Analytical Methods

Determination of Non-Steroidal Anti-Inflammatory Drugs in Water Samples Using Graphene Oxide/Fe3O4/Polyoxometalate as Sorbent

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Analytical Methods

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Best regards,

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Dear Editor,

We would like to submit a manuscript entitled "**Determination of Non-Steroidal Anti-Inflammatory Drugs in Water Samples Using Graphene Oxide/Fe_3O_4/Polyoxometalate as Sorbent**" as an article to ***Analytical Methods.***

The synthesis of mixed-component polyoxometalate-based frameworks as modern materials is becoming a very active research field. So, following our interests in using polyoxometalate-based frameworks and composites for the extraction of different analytes, in this study, we reported the preparation, characterization, and application of magnetic tri-component composite that was prepared based on the immobilized Keggin-type polyoxometalate ($H_4SiW_{12}O_{40}$ (SiW)) and Fe_3O_4 nanoparticles on the graphene oxide (GO) sheets (GO/Fe_3O_4/SiW) as sorbent. Then, the ability of our POM-based composite for the extraction and quantitative determination of non-steroidal anti-inflammatory drugs (i.e. ibuprofen, diclofenac, naproxen, tenoxicam, meloxicam) from water samples was investigated by using magnetic solid-phase extraction (MSPE) and High-performance liquid chromatography coupled with an ultraviolet detector. The POM-based composite enriched analytes through *via* π-stacking, and hydrogen bonding interactions between several oxo-groups from POM clusters, carboxylate, and hydroxy groups of oxidized GO. The results showed good repeatability, low detection limit, good relative extraction recovery, and wide linear range.

The article is original and has been written by the stated authors who are all-aware of its content and approve its submission. It has not been published previously and it is not under consideration for publication elsewhere. No conflict of interest exists and if accepted, the article will not be published elsewhere in the same form.

We believe these findings will be of interest to the readers of your journal. We are looking forward to hearing from you soon.

Sincerely yours,

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Response to reviewers' comments

(Manuscript ID: AY-ART-03-2025-000466)

Oct 4, 2025

Subject: Response Letter
Title: Determination of Non-Steroidal Anti-Inflammatory Drugs in Water Samples Using Graphene Oxide/Fe_3O_4/Polyoxometalate as Sorbent
Manuscript ID: AY-ART-03-2025-000466

Dear Professor Martina Catani

Associate Editor, Analytical Methods

Thank you very much for sending us the constructive comments of the reviewers of our manuscript. We would also like to express our sincere thanks and appreciation for the time and efforts made by reviewers for evaluating our manuscript. These substantially helped us improve the quality and presentation of the work. Below the points raised by the referees are repeated followed by a detailed reply and discussion. Also, all changes we made have been highlighted in yellow in the revised version. We hope that the new version of our manuscript is accepted for publication in *Analytical Methods*.

With warm regards on behalf of all authors,

Dr. Amirhassan Amiri
Department of Chemistry
Ferdowsi University of Mashhad

Reviewer(s)' Comments to Author:

Reviewer: 1

The manuscript is well written and well organized. The novelty of method is acceptable. I recommend the publication of manuscript after revision. The comments are as follow:

- Please add more analytical data into the abstract section.

  Response: Thank you for your comment. The corresponding contents have been added to the abstract.

- Please improve the keywords.

  Response: Thank you for your suggestion. The keywords have been improved.

- Please improve the introduction section. Add more related articles and literature review.

  Response: Thanks for your valuable comment. Please find the changes in the Introduction section.

- Please improve the quality of figures.

  Response: Thanks, as reviewer suggested the figure's quality have been improved.

- Fig. 6, please add the SDs in the figures.

  Response: Thanks for your valuable comment. It was done.

- Please revise the real samples. Use some biological samples such as urine and plasma.

  Response: Thank you for your valuable comment. Our objective in this study is to monitor the presence, and persistence of drug residues in water (e.g. surface water, wastewater, effluents). We fully agree that biological matrices (such as plasma, urine) are of great interest, and we intend to extend our method to those in a subsequent phase.

- However though the authors in the conclusions part claim for practicality, this is not evaluated using relevant metric tools eg BAGI software. Moreover, the green character of the method should also been evaluated using respective metric tools, eg AGREEprep, ComplexGAPI etc Please use the following reference and add the appropriate results: https://www.sciencedirect.com/science/article/abs/pii/S0021967324009889 https://www.sciencedirect.com/science/article/abs/pii/S0026265X24026729

  Response: Thanks for your comment. It was done. Also, the references were added.

- Please improve the conclusion section. Add more data in this section.

  Response: Thanks for your comment. As suggested the Conclusion has been revised and more data have been added.

- Please re-check the significant figures in whole manuscript.

Response: Thank you for your suggestion. It has been checked and revised.

Reviewer: 2

The present manuscript must undergo minor corrections as listed below prior to publication in this journal.

Abstract

- Suggest briefly stating the real-world significance of detecting NSAIDs in water samples (e.g., potential risks to aquatic ecosystems or human health). Consider quantifying the improvement over previous sorbents in terms of LOD or recovery to enhance impact.

  Response: Thank your valuable comment. The Abstract have been revised accordingly.

Introduction

The introduction provides a solid background but could benefit from:

- A more in-depth critical comparison of existing sorbents used in MSPE for NSAIDs.

  Clearer articulation of how the tri-component GO/Fe_3O_4/SiW addresses known limitations of prior materials (e.g., stability, selectivity, recovery).

  Response: Thank you for your suggestion. The Introduction have been revised (please see yellow highlights)

Experimental Section

Synthesis Descriptions:

- While the methods are detailed, the rationale behind specific synthesis parameters (e.g., choice of hydrothermal conditions or Fe_3O_4 concentration) should be explained to support reproducibility and understanding.

  Response: Thanks, the explanation has been added.

Characterization Techniques:

- Consider discussing how each characterization method (e.g., FTIR, XRD, SEM) directly supports the conclusion that the composite was successfully formed.

  Response: Thank your valuable comment. As reviewer suggested, this section has been revised.

Results and Discussion

Adsorption Mechanism:

- Although the manuscript discusses multiple interactions (π–π, H-bonding, electrostatic), experimental validation (e.g., pH effect on extraction, zeta potential) to support these mechanisms is mostly qualitative. If possible, include or cite supporting experimental data.

  Response: Thank you for your valuable comment. In the revised version, Zeta potential section has been added and also some related explanation has been added to the Optimization test section (yellow highlights).

Analytical Figures of Merit:

- The authors report impressive LODs. A statistical comparison with previously published materials in Table 4 (e.g., significance testing) could help strengthen the argument.

  Response: Thanks for your suggestion. It was done.

- Expand the discussion on how matrix effects were evaluated and how they were minimized or tolerated in real water samples.

  Response: Thanks for your suggestion. Some explanations were added.

Tables and Figures

Figure Quality:

- Ensure all figures are high-resolution and labeled consistently (e.g., clear units, legends).

  Response: Thanks for your suggestion. The quality of Figures has been improved.

Table 3 (Real Sample Analysis):

- It would be helpful to indicate whether the spiked recovery experiments were done in triplicate or more and clarify the sampling period/conditions (e.g., seasonality or urban vs. rural locations).

  Response: Thanks for your suggestion. Some explanations were added.

Conclusion

- The conclusion is clear but should suggest possible future improvements or applications (e.g., automation, coupling with MS detection, other pharmaceutical residues).

  Response: Thank you for your suggestion. The conclusion has been revised.

References

- Ensure uniform citation formatting and verify that the most recent and relevant references (2023–2024) are included.

  Response: Thank you for this comment. The refences checked and most recent articles have been added.

Determination of Non-Steroidal Anti-Inflammatory Drugs in Water Samples Using Graphene Oxide/Fe_3O_4/Polyoxometalate as Sorbent

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Abstract

The detection of nonsteroidal anti-inflammatory drugs (NSAIDs) in water samples is of critical importance due to their adverse effects on aquatic ecosystems, including toxicity to fish and invertebrates, and the potential risks to human health through contaminated drinking water sources. Precisely monitoring their content is crucial yet difficult due to their complex matrix and trace concentrations. This study represents a magnetic tri-component composite that was prepared based on the immobilized Keggin-type polyoxometalate ($H_4SiW_{12}O_{40}$ (SiW)) and Fe_3O_4 nanoparticles on the graphene oxide (GO) sheets (GO/Fe_3O_4/SiW) through a hydrothermal synthetic method. This composite benefits from the abundant delocalized π-electron system from its GO support and also the oxygen-rich surface from the functional groups of GO and SiW moieties, resulting in strong affinity toward target analytes through various mechanisms like π-stacking, hydrogen bonding, and electrostatic interactions. Along with the above advantages, Fe_3O_4 magnetic nanoparticles of GO/Fe_3O_4/SiW composite also result in additional potential which enables it to be employed as a very effective sorbent for the magnetic solid-phase extraction (MSPE) of five types of NSAIDs with different functional groups (ibuprofen, diclofenac, naproxen, tenoxicam, meloxicam). High-performance liquid chromatography coupled with an ultraviolet detector (HPLC-UV) was established which exhibited good linearity ranges (0.03–300 ng mL^{-1}) and the limit of detection ranges (0.01−0.03 ng mL^{-1}), which is significantly lower than many previously reported sorbents. To assess the method's accuracy, the inter-day and intra-day relative standard deviations (RSDs%) for five types of NSAIDs were measured, ranging from 3.7% to 5.0% across three concentration levels (0.1, 5, and 100 ng mL^{-1}). Moreover, the method achieved high recoveries ranging from 97.1% to 100.0%, demonstrating its outstanding efficiency in extracting NSAIDs. These enhancements highlight the composite's potential for reliable, sensitive, and rapid environmental monitoring of pharmaceutical pollutants at trace levels.

Keywords: Graphene oxide; HPLC-UV; Keggin-type polyoxometalate; Non-steroidal anti-inflammatory drugs; Magnetic solid-phase extraction; Water samples

Introduction

While pharmaceuticals have saved millions of lives, they are now one of the environmental contaminants, harming flora and fauna. Non-steroidal anti-inflammatory drugs (NSAIDs) like ibuprofen, diclofenac, naproxen, etc. are among the widely consumed pharmaceuticals and that is why they can be detected in various water bodies such as surface, drinking, or groundwater and wastewater[1] at levels ranging from ng L^{-1} to μg L^{-1} that can have chronic toxicological effects on living organisms due to high bioactivity.[2] Therefore, to determine the concentration of the NSAIDs in real samples, extraction, and preconcentration steps seem to be necessary. Up to now, various analysis methods have been employed for the determination of NSAIDs, including high-performance liquid chromatography (HPLC),[3] gas chromatography (GC),[4] and capillary electrophoresis (CE).[5] However, these approaches require sample preparation for enriching target analytes or separate matrices to achieve optimal detection limits.[6] Some popular sample preparation techniques can be mentioned to solid-phase extraction (SPE),[7] solid-phase microextraction (SPME),[8] liquid-phase microextraction (LPME),[9] and magnetic solid-phase extraction (MSPE).[10] Among these methods, the MSPE has attracted attention due to its simple operation since this method involves magnetic sorbent which is added to a sample solution to adsorb the target analyte(s), then an external magnet is needed for the easy separation of collected analytes on the sorbent which reduce extra steps such as centrifugation or filtration.[11,12] Therefore, developing new magnetic sorbents with high extraction ability, suitable chemical stability, and high selectivity is crucial because of the dependency of the MSPE method on magnetic sorbents.[13] So far, various sorbents such as carbon nanomaterials,[14,15] layered hydroxide (LDH),[16] metal-organic frameworks (MOFs),[17] molecularly imprinted polymers,[18] and many more have been used in this method. However, they have some drawbacks such as poor stability in water and different solvents, low performance at reusability tests, and the disposal problem. For instance, carbon nanomaterials tend to aggregate, due to strong π–π stacking and van der Waals interactions between graphitic layers, leading to a decrease in accessible surface area and, consequently, lower extraction efficiency.[19] Molecularly imprinted polymers have problems in reproducibly; the template molecules are usually strongly retained in the polymer matrix, making complete removal challenging.[20] MOFs may undergo hydrolysis in aqueous media due to labile metal–ligand coordination bonds, compromising structural integrity.[21–23] Thus, to address these problems, there is a need for designing and engineering sorbents with novel approaches by purposeful integrating components, resulting in a sorbent with enhanced stability, reusability, and selectivity, effectively overcoming the main drawbacks of previously reported materials in NSAID extraction.

Polyoxometalates (POMs), also known as metal−oxygen clusters, are made from non-precious transition metals (mostly tungsten and molybdenum) at their highest oxidation states.[24,25] Owing to their chemical versatility, electron/proton storage capacities, oxygen-rich surface, inherent resistance to oxidative decomposition, and redox capability, POMs can be employed in many applications like catalysis/photocatalysis/electrocatalysis,[26–29] optical and electronic applications,[30] sorbent,[31–33] medicine,[34,35] etc. Despite the above advantages, POMs suffer from low surface area and instability at acidic or basic conditions in their soluble form as POMs are water-soluble species which makes their reusability (as sorbent) difficult. To address these limitations, one of the effective ways can be mentioned to immobilize them on a support substrate such as MOFs,[36] molecularly imprinted polymer (MIP),[37] and carbon-based nanomaterials (like carbon nanotubes (CNTs),[19] graphene oxide (GO)),[38] Also, the dispersion of POMs on appropriate supports can improve the availability of their active sites for the specific application.[39] Among the mentioned supports, C-based nanomaterials have gained special attention due to their low cost, high adsorption capacity, easily modifiable surface, and mechanical resistance.[40]

Graphene oxide (GO) represents a two-dimensional nanosheet material with a delocalized π-electron system in which several oxygen-rich functional groups like carboxylic acids, hydroxyl, and epoxy protrude from the nanosheet[41] which imparts hydrophilic properties to GO, resulting in better interaction with compounds containing more polar groups.[42] In addition, GO can easily anchor other nanomaterials on its surface like magnetic nanoparticles, metal-oxides (like TiO_2, POMs, etc.), MOFs, and so on through the possible formation of covalent or non-covalent bonds (like H-bonding, π-stacking, electrostatic interaction, and hydrophobic interaction) via its oxygen-rich surface and functional groups of other materials to form GO-based composite with desirable properties.[43,44] These composites benefit from the advantages of all their components due to the synergistic effects between moieties. Owing to these properties, GO sheets have been reported as ideal fundamental materials to immobilize POMs on their surface to produce GO/POM composites.[45,46] The processes of anchoring POMs onto GO can be described using the sol-gel approach,[47] electrostatic interactions,[48] ion exchange,[6] covalent grafting,[49] and impregnation[50] methods. It is important to note that POMs with negative charges can electrostatically attract on the GO surface due to the pH-dependent positive charge of its oxygen-containing functional groups. It has been found that the electrostatic interactions between the GO surface and POM facilitate electron transfer from the POM to the graphene sheet, leading to stronger anchoring of POMs and less possibility of their leaching during the extraction/catalysis process [39]. However, despite the advantages of GO/POM composites, their lightweight causes them to float on the solution, making rapid separation and full recovery difficult. Thus, to overcome these limitations, introducing magnetic nanomaterials like Fe_3O_4 can not only enhance the weight of the composite but also make it uniformly dispersed in the sample solution, allowing for complete interaction with the analytes. Hence, one of the efficient synthetic methods to achieve tri-component composites based on GO, POMs, and Fe_3O_4 is the solvothermal approach in which magnetic GO/Fe_3O_4/SiW composite with high binding amount, low agglomeration, and uniformly dispersed POM and Fe_3O_4 on the GO surface can be synthesized.[51]

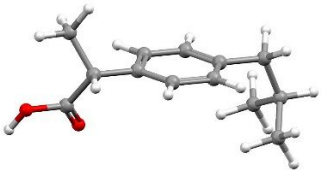
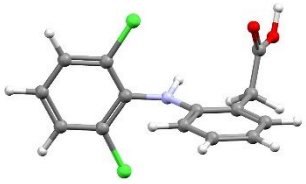
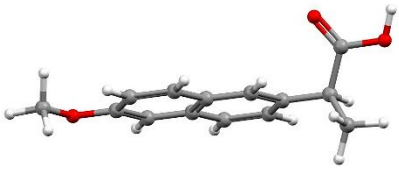
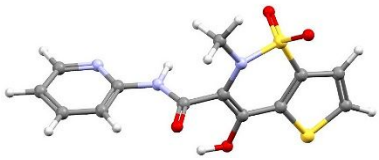
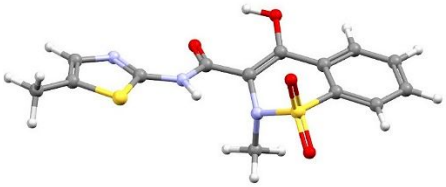
With the above points in mind and adding this point that many existing sorbents face challenges related to recovery efficiency, reproducibility, and selectivity toward NSAIDs, herein, a magnetic tri-component composite (GO/Fe_3O_4/SiW) based on the GO, Keggin-type POM ($H_4SiW_{12}O_{40}$ (SiW)), and Fe_3O_4 nanoparticles was designed, synthesized, and characterized. Then the feasibility of GO/Fe_3O_4/SiW as MSPE sorbent for the adsorption of NSAIDs from environmental water samples was investigated. Finally, the ultra-performance liquid chromatography (HPLC) method, as a highly sensitive analytical method for the determination of NSAIDs, coupled with ultraviolet (UV) detector was applied to measure the extracted NSAIDs by the MSPE method. The GO/Fe_3O_4/SiW composite integrates the advantages of its components while mitigating their limitations, for example, the magnetic Fe_3O_4 part ensures rapid separation and high reusability, enhancing stability and operational convenience. The immobilized POM (SiW) introduces strong interactions such as H-bonding, electrostatic, and π-stacking thereby improving selectivity for NSAIDs with diverse functional groups. Moreover, the synergy between GO's delocalized π-electron system and SiW's oxygen-rich surface enhances recovery and reproducibility, leading to high extraction efficiency. Based on our searches, no research has been reported on the possibility of employing a tri-component magnetic composite sorbent (containing GO, POMs, and Fe_3O_4) in SPE of NSAIDs from water samples, representing the novelty of this work.

Experimental

Chemicals and solutions

NSAIDs including Ibuprofen, Diclofenac, Naproxen, Tenoxicam, and Meloxicam, and all other chemicals were obtained from Merck and used with any additional purification (Table 1). The stock solution of NSAIDs (100 mg L^{-1}) was prepared in methanol and stored in a cool, dark environment at 4°C. Then, the stock solution was diluted to the required concentrations with deionized water to obtain standard and working water solutions. Water samples from rivers and wastewater were collected from Mashhad, Iran.

Table 1. The molecular structure and chemical properties of NSAIDs drugs.[1] Color codes: Grey: Carbon, Yellow: Sulfur, White: Hydrogen, Red: Oxygen, Green: Chlorine atoms, Blue: Nitrogen (structures are drawn using Mercury software).[52]

Drugs	Molecular structure	pK_a	Log K_{ow}
Ibuprofen		4.91	3.97
Diclofenac		4.15	4.51
Naproxen		4.15	3.18
Tenoxicam		5.30	3.50
Meloxicam		4.08	3.54

Instrumentation

Chromatographic separations and detection of the NSAIDs were fulfilled by the use of a Knauer HPLC instrument equipped with a UV detector (Berlin, Germany). The ODS3 column (250 mm length) was employed for the separations. The mobile phase was a mixture of 0.05 M phosphate buffer and acetonitrile

(65: 35 v/v) with isocratic elution. The injection volume was 20 µL and detection was set at a wavelength of 210 nm. The magnetic characteristics of the adsorbent were determined using a vibrating sample magnetometer (VSMF, Kashan, Iran) located in Mashhad, Iran. Powder X-ray diffraction (PXRD) was used by XMD300 (Unisanits Bruker system), with Cu-Kα (λ = 1.54184 Å) radiation over a scan range of 2θ = 5 to 50° at room temperature. The morphology and dimension of GO/Fe_3O_4/SiW nanocomposite were recorded on a Transmission electron microscopy (TEM) by JEM-2010 transmission electron microscope at an acceleration voltage of 200 KV. Field-emission scanning electronic microscopy (FE-SEM) images were obtained by MIRA3 TESCAN (www.tescan.com). The elements in the nanocomposite sample were elucidated through energy-dispersive X-ray (EDX), coupled with LEO-1450 VP at an acceleration voltage of 10.00 kV and a resolution of approximately 500 nm (Zeiss, Germany). Moreover, FT-IR was conducted in the range 4000−400 cm^{-1} on a Thermo Nicolet/AVATAR 370 Fourier transform spectrophotometer using KBr discs. FT-IR spectra were recorded on a Buck 500 spectrometer. The Soner 203 Ultrasonic Cleaner (Model 188203-22, AC 220V, 50Hz, Rocker) was used for ultrasonic cleaning of the samples.

Synthesis of $H_4SiW_{12}O_{40}.xH_2O$

The $H_4SiW_{12}O_{40}.xH_2O$ (SiW) was synthesized according to the reference.[53] First, 5 g sodium metasilicate is dissolved in 50 mL of distilled water to form solution A. Next, 150 mL of boiling distilled water is used to dissolve 91 g of sodium tungstate (solution B). Then, a solution of 4 M HCl (82 mL) is added dropwise to the boiling solution B to dissolve the residue. Subsequently, after adding solution A, 25 mL of 4 M HCl is added. Upon completion of the acid addition, the measured pH was within the range of 5 to 6 and maintained at 100 °C for 1 h. Then, 25 mL of sodium tungstate (1M) was added, followed immediately by adding 40 mL of HCl (4M). After cooling the solution, it was filtered and then transferred to a 1-L separatory funnel and diethyl ether (40 mL) with a solution mixture containing diethyl ether and concentrated hydrochloric acid (1:1, 60 mL) were added. Finally, the aquas solution is separated from the separatory funnel and SiW is crystallized through slow evaporation. Yield: 65 g (75 % based on W). FTIR (KBr pellet, cm^{-1}): 3409, 1616, 1018, 981, 925, 882, 785, 539.

Synthesis of Graphene oxide (GO)

GO was synthesized following Hummers' method.[54] Initially, graphite flake powder (4.0 g) and $NaNO_3$ (4.0 g) were added to 100 mL of concentrated H_2SO_4 while stirring in an ice bath for 2 hours. After that, 12 g of $KMnO_4$ was gradually added, maintaining the temperature below 15 °C. Then, the mixture was heated at 35 °C (48 h). Following, the reaction was diluted with 200 mL of distilled water, and the temperature was quickly raised to 98 °C. Finally, 400 mL of distilled water and 20 mL of H_2O_2 were added with continuous stirring. The resulting GO powder was washed with water until its pH reached 7, then it was dried under vacuum at 40 °C. FTIR (KBr pellet, cm^{-1}): 3367, 1715, 1611, 1384,1031, 750, 535, 472.

Preparation of GO/Fe_3O_4/SiW nanocomposite

First, 0.04 g of GO in 2 mL methanol was dispersed by sonicating (30 min). Next, a solution containing 0.27 g of SiW in 4 mL of water and 0.05 g of dispersed Fe_3O_4 in 2 mL of water was added to it and the reaction mixture remained in an ultrasonic bath at room temperature for 120 min and then transferred to the autoclave, which was heated at 200 °C for 8 h. Then, the external magnet was used to separate the obtained GO/Fe_3O_4/SiW composite, after cooling to room temperature and soaked in distilled water for three days to remove any unsupported SiW and Fe_3O_4. The resulting nanocomposite (Fig. 1a) was dried under vacuum conditions at 70 °C for 12 h.[27] The solvothermal method was chosen because it has a proven ability to facilitate the homogeneous growth and stable attachment of Fe_3O_4 and SiW onto GO sheets.[55] The Fe_3O_4

concentration was optimized to provide sufficient magnetic separation capability without causing nanoparticle aggregation, which could reduce the available surface area and active sites for adsorption.[56] Yield: 0.04 g. FTIR (KBr pellet, cm^{-1}): 3192, 1722, 1580, 1235, 1017, 973, 924, 804, 878, 702, 637, 583, 562, 443.

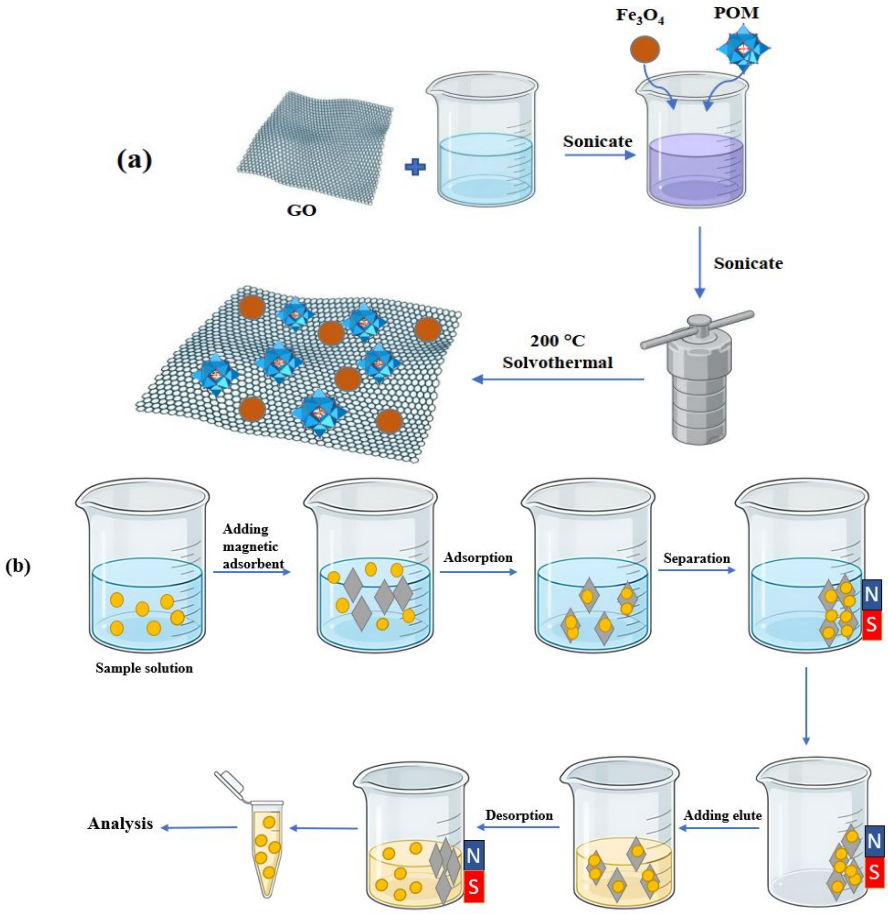


Fig. 1. (a) The preparation route of GO/Fe_3O_4/SiW anocomposite; (b) General MSPE procedure using GO/Fe_3O_4/SiW sorbent.

MSPE procedure

First, 20 mg of GO/Fe_3O_4/SiW sorbent was added to the sample solution containing NSAIDs (10 mL) followed by sonication for 4 min. After extraction, the GO/Fe_3O_4/SiW with analytes were separated from the matrix solution under the assistance of an external magnet and transferred into a 1 mL tube and the supernatant was discarded (Fig. 1b). Then, the extracted analytes were desorbed with 250 µL of acetonitrile, utilizing sonication for 1.5 min. The mixture was then separated and 20 µL of the supernatant was injected into the HPLC for analysis.

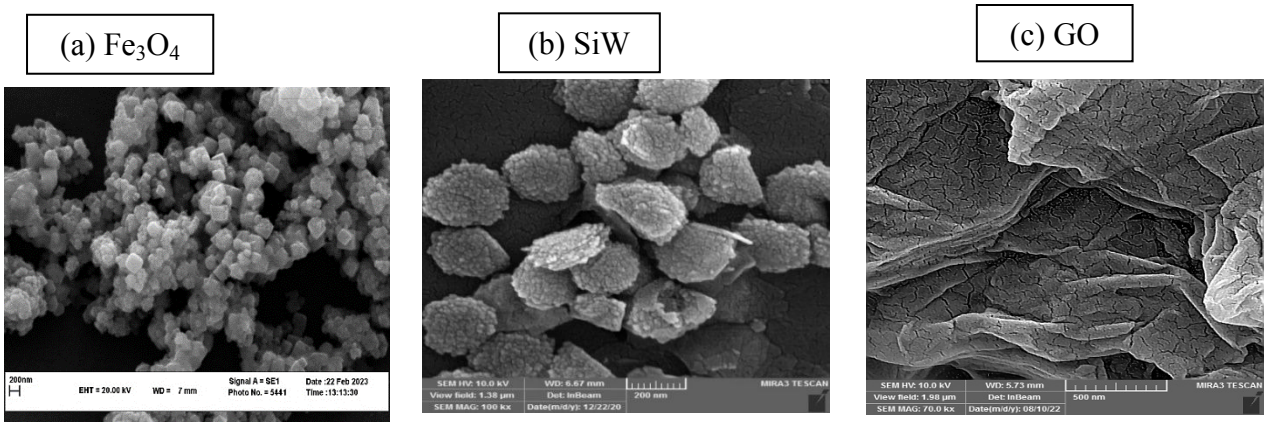
Results and discussion

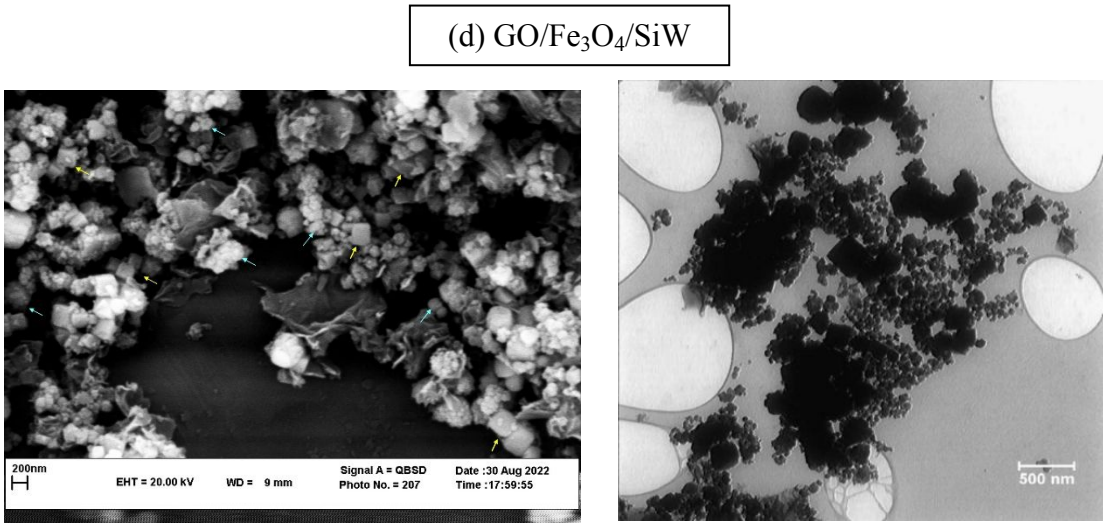
The Fe_3O_4/SiW_{12}/GO sorbent was synthesized by a reaction between its three components under hydrothermal synthesis conditions and the yield of compounds was calculated according to the formula of the previous works (Fig. 1a).[57] The characterization techniques employed in this study, including FE-SEM,

TEM, EDX, PXRD and FTIR, provided compelling evidence for the successful synthesis of the GO/Fe_3O_4/SiW composite.

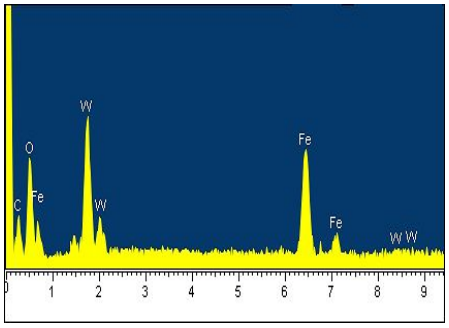
Morphology and elemental analysis

FE-SEM and TEM images revealed the morphology of individual components (Fig.2), showing Fe_3O_4 nanoparticles with a regular cubic shape (Fig 2a), [58] GO sheets with smooth surfaces (Fig. 2b), and spherical SiW particles (Fig. 2c). The SEM image of the composite demonstrated that GO sheets were effectively occupied by uniformly dispersed Fe_3O_4 and SiW, indicating successful immobilization and good dispersion, which are crucial for optimal adsorption performance. Elemental analysis via EDX (Fig. 2e) confirmed the presence of key elements (C, O, Fe, W, and Si) corresponding to GO, Fe_3O_4, and SiW, further validating the proper composition of the composite.





(e)



Element	Weight%	Atomic%
C	39.47	60.85
O	29.79	31.39
Fe	12.28	7.20
W	18.46	0.23
Totals	100.00	

Fig. 2. FESEM images: a) Fe_3O_4, b) SiW, c) GO, d-left) $GO/Fe_3O_4/SiW$ (yellow arrows represent Fe3O4 and blow arrows represent SiW), d-right) TEM image of $GO/Fe_3O_4/SiW$, and e) EDX of $GO/Fe_3O_4/SiW$ nanocomposite.

PXRD analysis

The powder XRD analysis (Fig. 3) provided additional confirmation by exhibiting diffraction peaks characteristic of each component at specific at $2\theta = 11$ (GO),[59] 36.5 (Fe_3O_4),[60] and 28.5 (SiW)[61], confirming that Fe3O4 and SiW moieties were successfully anchored onto the GO surface without compromising their crystalline structures.

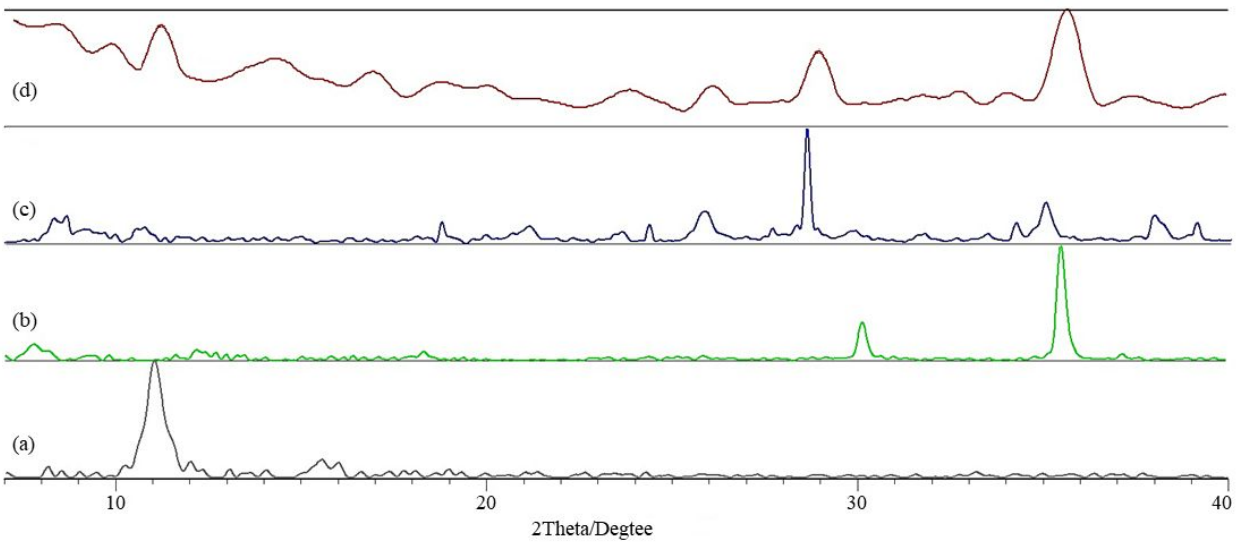


Fig. 3. The XRD patterns: (a) GO, (b) Fe_3O_4, (c) SiW, (d) composite (GO/Fe_3O_4/SiW).

FTIR spectra

Infrared spectroscopy of GO/Fe_3O_4/SiW is consistent with the presence of functional groups from all components observed by a single spectrum of GO,[62] Fe_3O_4,[60] and SiW[61] which confirms that our composite is synthesized successfully (Fig. 4). For example, SiW showed four characteristic bands for the stretching vibrations of W=O (973 cm^{-1} and 702 cm^{-1}), Si−O (924 cm^{-1}), and W−O (804 cm^{-1}). In addition, characteristic bands at 583-637 cm^{-1} in the GO/Fe_3O_4/SiW composite are attributed to Fe–O stretching vibration, and the vibration band for C=O groups attached on the GO surface are attributed at 1580 and 1722 cm^{-1}. These combined evidences strongly support that the GO/Fe_3O_4/SiW nanocomposite was synthesized correctly with the desired structural and chemical features necessary for effective adsorption of NSAIDs.

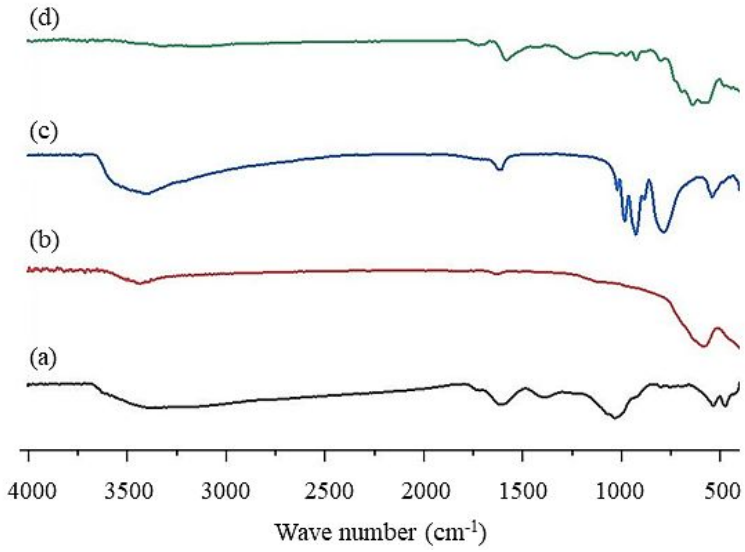


Fig. 4. FTIR spectra: (a) GO, (b) Fe_3O_4, (c) SiW, (d) composite (GO/Fe_3O_4/SiW).

Magnetism analysis

The magnetic characteristics of both pure Fe_3O_4 and GO/Fe_3O_4/SiW were investigated using a vibrating sample magnetometer (VSM) at ambient temperature. The magnetization curves for Fe_3O_4 and GO/Fe_3O_4/SiW indicated that the magnetic remanences are almost negligible, suggesting that there is very little residual magnetization after the external magnetic field has been taken away, which is typical of superparamagnetic behavior. Also, the maximum saturation magnetization of GO/Fe_3O_4/SiW showed a reduction (43 emu g^{-1}) compared to the Fe_3O_4 nanoparticle (65 emu g^{-1}) due to the immobilization of Fe_3O_4 nanoparticle on the non-magnetic surface of GO.

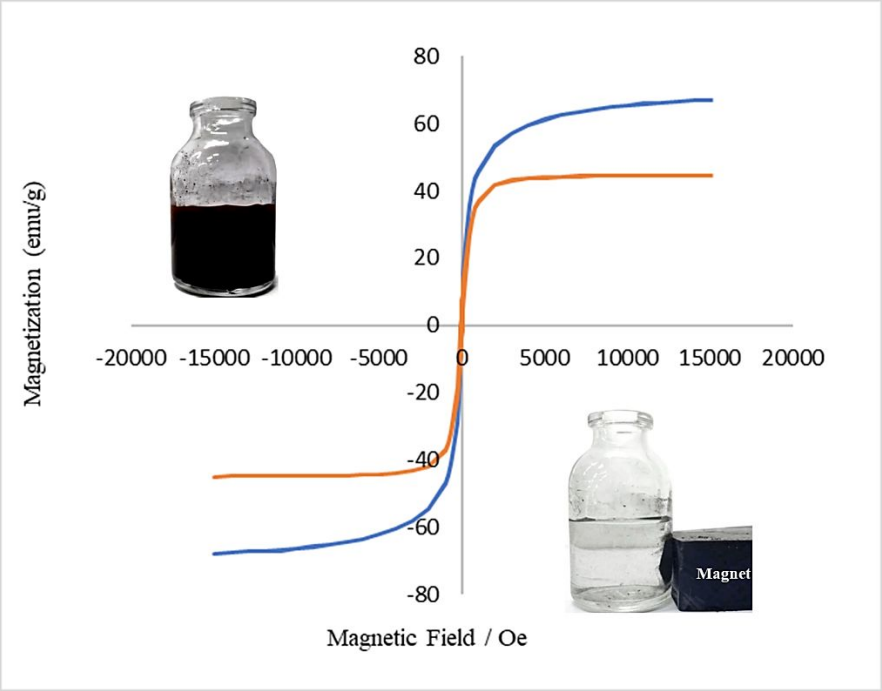


Fig. 5. Magnetization curves of (blue) Fe_3O_4, (orange) GO/Fe_3O_4/SiW, in-set the response of composite by the external magnet.

Zeta potential

The pH of the GO/Fe_3O_4/SiW nanocomposite can significantly influences its adsorption performance by modulating its surface charge and, consequently, the electrostatic interactions with NSAID molecules during the MSPE process. As shown in Fig. 6, the zeta potential measurements ranged from –5.97 mV at pH 4 to –28.60 mV at pH 10, indicating a transition from mildly positive or neutral to strongly negative surface charge across this pH range. This negative charge is primarily attributed to the deprotonation of functional groups on GO and the inherent negative charge of the SiW moieties.[63,64] Most of the NSAIDs studied (ibuprofen, diclofenac, naproxen, tenoxicam, meloxicam) have pKa values between 4.08 and 5.30 (Table1) which means they have acidic nature, favoring electrostatic attraction with the negatively charged sorbent surface.

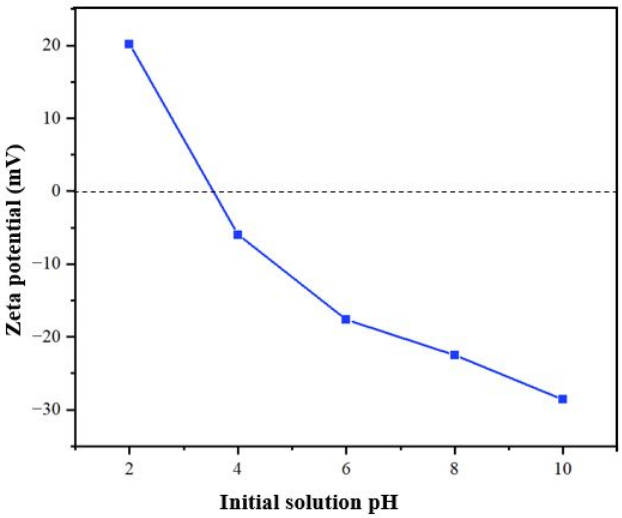


Fig. 6. Zeta potential of aqueous suspension GO/Fe_3O_4/SiW

Optimization test

Optimization of MSPE was performed on five standard samples of NSAIDs to achieve the highest extraction efficiency. All experiments were conducted in triplicate at room temperature, and the means of the results were used for the optimization process. First, the influence of the sorbent amount on the extraction efficiency of NSAIDs was evaluated within the range of 5–25 mg (Fig. 7a). Based on the obtained results, 20 mg of GO/Fe_3O_4/SiW as sorbent is adequate for the quantitative extraction of NSAIDs. Then, the effect of the extraction solvents was investigated by applying five organic solvents that differ in polarity (chloroform (2.7), acetonitrile (5.8), toluene (4.4), methanol (5.1), and dichloromethane (3.1)) (Fig. 7b).[65] Among the above solvents, acetonitrile showed the best extraction efficiency due to its highest polarity index. In continuing, different volumes of acetonitrile from 0.5 to 1.5 mL were examined for the desorption of the analytes (Fig. 7c). As the amount of desorption solvent rose from 0.5 to 1 mL, the efficiency of extraction increased. However, there was no significant change for most of the analytes by increasing the volume by more than 1 mL, so, 1 mL was determined to be the optimum amount of desorption solvent for the following experiments. To investigate the influence of desorption time, five times were selected (1–10 minutes) and the maximum extraction efficiency was observed in 6 minutes (Fig. 7d). Therefore, 6 min was implemented for the desorption of NSAIDs from GO/Fe_3O_4/SiW nanocomposite. It is important to note that extraction time refers to the duration of time which the GO/Fe3O4/SiW sorbent was actively in contact with the analytes, and this was evaluated by varying the time from 1 to 10 minutes (Fig. 7e). The peak area of all NSAIDs improved when the extraction time increased to 6 minutes, so it was selected as the ideal extraction time. Finally, the impact of pH on the extraction efficiency of NSAIDs was investigated to identify the optimal interaction between the analyte and sorbent. When the pH of the sample solution ranges from 2.0 to 4.0, the analyte remains in molecular form, as NSAIDs are acidic with pKa values below 5.3 (Table 1), and can be captured by GO/Fe_3O_4/SiW through hydrogen bonding and π-stacking interactions. The extraction efficiency of NSAIDs improves with increasing pH in the range of 4.0 to 6.0. At this pH, the surface charge transitions from slightly positive to neutral, favoring electrostatic attraction between the positively charged or neutral surface (due to protonation) and the negatively charged NSAID species (pKa values between 4.08 and 5.30), which predominately exist in their anionic forms above pH 5.0. When the pH exceeds 7.0, deprotonation of both the GO/Fe_3O_4/SiW functional groups and

the NSAIDs reduces electrostatic attraction, leading to diminished adsorption efficiency. Therefore, pH 6.0 was determined to be the optimal pH for extraction performance and repeatability (Fig. 7f). Therefore, the adsorption mechanism between the analytes and GO/Fe_3O_4/SiW sorbent can be described by π-stacking (between the aromatic backbone of NSAIDs and GO, electrostatic interactions (between analytes and sorbent with different charges), and H-bonding (between functional groups of NSDAIDs and hanged oxygen surface of sorbent (oxo-groups from SiW, carboxylate, and hydroxy groups from GO)). The pH-dependent zeta potential data provide experimental support for these mechanisms, confirming the role of electrostatic interactions modulated by surface charge changes within the pH range studied.

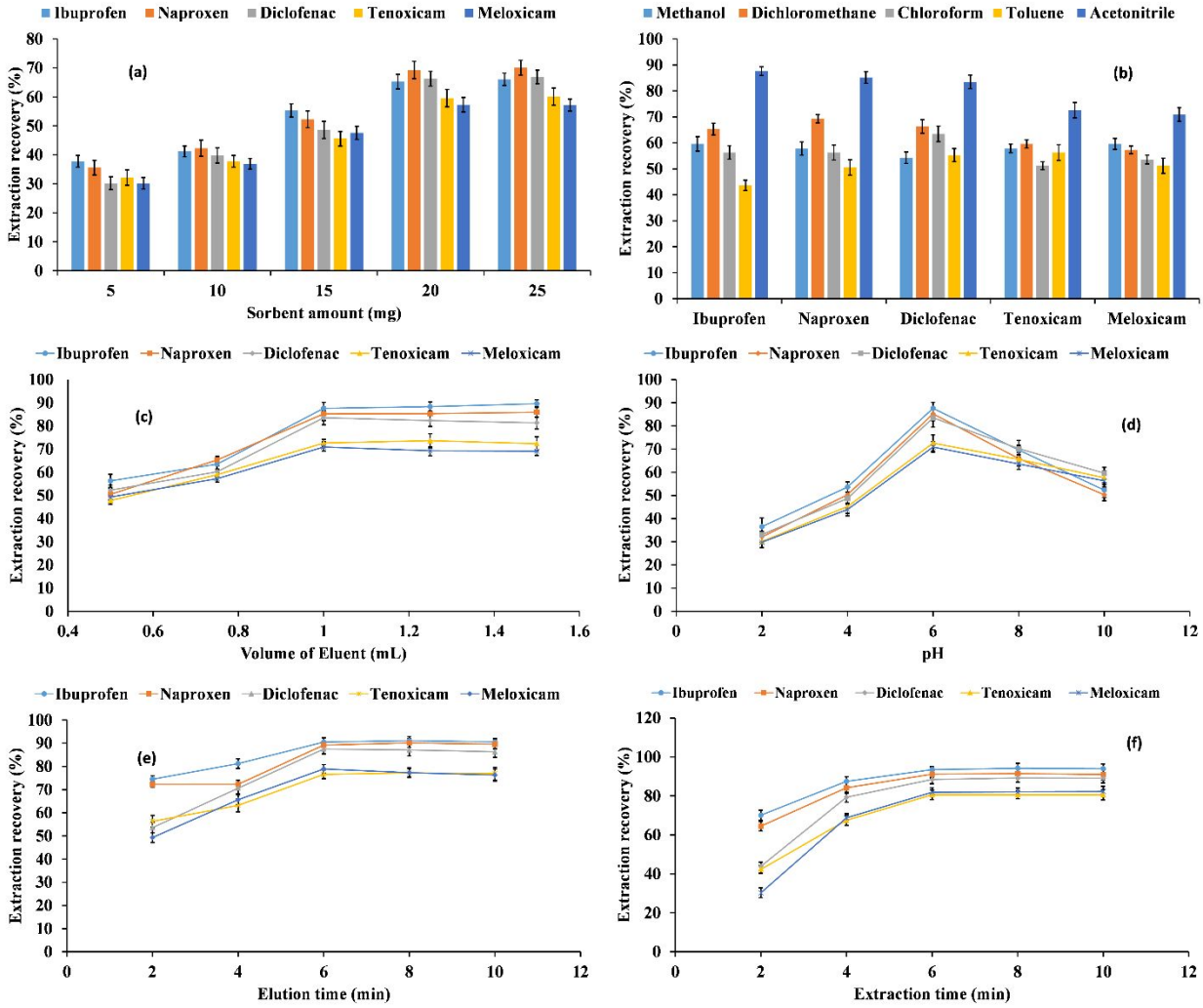


Fig. 7. Optimization of the extraction conditions on the extraction efficiency: a) Sorbent amount; b) Desorption solvent; c) Desorption solvent volume; d) pH; e) Desorption time; f) Extraction time.

Analytical performance

Under optimized conditions, a few key analytical properties of the MSPE-HPLC-UV technique such as the linearity, the lower limit of detection (LOD), and precision were investigated (Table 2). Various concentrations of NSAIDs were employed to acquire the calibration plots for HPLC-UV analysis. The

MSPE-HPLC-UV method showed good linearity for ibuprofen (0.03–300 ng mL^{-1}), naproxen (0.03–300 ng mL^{-1}), diclofenac (0.06–300 ng mL^{-1}), tenoxicam (0.1–200 ng mL^{-1}), and meloxicam (0.1–200 ng mL^{-1}) with the correlation coefficient (R) greater than 0.9925. The LODs (at a signal-to-noise ratio of 3) are found to be 0.01–0.03 ng mL^{-1} for all NSAIDs. To assess precision, five consecutive MSPE-HPLC-UV methods were carried out at three concentration levels (0.1, 5, and 100 ng mL^{-1}), resulting in RSD% ranging from 3.7 to 5.0%.

Table 2. Summary of the results of merit of the MSPE method of the NSAIDs

Analyte	Linear range (ng mL^{-1})	LOD (ng mL^{-1})	Correlation coefficient (r)	Repeatability (RSD%, n=5)		
				0.1 (ng mL^{-1})	5 (ng mL^{-1})	100 (ng mL^{-1})
Ibuprofen	0.03−300	0.01	0.9963	5.0	4.8	4.7
Naproxen	0.03−300	0.01	0.9925	4.6	4.3	3.7
Diclofenac	0.06−300	0.02	0.9942	4.7	4.4	4.1
Tenoxicam	0.1−200	0.03	0.9937	4.9	4.3	3.9
Meloxicam	0.1−200	0.03	0.9941	4.5	4.0	3.8

Evaluation of method practicality

The environmental performance of the proposed analytical method was further evaluated using the BAGI (Baranowska–Gadek Analytical Greenness Index) tool[66,67]. The BAGI evaluation of the proposed method (Fig. 8a) yielded an overall score of 75.0, which reflects a good level of environmental friendliness. The spider diagram demonstrates balanced performance across most categories, indicating reduced solvent use, minimal hazardous reagents, and relatively low waste generation. Only one criterion scored lower, suggesting a potential area for further improvement. These results confirm that the method provides a reasonable compromise between analytical efficiency and environmental sustainability. Also, the greenness and sustainability of the MSPE-HPLC-UV method were evaluated using the AGREEprep algorithm[68], yielding an overall score of 0.61 (Fig. 8b). This relatively high score reflects a strong green profile for the sample preparation component of the method. Major strengths include the low energy consumption, employment of eco-friendly solvents and materials, minimal waste generation, reusability of materials, and high throughput. However, some criteria scored lower—namely criterion 1 (in situ sample preparation), criterion 5 (size economy of the sample), and criterion 7 (integration and automation), which point to limitations in automation and field preparedness.

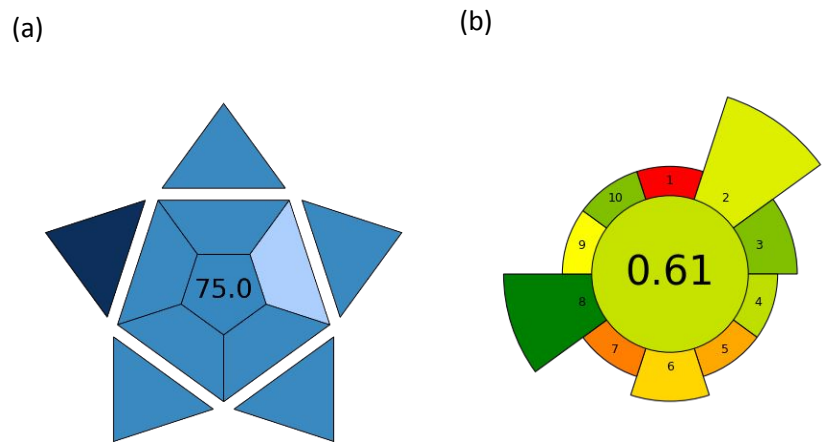


Fig. 8. (a) The results of BAGI assessment of the presented procedure, (b) the results of AGREEprep assessment of the presented procedure.

Real sample analysis

The efficiency of the MSPE-HPLC-UV method with the GO/Fe3O4/SiW sorbent was examined by the extraction of NSAIDs in real water samples (river, tap, and wastewater). These environmental water samples were collected during the summer season from urban areas of Mashhad, Razavi Khorasan Province, Iran, transferred into headspace-free, dark glass vials, and stored at 4 °C to maintain their integrity for analysis. No NSAIDs were detected in the collected samples, as shown in Table 3. To investigate the matrix effect of the MSPE-HPLC-UV method, the relative recoveries of target NSAIDs were examined at three concentration levels (0.1, 5, and 100 ng mL^{-1}). The spiked recovery experiments were performed three times at each concentration level, and the mean recoveries with corresponding RSDs are presented in Table 3. Relative recoveries of NSAIDs in real water ranged from 97.1% to 100.0% with RSDs between 4.1% and 6.0%. These results demonstrate that matrix effects were either effectively minimized by the extraction procedure or were within acceptable limits, confirming the reliability of the MSPE-HPLC-UV method for real environmental water analysis.

Table 3. The contents, precisions, and accuracies of NSAIDs in real water samples with the MSPE 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 (%)
Drinking water	Ibuprofen	ND	99.6	5.1	99.8	4.9	100.0	4.9
	Naproxen	ND	99.5	4.8	99.6	4.5	99.8	4.3
	Diclofenac	ND	99.1	5.0	99.3	4.9	99.5	4.5
	Tenoxicam	ND	99.3	5.1	99.3	4.7	99.6	4.6
	Meloxicam	ND	98.9	4.7	99.0	4.3	99.4	4.1
River water	Ibuprofen	ND	99.1	5.3	99.3	5.0	99.7	4.8
	Naproxen	ND	99.2	4.7	99.4	4.5	99.5	4.5
	Diclofenac	ND	98.8	4.6	98.9	4.3	99.3	4.1
	Tenoxicam	ND	98.7	4.9	99.0	4.4	99.3	4.3
	Meloxicam	ND	98.6	4.6	98.7	4.6	99.1	4.4
Wastewater	Ibuprofen	ND	97.7	5.6	98.1	5.2	98.7	5.1

Naproxen	ND	98.3	6.0	98.4	5.7	98.6	5.2
Diclofenac	ND	98.1	5.8	98.3	5.3	98.4	4.9
Tenoxicam	ND	97.5	5.6	97.9	5.2	98.8	5.0
Meloxicam	ND	97.1	5.3	97.3	5.1	97.8	4.8

The effectiveness of the MSPE-HPLC-UV technique for extracting NSAIDs was assessed by comparing its results with those obtained from similar methodologies (Table 4).[6, 69–72] The comparative data clearly demonstrate that the proposed MSPE method offers distinct advantages over previously reported approaches. In terms of sensitivity, MSPE achieves an exceptionally low LOD of 0.01–0.03 ng mL^{-1}, which is at least one order of magnitude lower than classical SPE (1.8–32.3 ng mL^{-1}) and also superior to other miniaturized extraction techniques such as HF-SLPME (1.51–2.95 ng mL^{-1}), SBSE (6.90–7.69 ng mL^{-1}), DLLME-SFO (0.13–0.39 ng mL^{-1}), and D-µSPE (0.02–0.03 ng mL^{-1}). This demonstrates the outstanding potential of MSPE for ultra-trace determination in water samples. The precision of MSPE (RSD: 3.7–5.0%) is comparable to or better than most other methods, and well within the acceptable range for environmental analysis. While DLLME-SFO and SBSE exhibit slightly broader RSD intervals (up to 9.2%), the MSPE method maintains consistent reproducibility. In addition, the linear range obtained by MSPE (0.03–300 ng mL^{-1}) is considerably wide compared to methods such as DLLME-SFO (1–100 ng mL^{-1}) and D-µSPE (0.08–200 ng mL^{-1}), offering greater flexibility for analyzing samples with varying concentration levels. Although HF-SLPME provides the broadest interval (2–30,000 ng mL^{-1}), its relatively higher LOD limits its suitability for trace-level monitoring. Collectively, these findings highlight that the proposed MSPE method not only surpasses conventional SPE but also demonstrates superior analytical performance compared to state-of-the-art microextraction techniques. Its combination of ultra-low detection limits, adequate precision, and broad linearity underscores its applicability as a highly reliable tool for trace-level environmental monitoring.

Table 4. Comparison of the MSPE method with other methods for determination of NSAIDs in real samples

Method	Detection system	Sample	LOD (ng mL^{-1})	Linear range (ng mL^{-1})	RSD%
SPE[69]	HPLC–UV	Water	1.8−32.3	2−300	1.9−7.1
HF-SLPME[70]	HPLC–UV	Water	1.51−2.95	2−30000	2.42−3.55
SBSE[71]	HPLC–UV	Water	6.90−7.69	20−2000	4.1−9.2
DLLME-SFO[72]	HPLC–UV	Water	0.13−0.39	1−100	3.45−6.34
D-µSPE[6]	HPLC–UV	Water	0.02−0.03	0.08−200	4.1−6.1
MSPE	HPLC–UV	Water	0.01−0.03	0.03−300	3.7−5.0

abbreviations: SPE: solid-phase extraction; HF-SLPME: Hollow fiber solid-liquid phase microextraction; SBSE: Stir bar sorptive extraction; DLLME-SFO: Dispersive liquid-liquid microextraction based on solidification of floating organic droplet; D-µSPE: Dispersive micro-solid-phase extraction .

Conclusion

The purpose of this research was to evaluate the efficacy of a novel tri-component composite, produced by GO, POM, and magnetic Fe_3O_4 (GO/Fe_3O_4/SiW), for the extraction and preconcentration of various NSAIDs, including ibuprofen, diclofenac, naproxen, tenoxicam, and meloxicam, from water samples. The magnetic properties of Fe_3O_4 not only facilitated rapid magnetic separation but also eliminated the need for time-consuming filtration or centrifugation steps, thereby significantly reducing analysis time. To the best

of our knowledge, this is the first report demonstrating the application of GO/Fe_3O_4/SiW composites for MSPE of NSAIDs with diverse functional groups, highlighting its novelty and potential in environmental analysis. Comprehensive characterization techniques, such as FTIR, SEM, and XRD, confirmed the successful immobilization of Fe_3O_4 nanoparticles and SiW moieties on the GO surface. Analysis such as FTIR, SEM, and XRD proved that Fe_3O_4 and SiW moieties are anchored on the surface of the GO which makes the surface of this composite rich in oxo-containing functional groups which provides valuable insights into the adsorption mechanisms. For instance, H-bonding and halogen bonding between functional groups of NSDAIDs and oxo-groups from SiW, carboxylate, and hydroxy groups from GO of sorbent can be described as one of the possible adsorption mechanisms. In addition, electrostatic interactions and π-stacking between the aromatic rings of NSAIDs and the delocalized π-electron system of GO are other defined mechanisms for the system. Optimization studies demonstrated that the method exhibits high sensitivity, with linear detection ranges spanning from 0.03 to 300 ng mL^{-1} and low limit of detection (ranging from 0.01 and 0.03 ng mL^{-1}) and good recoveries (ranging from 97.1% to 100.0%) for the target NSAIDs. Overall, the developed MSPE-HPLC-UV technique presents a simple, rapid, and cost-effective approach with outstanding sensitivity for NSAID monitoring in environmental water samples. Furthermore, the versatility of the GO/Fe_3O_4/SiW sorbent suggests its applicability for the pre-concentration and detection of a variety of other analytes such as pesticides, hormones, and amino acids in complex matrices like food, biological fluids, and environmental samples, potentially broadening its impact in analytical and environmental chemistry. Looking forward, future work could focus on automating the MSPE process to enable high-throughput analysis and integrating the sorbent with advanced detection techniques such as mass spectrometry (MS) for enhanced sensitivity and specificity. Additionally, coupling this approach with tandem MS could improve selectivity for complex matrices. The versatile nature of the GO/Fe_3O_4/SiW sorbent suggests its potential for expanding applications to other pharmaceutical residues, pesticides, hormones, and environmental pollutants in diverse samples, including biological fluids, food matrices, and wastewater. Further research may also explore the possibility of adapting the method for on-site or portable analysis systems to facilitate real-time environmental monitoring.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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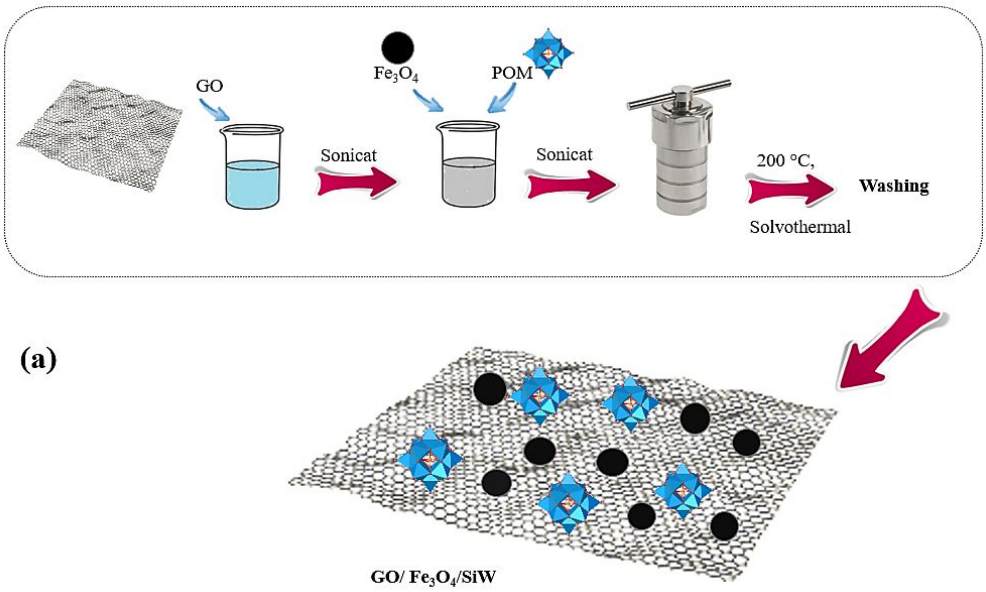
GO
Fe_3O_4
POM
Sonicat
Sonicat
200 °C,
Solvothermal
Washing
(a)
GO/ Fe_3O_4/SiW

Data availability

The datasets generated and analyzed during the current study are available within the manuscript itself. All relevant data are presented in the form of figures, tables, and supplementary information accompanying this article.