the extraction process was examined within a period of 10–50 min. The results indicated that the amount of extracted analyte reached a maximum at 30 min (Fig. 6). Thus, 30 min will be chosen in future experiments.

#### The effect of ionic strength of solution

The addition of salt raises the ionic strength of the donor phase and decreases the tendency to the organic phase, thereby improving the extraction efficiency of the organic analyte in most conventional extraction techniques. In the present work, NaCl salt from 0 to 30 % (w/v) was added

to the samples and it was observed that salting elevated the extraction efficiency up to 15 % (w/v).

#### The effect of stirring speed of the solution

The mass transfer rate in the donor phase increases and both the time needed to reach equilibrium and the extraction time decrease by stirring the solution. In this study, the results obtained from the use of different stirring rates (0-700 rpm) revealed an increase in the extraction of PCs by raising the stirring rate to 500 rpm, which was therefore selected as the optimal speed.

#### Quantitative evaluation and analysis of real samples

Following the optimization of the microextraction conditions, quantitative features of the proposed method, including correlation coefficient, limit of detection (LOD), and linear range of the calibration curve were evaluated herein as presented in Table 1. The dynamic linear range (DLR) of this method was examined by the extraction of different aqueous samples at a range of concentrations and a good DLR (0.01-200 ngmL<sup>-1</sup>) was found with a correlation coefficient range of 0.995-0.999. The relative standard deviation (R.S.D) values (Table1) suggest good repeatability of the manufactured fiber. To assess the method's applicability to determine the examined PCs in real specimens and investigate the effects of the sample matrix on quantifying, the technique was utilized to analyze plasma and river water samples. TFME of (a) non-spiked and (b) spiked urine samples with 10 ngmL<sup>-1</sup> of PCs were performed, and GC-MS was used for analysis. To evaluate the method's ability in real sample analysis, RSDs were regarded in the sample analysis via the technique. Table 2 represents the findings demonstrating that the technique can be used to extract and determine the evaluated PCs in the real specimens.

## CONCLUSION

This study is the first to develop a highly sensitive method based on the SPME using the synthesized fiber to measure PCs in an aqueous sample. The applied method has a good DLR, repeatability, and high sensitivity, which can therefore be employed for other research on aromatic compounds with low concentrations in water and soil. The present results establish that the prepared composite fiber is of high extractability. High sensitivity, no use of organic solvents, high selectivity, and low LODs are the unique advantages of the introduced technique.

Table 2: Results obtained for the analysis of the spiked water samples (1 mg L<sup>-1</sup>) by the proposed method under optimized conditions.

Sample	After addition (ngmL <sup>-1</sup> )								
	Phenol	4-Chlorophenol	2,4 Dichlorophenol	2,6 Dichlorophenol	2, 4, 6-Trichlorophenol	3-Nitrophenol	4- Nitrophenol	3-Nitroaniline	4- Nitroaniline
Sofy river	10.2(0.1)	10.1(0.1)	10.2(0.3)	10.1(0.1)	10.3(0.2)	10.3(0.3)	10.2(0.2)	10.4(0.3)	10.4(0.2)
Aji river	10.3(0.3)	10.2(0.2)	10.1(0.2)	10.1(0.2)	10.2(0.4)	10.2(0.6)	10.2(0.3)	10.2(0.2)	10.2(0.1)
Plasma	10.3(0.3)	10.4(0.1)	10.1(0.1)	10.2(0.2)	10.2(0.2)	10.2(0.3)	10.4(0.4)	10.1(0.2)	10.2(0.3)

## CONFLICT OF INTEREST

The authors declare no conflicts of interest.

## REFERENCES

- M.E Phd D, Agrawal Y. Multifarious applications of halloysite nanotubes: A review. *Reviews on Advanced Materials Science*. 2012;30:282-95.
- Joussein E, Petit S, Churchman J, Theng B, Righi D, Delvaux BJ. Halloysite clay minerals-a review. 2005;40(4):383-426. <https://doi.org/10.1180/0009855054040180>
- Wesley L. Some basic engineering properties of halloysite and allophane clays in Java, Indonesia. *Geotechnique*. 1973;23(4):471-94. <https://doi.org/10.1680/geot.1973.23.4.471>
- Zhang Y, He X, Ouyang J, Yang H. Palladium nanoparticles deposited on silanized halloysite nanotubes: synthesis, characterization and enhanced catalytic property. *Scientific Reports*. 2013;3(1):2948. <https://doi.org/10.1038/srep02948>
- Massaro M, Casiello M, D'Accolti L, Lazzara G, Nacci A, Nicotra G, et al. One-pot synthesis of ZnO nanoparticles supported on halloysite nanotubes for catalytic applications. *Applied Clay Science*. 2020;189:105527. <https://doi.org/10.1016/j.clay.2020.105527>
- Piryaei M, Abolghasemi MM, Sobhi M. A New Method for Extracting and Measuring Methoxyfenozide Using ND/PAN-K10 SPE Using High Performance Liquid Chromatography. *Nanochemistry Research*. 2023;8(3):197-204.
- Piryaei M, Abolghasemi MM, Hasani S. Zeolite Imidazolate Framework8 (ZIF-8) Decorated on ZnO Nanorods Resulting in Layered Double Hydroxide Layers for Determination of Phenolic Pollution in Water. *Nanochemistry Research*. 2023;8(3):224-30.
- Piryaei M, Abolghasemi M. A sandwich-type three-dimensional layered double hydroxide nanosheet array as a novel fiber coating for headspace solid-phase microextraction of phenols from water samples. *Nanochemistry Research*. 2023;8(2):87-94.
- Arthur CL, Pawliszyn J. Solid phase microextraction with thermal desorption using fused silica optical fibers. *Journal of Analytical chemistry*. 1990;62(19):2145-8. <https://doi.org/10.1021/ac00218a019>
- Magdic S, Boyd-Boland A, Jinno K, Pawliszyn JB. Analysis of organophosphorus insecticides from environmental samples using solid-phase microextraction. *Journal of Chromatography A*. 1996;736(1):219-28. [https://doi.org/10.1016/0021-9673\(95\)01349-0](https://doi.org/10.1016/0021-9673(95)01349-0)
- Abolghasemi MM, Karimi B, Yousefi V. Periodic mesoporous organosilica with ionic liquid framework as a novel fiber coating for headspace solid-phase microextraction of polycyclic aromatic hydrocarbons. *Analytica Chimica Acta*. 2013;804:280-6. <https://doi.org/10.1016/j.aca.2013.10.022>
- Abolghasemi MM, Yousefi V, Hazizadeh B. An inorganic-organic hybrid material based on ZnO nanoparticles anchored to a composite made from polythiophene and hexagonally ordered silica for use in solid-phase fiber microextraction of PAHs. *Microchimica Acta*. 2014;181(5):639-45. <https://doi.org/10.1007/s00604-014-1165-1>
- Abolghasemi M, Yousefi V, Piryaei M. Synthesis of Carbon Nanotube/Layered Double Hydroxide nanocomposite as a novel fiber coating for the headspace solid-phase microextraction of phenols from water samples. *Journal of Separation Science*. 2015;38. <https://doi.org/10.1002/jssc.201401191>
- Gholivand MB, Piryaei M, Abolghasemi MM. Anodized aluminum wire as a solid-phase microextraction fiber for rapid determination of volatile constituents in medicinal plant. *Analytica Chimica Acta*. 2011;701(1):1-5. <https://doi.org/10.1016/j.aca.2011.05.046>
- Majdafshar M, Piryaei M, Abolghasemi MM, Rafiee E. Polyoxometalate-based ionic liquid coating for solid phase microextraction of triazole pesticides in water samples. *Separation Science and Technology*. 2019;54(10):1553-9. <https://doi.org/10.1080/01496395.2019.1572625>
- Starukh G, Rozovik O, Oranska O. Organo/Zn-Al LDH Nanocomposites for Cationic Dye Removal from Aqueous Media. *Nanoscale Research Letters*. 2016;11(1):228. <https://doi.org/10.1186/s11671-016-1402-0>
- Zeng R-C, Li X-T, Liu Z-G, Zhang F, Li S-Q, Cui H-Z. Corrosion resistance of Zn-Al layered double hydroxide/poly(lactic acid) composite coating on magnesium alloy AZ31. *Frontiers of Materials Science*. 2015;9(4):355-65. <https://doi.org/10.1007/s11706-015-0307-7>
- Le Ba T, Alkurdi AQ, Lukács IE, Molnár J, Wongwises S, Gróf G, et al. A novel experimental study on the rheological properties and thermal conductivity of halloysite nanofluids. 2020;10(9):1834. <https://doi.org/10.3390/nano10091834>
- Zhou T, Jia L, Luo Y-F, Xu J, Chen R-H, Ge Z-J, et al. Multifunctional nanocomposite based on halloysite nanotubes for efficient luminescent bioimaging and magnetic resonance imaging. *International Journal of Nanomedicine*. 2016;11:4765-76. <https://doi.org/10.2147/IJN.S110081>
- Matusik J, Rybka K. Removal of chromates and sulphates by Mg/Fe LDH and heterostructured LDH/halloysite materials: Efficiency, selectivity, and stability of adsorbents in single- and multi-element systems. *Materials*. 2019;12(9):1373. <https://doi.org/10.3390/ma12091373>
- Rajaei M, Kim NK, Bickerton S, Bhattacharyya D. A comparative study on effects of natural and synthesised nano-clays on the fire and mechanical properties of epoxy composites. *Composites Part B: Engineering*. 2019;165:65-74. <https://doi.org/10.1016/j.compositesb.2018.11.089>
- Shi X, Wang C, Dong B, Kong S, Das R, Pan D, et al. Cu/N doped lignin for highly selective efficient removal of As(v) from polluted water. *International Journal of Biological Macromolecules*. 2020;161:147-54. <https://doi.org/10.1016/j.ijbiomac.2020.06.016>
- Sayed H, Mahmoud R, Mohamed HFM, Gaber Y, Shehata N. Co and Ni Double Substituted Zn-Fe Layered Double Hydroxide as 2D Nano-Adsorbent for Wastewater Treatment. *Key Engineering Materials*. 2022;922:193-213. <https://doi.org/10.4028/p-tpns6c>
- Piryaei M. Determination of the volatile compounds from *Satureja hortensis* L with a Metal-organic framework on copper nanoarrays. *Nanochemistry Research*. 2023;8(1):50-6.
- Abolghasemi MM, Piryaei M. Head space solid phase microextraction of 15 pesticides in water samples using MnO<sub>2</sub> nanowires decorate on graphenized pencil lead fiber. *Separation Science and Technology*. 2022;57(3):419-25. <https://doi.org/10.1080/01496395.2021.1901743>
- Abolghasemi MM, Laki RM, Piryaei M. The New Simple and Manual Coated Serum Vial Solid-Phase Microextraction



- Method for Pre-Concentration of Polycyclic Aromatic Hydrocarbons in Water Samples. *Polycyclic Aromatic Compounds*. 2022;42(10):7247-55. <https://doi.org/10.1080/10406638.2021.1998147>
27. Abolghasemi MM, Habibiyan R, Jaymand M, Piryaei M. A star-shaped polythiophene dendrimer coating for solid-phase microextraction of triazole agrochemicals. *Microchimica Acta*. 2018;185(3):179. <https://doi.org/10.1007/s00604-017-2639-8>
28. Piryaei M, Yosefzadeh S. New Fiber Coating with Silica Coated  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> Nanoparticles for Extraction and Determination of Volatile Compounds of *Ziziphora tenuior* L. *Nanochemistry Research*. 2022;7(1):9-14.
29. Hosseinzadeh Z, Piryaei M, Babashpour Asl M, MM A. ZnO polythiophene SBA-15 nanoparticles as a solid-phase microextraction fiber for fast determination essential oils of *Matricaria chamomilla*. *Nanochemistry Research*. 2018;3(2):124-30.