



A nanohybrid composed of polyoxotungstate and graphene oxide for dispersive micro solid-phase extraction of non-steroidal anti-inflammatory drugs prior to their quantitation by HPLC

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Abstract

A nanohybrid was prepared from polyoxotungstate anion and graphene oxide (POT/GO) and characterized in terms of porosity by applying Fourier transform infrared and transmission electron microscopy. The nanohybrid was applied as a sorbent for the dispersive micro solid-phase extraction of the non-steroidal anti-inflammatory drugs (NSAIDs) ibuprofen, diclofenac, and naproxen. Different types of sorbents were compared, and the POT/GO nanohybrid was found to have the best adsorption affinity. The NSAIDs were quantified via HPLC with UV detection. Under the optimum conditions, the limits of detection (at an S/N ratio of 3) range between 0.02–0.03 ng.mL⁻¹, and the linear response ranges extend from 0.08–200 ng.mL⁻¹, respectively. The relative standard deviations (RSDs) for five replicates at three concentration levels (0.1, 5 and 100 ng.mL⁻¹) of NSAIDs ranged from 4.1 to 6.1%. The applicability of the method was confirmed by analyzing spiked real water samples, and satisfactory results were obtained, with recoveries between 95.6 and 99.6%.

Keywords Polyoxometalate · Carbon-based nanomaterial · Poly(diallyldimethylammonium chloride) · Sample preparation · Tap water analysis · River water analysis · Wastewater analysis · Anion exchange polymer

Introduction

Non-steroidal anti-inflammatory drugs (NSAIDs) are broadly utilized for the treatment of fever, pain, and inflammation. The trace level of the NSAID residues in various environmental water samples can create significant threats to the lives of humans and animals [1]. Therefore, the development of a

highly sensitive, cost-effective and fast method for the determination of NSAIDs is of great significance for environmental safety assessment.

For the determination of NSAIDs, several methods such as high-performance liquid chromatography (HPLC) [2], gas chromatography (GC) [3], and capillary electrophoresis (CE) [4] are described in the literature. But, in many of these analytical approaches to achieve the desired detection limits, require sample preparation for the analyte preconcentration and/or matrix elimination. A number of sample preparation methods, such as solid-phase extraction (SPE) [5], and solid-phase microextraction (SPME) [6], magnetic solid-phase extraction (MSPE) [7], liquid-phase microextraction (LPME) [8] have been used for the extraction of NSAIDs in various water samples.

The dispersive micro solid-phase extraction (D- μ SPE) methods, which based on the dispersion of the sorbent into the sample solution, has become one of the most commonly used sample preparation methods for the extraction of various compounds [9, 10]. In the D- μ SPE method, sorbent plays a crucial role in extraction efficiency. Several materials have

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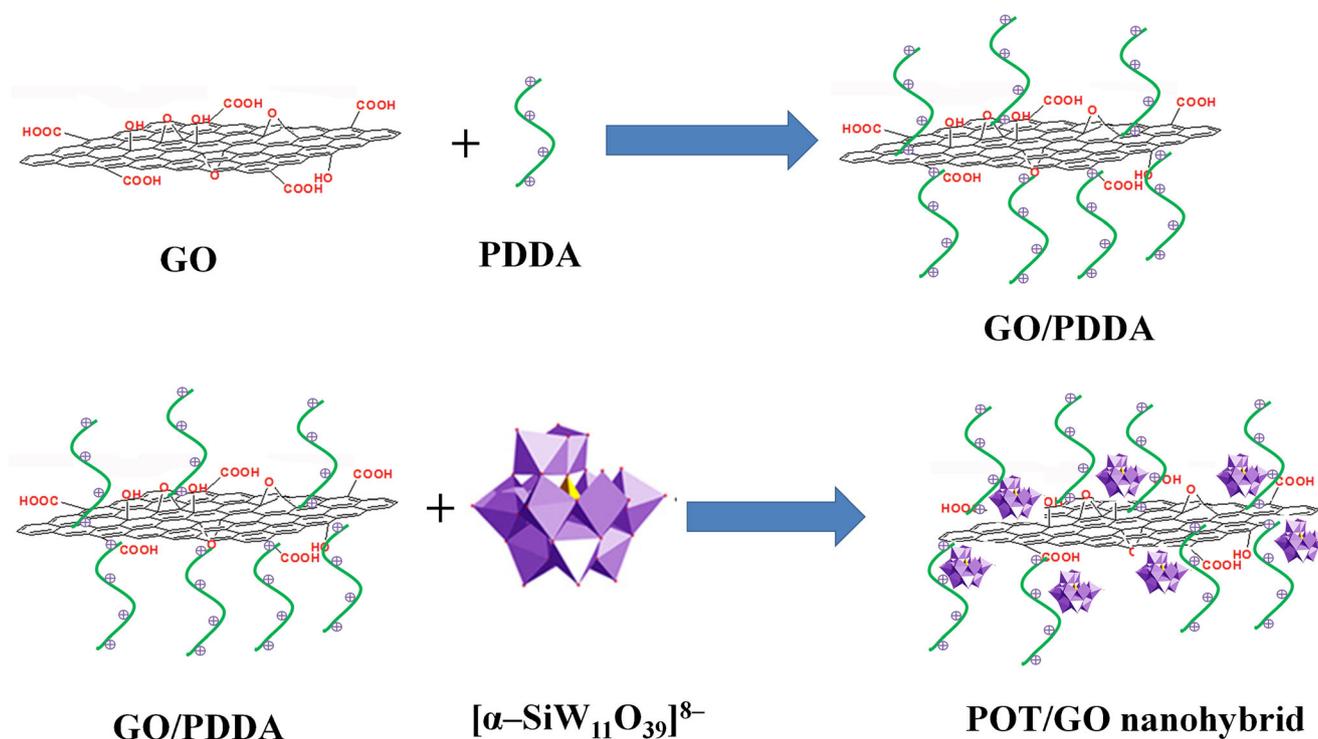
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been applied as sorbents in D- μ SPE method including graphene [11, 12], layered double hydroxide (LDH) [13], molecularly imprinted polymer (MIP) [14], metal-organic framework (MOF) [15], and conductive polymers (CPs) [16].

Polyoxometalates (POMs) are a large class of anionic metal-oxide clusters with d-block transition metals in their highest oxidation state [17]. Owing to their chemical versatility, POMs have been employed in medicine, photochromism, separation, electrochemistry, magnetism and also catalysis [18–24]. The modification of properties can be basically done by adjusting the primary structural properties at the atomic or molecular level by applying deflection in POM structures as Lacunary Polyoxometalates (LPOMs). LPOMs are a sub-branch of POMs with a set of incomparable properties like rigidity, multicentricity, oxidative and thermal stability, as well as unique properties in structural and chemical behaviors [25]. But due to the important problems of the POMs like the low specific surface area and easy to gather in the water, that affected their application as sorbent. To overcome these drawbacks, POMs can be immobilized onto suitable supporting

substrates. Graphene (G) nanosheets, a two-dimensional lattice of sp^2 -hybridized carbon atoms packed into a dense honeycomb, has received extensive attention as effective sorbents in separation science due to its chemical and thermal stability, high surface area, special π -stacking property and mechanical properties [26]. Graphene oxide (GO) is a chemically modified graphene containing various reactive oxygen functional groups such as epoxy, hydroxyl and carboxylic acids. To immobilize POMs onto surface, GO sheets ideal fundamental materials. The immobilization of POMs onto graphene can be improved robustness, the electrical conductivity, and adsorption capacity [27, 28].

We present a synthetic method for the preparation of nano hybrid material based on polyoxotungstate of type $K_8[\alpha-SiW_{11}O_{39}] \cdot 13H_2O$ and GO (POT/GO) through a simple anion exchange polymer [poly(diallyldimethylammonium chloride) (PDDA)] as a linker of two components. To the best of our knowledge, the use of POT/GO nano hybrid as a sorbent has not been reported. The sorbent was successfully employed as D- μ SPE sorbent for the extraction of the NSAIDs in the



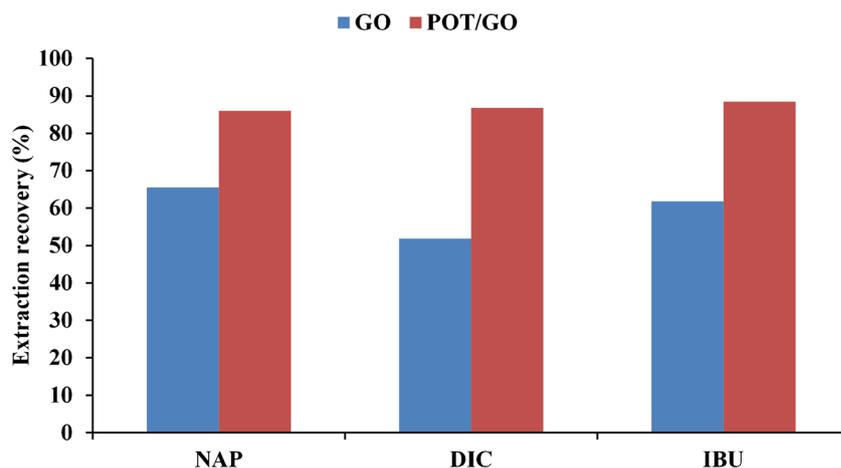
GO; graphene oxide

PDDA; poly(diallyldimethylammonium chloride)

POT/GO; polyoxotungstate/graphene oxide

Fig. 1 Schematic of the preparation POT/GO nano hybrid

Fig. 2 Effect of sorbent type on the extraction efficiency



environmental water samples prior to high-performance liquid chromatography-ultraviolet (HPLC-UV) detection.

Experimental

Chemicals and materials

Diclofenac (DIC), Ibuprofen (IBU), and naproxen (NAP) were purchased from Sigma-Aldrich (Steinheim, Germany, www.sigmaaldrich.com). Also, poly(diallyldimethylammonium chloride) (PDDA) were purchased from Sigma-Aldrich (Steinheim, Germany, www.sigmaaldrich.com). The stock solution of the NSAIDs was prepared in methanol (HPLC-grade) at a concentration of 1 mg mL^{-1} . The working standard solutions were prepared daily by appropriate dilutions of the stock solution with deionized water.

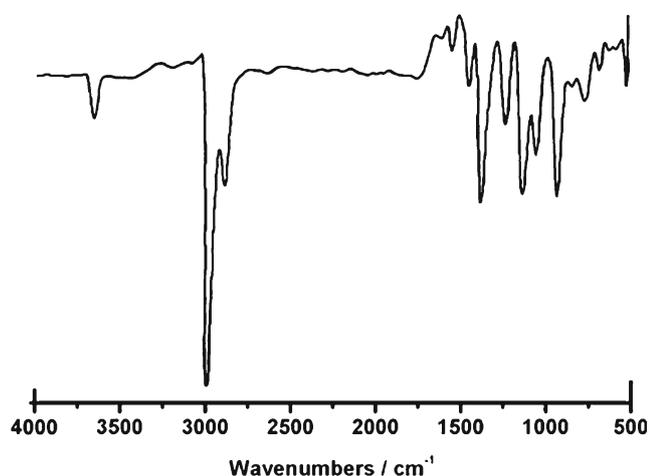


Fig. 3 The infrared spectrum of $\text{K}_8[\alpha\text{-SiW}_{11}\text{O}_{39}] \cdot 13\text{H}_2\text{O}$

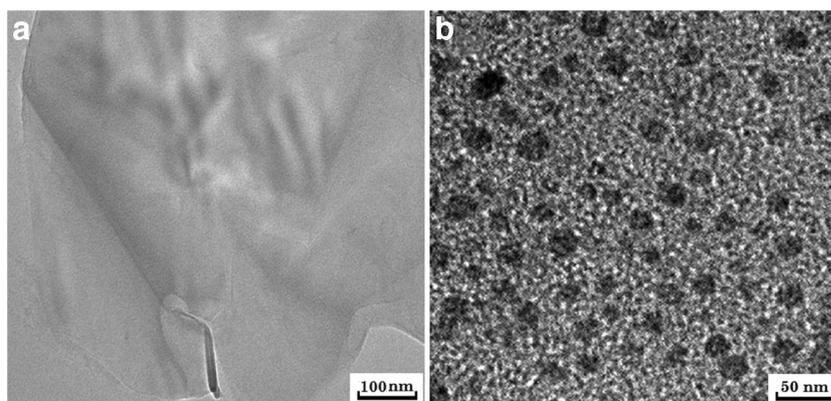
Instrumentation

The separation and detection of the NSAIDs were performed with Knauer HPLC instrument equipped with a UV detector (Berlin, Germany, www.knauer.net). The separations were performed on the ODS3 column ($5 \mu\text{m}$ particle diameter, $4.6 \text{ mm ID} \times 250 \text{ mm length}$). The mobile phase at a flow rate of 1.0 mL min^{-1} was a mixture of 0.05 M phosphate buffer and acetonitrile ($65:35 \text{ v/v}$) with isocratic elution. The wavelength of the UV detector was set at 220 nm . FT-IR spectra were recorded on a Buck 500 spectrometer (www.buck-scientific-norwalk.myshopify.com). The morphology and dimension of the GO and POT/GO nanohybrid were observed by a Transmission electron microscopy (TEM) (Leo, model 912 AB, Germany, www.leo-em.co.uk).

Synthesis of the polyoxotungstate/graphene oxide (POT/GO) nanohybrid

Graphene oxide (GO) was oxidized from graphite powder by a modified Hummer method [29] (Electronic Supporting Material). $\text{K}_8[\alpha\text{-SiW}_{11}\text{O}_{39}] \cdot 13\text{H}_2\text{O}$ was synthesized according to reference [30] (Electronic Supporting Material). The POT/GO nanohybrid was synthesized according to the reported method with some modifications [31]. First, 100 mg of GO was dispersed in 50 mL of deionized water and sonicated for 20 min . Then 1 mL of PDDA solution ($20\% \text{ wt\%}$ in water) was added to the previous solution to disperse of PDDA on the surface of GO. After sonication for 60 min , the mixture centrifuged and the resulting materials washed with deionized water. After that, the POT solution (50 mg of $\alpha\text{-SiW}_{11}\text{O}_{39}$ dissolved in 5 mL of deionized water) was added to the mixture and mixed for 24 h . Subsequently, the resulting material centrifuged and washed with deionized water three times. Finally, the POT/GO nanohybrid was

Fig. 4 **a** TEM images of GO and **b** POT/GO nanohybrid



dried in a vacuum oven at 60 °C for 12 h. Figure 1 illustrates the procedure used to preparation of POT/GO nanohybrid.

Extraction procedure

The 50 mL of the sample solution was placed in a glass vial and the pH value of the sample solution was set at 4.0. Then 20 mg of the POT/GO adsorbent was dispersed in the sample solution for the extraction of target analytes and sonicated. After extraction (4 min), the mixture centrifuged at 5000 rpm, for 3 min and the supernatant was discarded. Then, the extracted analytes were eluted with 200 μ L of acetonitrile, under sonication, for 2 min. After centrifugation, the elution solvent was transferred to an Eppendorf vial; the solvent was evaporated to dryness and finally, reconstituted with 20 μ L of acetonitrile, prior to the HPLC analysis.

Results and discussion

Sorbent type

In order to the choice of the most suitable sorbent, the extraction ability of GO, and POT/GO nanohybrid were studied. As shown in Fig. 2, the highest extraction efficiency for the DSPE

of NSAIDs was obtained with the POT/GO nanohybrid as sorbent. We attribute the better performance of the POT/GO nanohybrid to the following major factors: (i) large surface area of GO, (ii) special π -stacking property of GO nanosheets, (iii) the well dispersed POT on the GO nanosheets, and (iv) the crumpled, and porous morphology structure of POT/GO nanohybrid, which mainly enhanced the active sites on the sorbent for the extraction of the analytes.

Characterization of materials

To investigate the formation of $[\alpha\text{-SiW}_{11}\text{O}_{39}]^{8-}$ lacunary Keggin-type anions, the FT-IR spectroscopy was used (Fig. 3). Four bands appeared at 1255, 1385, 1151 and 954 cm^{-1} that attributed to (Si–O_a), (W=O_t), (W–O_b), and (W–O_c) stretching vibrations, respectively (where O_t = terminal oxygen, O_b = bridging oxygen, O_a = internal oxygen's, and O_c = bridging oxygen atoms within the edge-sharing octahedral).

The TEM images of GO and POT/GO nanohybrid are illustrated in Fig. 4. The TEM images of GO (Fig. 4a) and POT/GO nanohybrid (Fig. 4b) exhibit crumpled layered structure of the graphene oxide sheets. In the TEM image of POT/GO nanohybrid, POT clusters can be observed clearly as small dark spots. Besides that, the POT clusters are dispersed on the graphene surface in a uniform state.

Table 1 Analytical figures of merit of the D- μ SPE method of the NSAIDs

Analyte	Linear range (ng.mL ⁻¹)	LOD (ng.mL ⁻¹)	Correlation coefficient (r)	EF	ER%	Intra-day precision (n = 5) at three concentration (ng.mL ⁻¹)			Inter-day precision (n = 5)
						0.1	5	100	
NAP	0.1–200	0.03	0.9984	2150	86.0	5.7	4.4	4.1	6.0
DIC	0.1–200	0.03	0.9959	2170	86.8	6.1	5.3	5.1	6.6
IBU	0.08–200	0.02	0.9974	2212	88.5	5.4	4.8	4.2	5.5

Table 2 The contents, precisions, and accuracies of NSAIDs in real water samples with the D- μ SPE method

Sample	Analyte	Mean (ng.mL ⁻¹)	Spiked amount (ng.mL ⁻¹)					
			0.1		5		100	
			Relative recovery (%)	RSD (%)	Relative recovery (%)	RSD (%)	Relative recovery (%)	RSD (%)
Tap water	NAP	ND	98.4	5.8	98.8	5.4	99.1	5.1
	DIC	ND	98.9	6.6	99.4	6.1	99.5	6.0
	IBU	ND	99.0	5.5	99.6	5.2	99.6	4.9
Wastewater ^a	NAP	ND	96.6	6.7	97.4	6.2	97.9	5.9
	DIC	ND	97.1	6.9	97.5	6.6	97.8	6.5
	IBU	ND	96.0	6.2	96.7	5.9	97.0	5.7
Wastewater ^b	NAP	ND	95.8	7.1	96.2	6.8	96.4	6.4
	DIC	9.5	96.2	7.4	96.4	7.2	96.7	6.7
	IBU	7.6	95.6	6.7	95.9	6.6	96.3	6.5
River water	NAP	ND	96.8	7.2	97.5	6.9	97.8	6.7
	DIC	ND	97.9	7.0	98.1	6.6	98.3	6.4
	IBU	4.5	97.6	6.6	97.9	6.3	98.0	6.3

ND Not detected

^a Wastewater from research laboratory

^b Hospital wastewater

Optimization of extraction conditions

To obtain the optimized conditions for the improve of the extraction efficiency, several important parameters, including desorption conditions, amount of sorbent, sample pH, and extraction time were optimized. Respective data and Figures are given in the Electronic Supporting Material (Figs. S1–S5). The following experimental conditions were found to give best results: (a) sample pH, 4; (b) optimal ionic strength: no salt addition; (c) 20 mg of the POT/GO nanohybrid; (d) desorption solvent, acetonitrile; (e) volume of the desorption solvent, 200 μ L; (f) desorption time, 2 min; and (g) extraction time, 4 min.

Method validation

Some important analytical features of the D- μ SPE-HPLC-UV method in the term of linearity, limits of detection (LODs), precision, enrichment factor (EF), and absolute extraction recovery (ER%) were investigated. The results are listed in Table 1. The method was linear in the ranges of 0.08–200, 0.1–200, and 0.1–200 ng.mL⁻¹ for ibuprofen, naproxen, and diclofenac, respectively, with the correlation coefficient higher than 0.9959. The LODs (at an S/N ratio of 3) are founded to be 0.02 ng.mL⁻¹ for ibuprofen, 0.03 ng.mL⁻¹ for naproxen, and diclofenac. The intra-day precision was evaluated by loading standards sample solution at three concentration levels (0.1, 5

Table 3 Comparison of the D- μ SPE method with other methods for determination of NSAIDs in real samples

Method	Sample	Detection system	LOD (ng.mL ⁻¹)	Linear range (ng.mL ⁻¹)	RSD (%)	Ref.
TAALLME	Plasma, and water	HPLC–UV	0.1–0.3	0.5–4000	5.4–7.7	[32]
SRSE	Water	HPLC–UV	0.09–0.25	1–200	2.5–9.8	[33]
SBSE	Water	HPLC–UV	6.90–7.69	20–2000	4.1–9.2	[34]
DLLME-SFO	Wastewater	HPLC–UV/Vis	0.13–0.39	1–100	3.45–6.34	[35]
MSPE	Water	HPLC–UV	0.05–0.08	0.15–500	4.5–7.3	[7]
D- μ SPE	Water	HPLC–UV	0.02–0.03	0.08–200	4.1–6.1	This study

TAALLME Tandem air-agitated liquid-liquid microextraction, SRSE stir rod sorptive extraction, SBSE stir bar sorptive extraction, DLLME-SFO dispersive liquid-liquid microextraction based on solidification of floating organic droplet

and 100 ng.mL⁻¹), and relative standard deviations (RSDs) were in the range of 4.1 to 6.1%. The inter-day precision was determined by performing three consecutive extractions (spiked at 0.1 ng.mL⁻¹) each day over a period of three working days. The inter-day RSDs varied from 5.5 to 6.6%. The EFs were in the range of 2150 and 2212. The absolute extraction recoveries (ER%) were found in the range of 86.0–88.5%.

Analysis of real samples

To study the applicability of the D- μ SPE-HPLC-UV method with POT/GO sorbent, four kinds of environmental water samples (including tap water, river water, and two wastewater samples) were selected. The real water samples were collected in dark glass bottles without headspace and maintained in a cool place (4 °C) until analysis. One wastewater sample was collected from the local hospital, and the other wastewater sample was from a research laboratory. It showed that trace concentration level of the target NSAIDs was observed in the several water samples (Table 2). To study the matrix effect of the D- μ SPE-HPLC-UV method, the relative recoveries of the target NSAIDs were studied at three concentration levels of the NSAIDs (0.1, 5 and 100 ng.mL⁻¹) (Table 2). The relative recoveries for the NSAIDs were obtained in the range from 95.6–99.6% with RSDs between 4.9% and 7.4%. The results show that the matrix effect has no significant effect on the efficiency of the D- μ SPE-HPLC-UV method.

Comparison of the method with previously reported results

The efficiency of the D- μ SPE-HPLC-UV method in terms of LOD, linearity, extraction, and precision was compared with the others reported in the literature and summarized in Table 3 [7, 32–35]. It can be seen that the D- μ SPE-HPLC-UV method shows advantages over other methods in the LODs and linearity. The method exhibited lower LODs, good precision, and wide linearity range. Therefore, the results show that the D- μ SPE-HPLC-UV method is efficient and sensitive and can be applied for routine monitoring of NSAIDs in water samples.

Conclusion

Graphene oxide (GO) and PDDA-functionalized GO were synthesized and used as the support lacunary tungstoheteropoly anion [α -SiW₁₁O₃₉]⁸⁻. The high surface area of the graphene allowed a high dispersion of the polyoxotungstate (POT). The nanohybrid exhibits high stability and excellent extraction efficiency for the DSPE of NSAIDs from water samples. After comparison with plain POT, this is attributed to the synergistic effects of GO and POT. High EFs, low LODs, wide linearity, and good relative

recoveries were obtained for the real samples. The synthesis of POT/GO nanohybrid opens a new way for the synthesis of a wide range of nanohybrid compounds with unique properties. Based on the obtained results, it is believed that the POT/GO nanohybrid has a high potential for use in various field of chemistry such as extraction, separation, catalysis, and electrochemistry.

Compliance with ethical standards The author(s) declare that they have no competing interests.

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