University of Pannonia
Chemical Engineering and Material Sciences Doctoral School

DEVELOPMENT OF HIGH-SENSITIVITY ANALYTICAL METHODS FOR THE ENVIRONMENTAL ANALYSIS OF ORGANIC MICROPOLLUTANTS AND DESIGN OF EFFECTIVE ADSORBENTS FOR THEIR REMOVAL FROM AQUEOUS MEDIA

PhD THESIS

Written by:
Kovács Nikoletta
Doctor of pharmacy

Supervisors:
Gerencsérné Dr. Berta Renáta
Dr. Maász Gábor

University of Pannonia
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Introduction

Access to sufficient quantities of clean drinking water is already a critical challenge in certain areas of the world. The progressive degradation of natural water quality poses long-term risks even to water resources in developed countries. Intensive industrial and agricultural activities, and the increasing demands of modern consumer societies, have led to the widespread occurence of emerging anthropogenic contaminants in surface waters. These substances, including pesticides, pharmaceutical residues, and industrial chemicals, often occur at concentrations of only a few ng/l. Their diverse physicochemical properties, in complex environmental matrices, make their detection and quantification a significant analytical challenge. Even at trace levels, some compounds may pose ecological risks and potential adverse effects on human health, including carcinogenicity or endocrine disruption.

During this doctoral research, sample preparation and analytical (UPLC-MS/MS) methods were developed for the determination of a broad spectrum of organic micropollutants. The influence of chromatographic conditions on mass spectrometric ionization and adduct formation of target compounds was investigated, and different stationary phases were tested to achieve optimal peak shapes and retention for molecules with various physicochemical properties. Particular attention was given to optimizing chemical derivatization for the detection of trace levels of estrogenic hormones and bisphenols, as well as to adjusting sample enrichment to achieve the required sensitivity while minimizing matrix effects.

Conventional wastewater treatment technologies are often insufficient for the effective removal of the emerging micropollutants, making treated municipal wastewater a significant source of organic contaminants released into the environment. To protect surface waters and drinking water resources, increasing emphasis has been placed on advanced, fourth-stage treatment technologies, which enable selective and efficient removal of micropollutants. These approaches are initially implemented at large-scale treatment plants and gradually extended to smaller facilities.

As part of this doctoral work, the targeted removal of organic micropollutants was investigated using magnetically separable adsorbents that can be integrated into existing treatment systems. Two model compounds were selected for study: the polar herbicide glyphosate and the non-polar endocrine-disrupting compound bisphenol A. For the latter, magnetite particles were hydrophobized using various surface-modifying agents to enhance adsorption efficiency. The effects of experimental parameters, including pH and electrolyte composition, were evaluated, and the performance of the adsorbents was assessed using both surface water and drinking water samples.

Objective

The aim of my research was to develop analytical methods suitable for the simultaneous, selective, and sensitive determination of organic micropollutants in environmental samples, especially in surface waters. A key focus was on the development of UPLC-MS/MS based protocols suitable for multi-component analysis, and the optimization of critical steps in sample preparation. This included the fine-tuning of solid-phase extraction parameters, the reduction of matrix effects, and the development of derivatization procedures aimed at enhancing sensitivity. A particular focus was placed on optimizing derivatization reactions to facilitate the detection of estrogenic hormones and bisphenols, as well as on improving the efficiency of the associated extraction steps.

Furthermore, this doctoral work aimed to develop a novel water treatment technology capable of effectively removing organic micropollutants, including endocrine-disrupting compounds, represented by two model compounds with distinct physicochemical properties: glyphosate and bisphenol A, from various types of water. The research focused on exploring the application of magnetically separable adsorbents and optimizing their surface modification to enhance removal efficiency. A key objective of the research was the investigation of the effects of experimental parameters, such as pH and electrolytes, on adsorption efficiency, as well as the evaluation of adsorbent regenerability and reusability. Furthermore, the laboratory-scale investigations were extended to environmental water samples to assess the performance of the adsorbents in surface water and drinking water matrices.

Methods

1. Analytical method development

UPLC-MS/MS measurements

Targeted analysis of the micropollutants in environmental survey measurements and adsorption experiments was carried out using an ACQUITY UPLC H-Class (Waters, MA, USA) ultra-performance liquid chromatograph coupled to a Xevo TQS micro triple quadrupole mass spectrometer (Waters, MA, USA) equipped with an electrospray ionization source. High-purity nitrogen (95+%, Genius XE 35 laboratory nitrogen generator, Peak Scientific, UK) was used as both desolvation and cone (curtain) gas, while high-purity argon (99.997%, Messer Hungarogáz Ltd.) was applied as the collision gas. Data evaluation was performed using MassLynx software (version 4.2 SCN1017; Waters, MA, USA). Quantification of target compounds was achieved via targeted MRM-based mass spectrometric detection. Chromatographic conditions were optimized according to the specific analytical objectives.

Solid phase extraction (SPE)

Solid phase extraction (SPE) was applied to cleanup environmental water samples and enrich the target compounds. Following pre-filtration (GF/A 1.6 µm, #1820-047, Whatman, then GF/F 0.7 µm, #516-0345, VWR), sample clean-up was performed using an automated SPE system (Dionex AutoTrace 280; Thermo Scientific, USA). For multi-component analyses, Strata X-CW (33 µm, 200 mg, 6 ml; Phenomenex) SPE cartridges were employed. The cartridges were conditioned with 3 ml HPLC-grade methanol and equilibrated with 3 ml water containing 0.1% v/v formic acid. Subsequently, 1000 ml of water sample was loaded at a flow rate of 10 ml/min. After loading, the cartridges were washed with 6 ml of 0.1% v/v formic acid in water, followed by 6 ml of a 20:80 v/v mixture of acetonitrile (HPLC) and 0.1% v/v formic acid in water. Residual water was removed by drying under a nitrogen stream. Elution was performed with 5 ml acetonitrile containing 20% v/v NH_4OH. The eluates were evaporated to dryness under nitrogen and reconstituted in 300 µl of LC-MS-grade acetonitrile. For hormone and bisphenol analyses, chemical derivatization was performed from the acetonitrile solution. For LC-MS/MS measurements of pharmaceuticals, pesticides, and other micropollutants, an appropriate amount of ultrapure water was added to the samples prior to injection according to the respective analytical method.

Chemical derivatization

For the analysis of estrogens and bisphenols, chemical derivatization was performed following solid phase extraction to enhance analytical sensitivity. To 100 µl of the reconstituted sample, 20 µl of 40 mmol/L dansyl chloride (5-(dimethylamino)naphthalene-1-sulfonyl chloride in acetonitrile) and 80 µl of 100 mmol/L sodium carbonate (ultrapure aqueous solution, pH 11) were added. The mixtures were incubated at 65 °C for 15 minutes (HB1DG Dry Block Heater, OHAUS Europe GmbH, Germany). After incubation, samples were cooled at 4 °C for 5 minutes, followed by liquid-liquid extraction with 40 µl toluene and centrifugation at 10,000 rpm for 5 minutes (FRONTIER FC5816R; OHAUS Europe GmbH, Germany). From the upper organic phase, 80 µl was collected, evaporated to dryness under a stream of nitrogen gas, and reconstituted in a 50:50% v/v mixture of LC-MS-grade methanol and ultrapure water for LC-MS/MS analysis.

Extraction of micropollutants from sewage sludge

For the analysis of micropollutants in sewage sludge, the efficiency of ultrasound-assisted extraction (UAE), focused ultrasound-assisted extraction (FUSE), microwave-assisted extraction (MAE), and Soxhlet extraction was evaluated. One gram (wet weight) of sewage sludge was accurately weighed into a 50 mL polypropylene Eppendorf tube, and 30 mL of extraction solvent (methanol:ultrapure water, 25:75% v/v) was added. For UAE, samples were treated in an ultrasonic water bath (RS-57, Realsonic, Hungary) at 50 °C for 30 minutes. FUSE was performed using an ultrasonic processor (UP400St, Hielscher, Germany), with the probe immersed 1 cm below the liquid surface, delivering 5000 Ws (~167 J/mL) to the sample. The temperature limit was set to 50 °C. MAE was conducted using a microwave-assisted extraction system (MULTIWAVE GO Plus, Anton Paar, Austria). Samples were placed in TFM-PTFE microwave vessels and treated at 600 W for 30 minutes, with a temperature limit of 50 °C. For Soxhlet extraction, 1 g of sludge (wet weight) was extracted with 300 mL of hexane:acetone (55:45% v/v) at 65 °C for 22 hours. Soxhlet extracts were evaporated to dryness under a nitrogen stream and reconstituted in 30 mL of methanol:ultrapure water (25:75% v/v). All extraction experiments were performed in triplicate, with untreated blanks prepared simultaneously. Following extraction, sludge samples were centrifuged at 3780 rpm for 10 minutes (FRONTIER FC5816R; OHAUS Europe GmbH, Germany). Subsequently, 20 mL of supernatant was collected and the volume adjusted to 300 mL. Samples were acidified with 0.1% v/v formic acid, filtered, and subjected to solid phase extraction.

2. Adsorption experiments

Adsorbent preparation, characterization, and modification

Magnetite nanoparticles used for glyphosate removal were synthesized by the co-precipitation method. The concentration of the purified magnetite suspension was determined by measuring the dry matter content after drying to constant weight at 105 °C. The synthesized material was identified as magnetite using X-ray diffraction (XRD; Philips PW 1830/PW 1820 diffractometer, reflection mode, CuKα radiation, 20°–80° 2θ range). The average particle size and size distribution were determined by transmission electron microscopy (TEM; JEM-1400, JEOL Ltd., Japan). The isoelectric point was determined via electrokinetic potential measurements at 25 ± 0.1 °C using a NanoZS (Malvern, UK) instrument with disposable zeta cells (DTS 1070). For hydrophobic surface modification, aqueous solutions of sodium oleate, sodium cholate, or pyrocatechol were added to the magnetite nanoparticles in the presence of 10 mmol/L NaCl, and the pH was adjusted to 6.5. The specific amount of surface modifier added was varied between 0.2–2 mmol/g. The magnetite suspension was mixed with the hydrophobizing agents in 5 mL polypropylene Eppendorf tubes for 24 h at room temperature at 55 rpm (MX-RL-Pro rotary mixer, DLab, China). The suspension was then centrifuged at 4500 rpm for 20 min (FRONTIER FC5816R; OHAUS Europe GmbH, Germany), and the hydrophobized magnetite particles were collected using a permanent NdFeB magnet, while the known volume of supernatant was discarded. The degree of surface coverage was determined using UV–Vis spectrophotometry (oleate $\lambda_{max} = 233$ nm, pyrocatechol $\lambda_{max} = 275$ nm) or droplet weight methods (cholate).

Adsorption/desorption experiments

Adsorption and desorption experiments were conducted in a batch setup. Adsorption tests were performed in closed 5 mL polypropylene Eppendorf tubes containing 0.5 % w/v sorbent in the presence of 10 mmol/L of either an indifferent (NaCl) or a specific ($CaCl_2$) electrolyte. The solid-to-liquid ratio was 1:200 (0.01 g magnetite in 2.0 mL solution). The suspensions were agitated for 24 h at 22 ± 1 °C, at 55 rpm and a rotor angle of 15° (MX-RL-Pro rotary mixer, DLab, China). After adsorption, the sorbent was separated from the clarified supernatant by centrifugation (4500 rpm, 20 min, FRONTIER FC5816R; OHAUS Europe GmbH, Germany) and using a permanent NdFeB magnet. The equilibrium concentrations of glyphosate and BPA in the supernatants were determined by UPLC-MS/MS.

Determination of glyphosate/AMPA

Chromatographic separation of glyphosate (GLY) and AMPA was performed on a HILIC-type analytical column (Anionic Polar Pesticide, 5 µm; 100 × 2.1 mm, p/n: 186009287; Waters, MA, USA). The injection volume was 1 µL, and the column temperature was maintained at 50 °C. The mobile phases consisted of ultrapure water with 0.9 % v/v LC-MS grade formic acid (A) and LC-MS grade acetonitrile with 0.9 % v/v LC-MS grade formic acid (B), at a flow rate of 500 µL/min. The gradient program was as follows: 0–4 min, 90 % B to 15 % B (curve 2, convex); 4–13 min, 15 % B; 13–18.5 min, 90 % B. Targeted MRM transitions were used for GLY and AMPA analysis: 168 → 63; 150 (collision energies: 15; 10 eV) and 110 → 63; 79 (collision energy: 15 eV for both transitions) in negative ion mode. The capillary voltage was set to 2.4 kV, cone voltage 15 V, source temperature 150 °C, desolvation gas temperature 600 °C, and desolvation gas flow 1000 L/h.

Determination of Bisphenol A (BPA)

BPA was analyzed using an Acquity UPLC BEH C18 analytical column (1.7 µm, 50 × 2.1 mm i.d., p/n: 186002350; Waters, MA, USA). The injection volume was 2 µL, and the column temperature was maintained at 60 °C. The mobile phase consisted of ultrapure water (A) and LC-MS grade acetonitrile (B) at a flow rate of 400 µL/min, using the following gradient program: 0–3 min, 5 % B; 3–6 min, 45 % B to 75 % B; 6–8 min, 5 % B. Targeted MRM transitions for BPA were 227 → 212; 133 (collision energies: 18 eV; 25 eV) in negative ion mode. Optimized MS parameters were as follows: capillary voltage 2.0 kV, cone voltage 25 V, source temperature 150 °C, desolvation gas temperature 500 °C, and desolvation gas flow 1000 L/h.

Results

1. Analytical method development for the analysis of environmental samples

As a result of the analytical method development, high-sensitivity UPLC-MS/MS and sample preparation methods were optimized and validated for the determination of 77 organic micropollutants in environmental water samples, with an average limit of quantification of 5 ng/L.

2. Optimization of sample preparation methods for environmental analysis

Solid-Phase Extraction (SPE)

The Strata X-CW SPE cartridges (33 µm, 200 mg/6 mL, Phenomenex) proved suitable for the efficient extraction of a wide range of micropollutants from various water samples, with recoveries for most components ranging from 70 % to 130 %. Lower recoveries were observed for highly polar compounds (logP < 1), such as metformin, guanilurea, morphine, atenolol, clothianidin, and thiamethoxam. For the most polar compounds glyphosate and AMPA, none of the tested SPE cartridges (Strata XL-A, 100 µm, 500 mg/6 mL; Strata XL-AW, 100 µm, 500 mg/6 mL; Strata FL-PR Florisil, 170 µm, 500 mg/6 mL; Phenomenex) provided satisfactory recoveries. For estrogens and bisphenols, in addition to Strata X-CW, the Oasis HLB (30 µm, 200 mg/6 mL, Waters) and Dionex SolEx C18 (40 µm, 1000 mg/6 mL, Thermo Scientific) cartridges were also suitable; specifically, for Bisphenol S, Oasis HLB achieved ~100 % recovery, whereas Dionex SolEx C18 and Strata X-CW provided only ~20 % recovery.

Sample enrichment and matrix effects

Without concentration, no significant matrix effects were observed for most compounds; however, detection at ng/L levels was not possible without SPE-based concentration. After 2000× concentration, 23 out of the 52 investigated compounds exhibited significant matrix effects (<−30 % or >30 %), whereas at 1000× and 500× concentration, only 12 and 10 compounds, respectively, showed significant matrix effects. The optimal concentration factor was determined to ensure adequate detection limits for the target analytes while maintaining acceptable matrix effects. For most compounds, this corresponded to a 500–1000× concentration.

Chemical derivatization for estrogen analysis

Chemical derivatization with dansyl chloride significantly enhanced the sensitivity of the target analytes compared to the measurement of native molecules in negative ion mode. The highest signal intensity was achieved using acetonitrile as the solvent, pH 11, 15 min reaction time, and toluene extraction. Using the optimized method, the limits of quantification (LOQ) improved as follows: Bisphenol A from 0.66 µg/L to 0.05 µg/L, Bisphenol F from 0.13 µg/L to 0.05 µg/L, Bisphenol S from 0.05 µg/L to 0.01 µg/L, Estrone from 0.58 µg/L to 0.03 µg/L, Estradiol from 2.53 µg/L to 0.06 µg/L, and Ethinylestradiol from 7.45 µg/L to 0.03 µg/L.

Comparison of extraction methods from sewage sludge

For most target analytes, no significant difference in extraction efficiency was observed between UAE and MAE. Only with FUSE was it possible to detect 12 compounds that remained below LOD or LOQ using the other three techniques. FUSE proved most effective for 20 moderately hydrophobic compounds, while Soxhlet extraction was most efficient for 11 highly hydrophobic molecules. The total signal-to-noise ratio (Σ S/N) was highest for FUSE, whereas the highest overall noise was observed with Soxhlet extraction (Σ S/N ranking: SOX > MAE > UAE > FUSE). These results indicate that FUSE represents a suitable alternative to Soxhlet extraction for the extraction of hydrophobic compounds.

3. Analytical method development for adsorption samples

For the adsorption experiments, UPLC-MS/MS methods were developed to enable accurate and reliable determination of target compounds in various matrices, including samples with an electrolyte content of 100 mmol/L. The LC-MS/MS method developed for glyphosate exhibited a linear range of 50–1000 µg/L in both tap water and surface water samples. The method's LOQ values were 38.71 µg/L in tap water and 43.23 µg/L in surface water. Repeatability, assessed for peak area at three concentration levels, met the RSD < 10 % criterion, while the retention time exhibited RSD < 1 %. For bisphenol A (BPA), the LC-MS/MS method showed linear ranges of 0.5–50 µg/L in tap water and 5–500 µg/L in surface water. The LOQ values were 0.58 µg/L in tap water and 1.27 µg/L in surface water. Repeatability for peak area at three concentration levels satisfied the RSD < 10 % requirement, and retention time repeatability met the RSD < 1 % criterion.

4. Adsorption experiments

Adsorbent characterization and surface modification

Based on dry matter content measurements, the concentration of the prepared magnetite suspension was 6.0048 g/100 g (61.57 g/L). XRD patterns (2θ = 30.08°, 35.49°, 43.46°, 57.08°, and 62.83° reflections) confirmed the synthesized material as magnetite. The particle size, estimated from the most intense XRD peak using the Scherrer method, was 7.92 nm. TEM images showed that the synthesized particles were spherical, with an average diameter of 8.22 ± 1.75 nm. The isoelectric point (IEP) of the bare magnetite was 8.2 ± 0.2 in an indifferent electrolyte solution (10 mmol/L NaCl). In a specific electrolyte (10 mmol/L $CaCl_2$), the particles remained positively charged at pH values above the IEP, with ζ-potential values >20 mV. With increasing adsorption of oleate, the ζ-potential of the magnetite nanoparticles decreased. The amount of oleate required to reverse the ζ-potential was approximately 0.7 mmol/g (~198 mg/g). The initial section of the oleate adsorption isotherm indicated high affinity, and the specific adsorbed amount at the first plateau of the isotherm was ~0.6 mmol/g (~170 mg/g). In the presence of Ca^{2+} ions, the IEP shifted towards higher specific oleate amounts (~1 mmol/g, ~283 mg/g, ~6 molecules/nm^2). The adsorption of cholate exhibited a characteristic S-type isotherm, suggesting weak interactions between cholate and magnetite particles. Above a critical equilibrium concentration (~1 mmol/L, ~410 mg/L), adsorbed cholate molecules facilitated further adsorption of additional cholate molecules. Below this critical concentration, cholate presence did not affect the ζ-potential of the magnetite nanoparticles. During pyrocatechol-magnetite adsorption, the adsorbed amount showed significant temporal increase, and ζ-potential measurements indicated substantial accumulation of negative charge on the particle surface over time.

Glyphosate adsorption on bare magnetite

The adsorption of glyphosate and AMPA onto native magnetite was primarily influenced by the pH of the medium, with acidic conditions favoring adsorption for both compounds. In the presence of Ca^{2+} ions, higher adsorption capacities were observed at low micropollutant concentrations under alkaline conditions, compared tot he indifferent electrolyte. The adsorption efficiency of the native magnetite exceeded 98%, with maximum adsorption capacities of 64 mg/g for glyphosate and 36 mg/g for AMPA at pH ~6 in the presence of Ca^{2+} ions. ATR-FTIR analyses indicated that the high-affinity, monolayer adsorption mechanism occurs via surface complexation. The removal efficiency of glyphosate from both drinking water and natural surface water using native magnetite nanoparticles was excellent (98–99%). However, adsorbent regeneration using the applied alkaline treatment (pH 10) was insufficient, with maximum desorption efficiencies of only ~25% for AMPA and ~30% for glyphosate.

Bisphenol A adsorption on hydrophobically modified magnetite

The adsorption efficiency of BPA from a 2.5 mg/L (0.011 mmol/L) solution increased with oleate modification of the magnetite surface up to an optimal point, after which subsequent increase in surface hydrophilicity led to reduced adsorption. The highest adsorption efficiency (77.5 ± 0.8 %) was observed at a specific oleate loading of 0.6 mmol/g (169.5 mg/g). The maximum adsorption capacity (3.59 mg/g) was measured on the oleate-modified surface in the presence of Ca^{2+} ions. Cholate-modified magnetite particles showed improved adsorption efficiency compared to native magnetite; however, unlike the oleate-modified material, no distinct maximum was observed. For a 2.5 mg/L BPA solution, the highest adsorption efficiency with cholate-modified magnetite was 56.4 ± 1.7 % at 0.8 mmol/g (326.9 mg/g) specific cholate loading. Catechol-modified MNPs exhibited a less pronounced increase in adsorption efficiency, with a maximum of 17.9 % at 0.5 mmol/g (55 mg/g) specific catechol loading. Langmuir isotherm-derived equilibrium constants (K_L) and Freundlich isotherm affinity parameters (1/n) indicate low affinity, suggesting weak, physical interactions between BPA and the modified adsorbents. Regeneration of the adsorbent was effective: BPA could be desorbed from oleate-modified magnetite with 98 % efficiency using organic wash. Adsorption performance in drinking water approached that in ultrapure water (~73–76 %), while in surface water it was ~69–70 %. In both water matrices, BPA concentrations were reduced below regulatory limits even for samples initially containing twice the limit (2.5 µg/L for drinking water and 130 µg/L for surface water). Regarding reusability, the adsorbent could maintain regulatory compliance for three cycles in drinking water and two cycles in surface water for twice-limit BPA concentrations.

Summary

The aim of my doctoral research was to develop analytical and adsorption methods suitable for the detection and removal of a wide range of organic micropollutants from environmental samples. UPLC-MS/MS methods were developed and validated for the determination of 77 micropollutants, with an average LOQ of 5 ng/L. Solid-phase extraction procedures were applied for preconcentration, and the optimal enrichment factors were determinde that ensured sufficient sensitivity while minimizing matrix effects. For estrogenic hormones and bisphenols, a well-known chemical derivatization process was applied and optimized, which improved the sensitivity by several orders of magnitude. Four extraction methods (UAE, MAE, FUSE, SOX) were compared for micropollutant extraction from sewage sludge, and FUSE was found the most effective. It provided the highest signal-to-noise ratio and served as a suitable alternative to Soxhlet extraction even for hydrophobic compounds.

Following analytical method development, the second main focus of my research was the removal of micropollutants using magnetically separable adsorbents. Glyphosate adsorption was studied on bare magnetite. The adsorption efficiency was primarily pH-dependent: highest under acidic conditions, while under alkaline conditions the presence of calcium ions enhanced the adsorption. Bare magnetite exhibited >98% removal efficiency, with maximum adsorption capacities of 64 mg/g for glyphosate and 36 mg/g for AMPA at ~pH 6 in the presence of Ca^{2+}. ATR-FTIR analyses confirmed surface complexation as the dominant adsorption mechanism. Glyphosate removal efficiency from natural waters was also 98–99%, though regeneration proved limited. For bisphenol A removal surface-modified magnetites were examined, of which oleate-coated MNPs (O-MNP) showed the best performance. The adsorption efficiency of the modified MNPs followed the order: catechol < cholate < oleate. The highest adsorption capacity of O-MNP was 3.59 mg/g in the presence of $CaCl_2$. BPA adsorption was a weak physisorption in nature, enhanced by the occlusive effect of Ca^{2+} ions. In natural surface and drinking waters, O-MNP effectively reduced BPA concentrations below regulatory limits. Regenerability was favorable, as >99% of BPA could be desorbed using organic solvents; however, the adsorbent maintained its efficiency only for 2–3 adsorption/desorption cycles.

Thesis

1. During my doctoral work high-sensitivity analytical (UPLC-MS/MS) and sample preparation methods were developed and optimized for the environmental analysis of organic micropollutants and for evaluating adsorption experiments targeting glyphosate and BPA. The main findings are summerized as follows:

1.1. The use of 0.1% v/v formic acid as an eluent modifier provides the highest signal intensity with negligible adduct formation, enabling simultaneous analysis of 77 organic micropollutants with an average quantification limit of 5 ng/L.

1.2. The Strata X-CW polymer-based mixed-mode SPE sorbent is suitable for the broad-spectrum extraction of micropollutants with a wide range of pK_a and logP values from various water matrices. For environmental samples, concentration factors up to a maximum of 500-1000 can be reliably applied, as higher values induce pronounced matrix effects.

1.3. The optimal derivatization conditions for estrogen hormones and bisphenols with dansyl chloride are: acetonitrile as the solvent, pH 11, a 15-minute reaction time, and toluene as the extraction solvent, yielding an analytical method that meets EU Watch List thresholds.

1.4. Focused ultrasonic solid-liquid extraction (FUSE) is the most effective method for extracting organic micropollutants from solid samples, offering high efficiency and signal-to-noise ratio. It also serves as a viable alternative to Soxhlet extraction for hydrophobic compounds.

1.5. The optimized gradient program ensures effective separation of BPA from ion-suppressive Na^+ ions, enabling reliable quantification in adsorption samples at electrolyte concentrations up to 100 mmol/L.

2. An adsorption process was developed based on native magnetite nanoparticles for the removal of polar, water-soluble organic micropollutants (glyphosate and AMPA) from aqueous media, including model electrolyte solutions and natural waters. The following key findings were made:

2.1. The adsorption of glyphosate and AMPA onto native magnetite is primarily influenced by the pH of the medium, with acidic conditions favoring adsorption for both compounds. At low micropollutant concentrations, Ca^{2+} ions enhance adsorption not only through dominant surface complexation but also via Ca-bridging under alkaline pH conditions.

2.2. The adsorption efficiency of native magnetite exceeds 98%, with maximum adsorption capacities of 64 mg/g for glyphosate and 36 mg/g for AMPA at pH 6 in the presence of Ca^{2+} ions. The high-affinity monolayer adsorption mechanism involves surface complex formation, confirmed by ATR-FTIR analysis.

2.3. The high removal efficiency of native magnetite nanoparticles for glyphosate was verified in tap and surface waters (98–99%). However, due to poor regenerability, their reuse in water treatment applications is currently not feasible in this form.

3. An adsorption process was developed based on surface-modified/hydrophobized magnetite nanoparticles for the removal of hydrophobic and poorly water-soluble organic micropollutants (bisphenol A, BPA) from aqueous media, including model electrolyte solutions and natural waters. The following key findings were made:

3.1. Adsorption isotherms confirm that the magnetite surface can be controllably hydrophobized using organic molecules with different structures, such as oleate, cholate, and catechol.

3.2. Following surface modification with oleate (0.6 mmol/g), cholate (0.8 mmol/g), and catechol (0.5 mmol/g), the extent of BPA adsorption increases in the following order: catechol (18%), cholate (56%), and oleate (77%).

3.3. The interactions between the modified adsorbents and BPA are weak and physical in nature. The highest adsorption capacity (3.59 mg/g) is reached on the oleate-modified surface in the presence of Ca^{2+} ions. BPA can be desorbed from oleate-modified magnetite with 98% efficiency.

3.4. Using oleate-modified magnetite, BPA concentrations can be reduced below the limit values for tap water (2.5 μg/L) and surface water (130 μg/L); however, reuse of the material in water treatment applications is not feasible in its current form.

Publications related to the topic of the dissertation

Journal articles

Nikoletta Kovács, Gábor Maász, Ildikó Galambos, Renáta Gerencsér-Berta, Judith Mihály, Etelka Tombácz,”Hydrophobic interactions of bisphenol A with organically modified magnetite nanoparticles”, Colloids and Surfaces A : Physicochemical and Engineering Aspects 709 Paper: 136146 , 11 p. (2025)
IF (2025): 5.4 (Q2)

Zita Zrínyi, **Nikoletta Kovács**, Renáta Gerencsér-Berta, Ildikó Galambos, Barbara Kovács, Tamás Kucserka, István Gábor Hatvani, Anna Viktória Vancsik, László Bauer, Lili Szabó, Zoltán Szalai, Gábor Maász, Attila Csaba Kondor,”Wastewater-impacted streams within an agricultural catchment: occurrence, attenuation, and risks of organic micropollutants”, Journal of Hazardous Materials Advances 17 Paper: 100572 , 11 p. (2025)
IF (2025): 7.7 (Q1)

Nikoletta Kovács, Gábor Maász, Ildikó Galambos, Renáta Gerencsér-Berta, Judith Mihály, Etelka Tombácz,”Glyphosate/AMPA adsorption on magnetite under different conditions: The effect of pH and electrolytes”, Journal of Molecular Liquids 393 Paper: 123674 , 9 p. (2024)
IF (2024): 5.2 (Q1)

Oral and poster presentations

Zita Zrínyi, **Nikoletta Kovács**, Renáta Gerencsér-Berta, Gábor Maász, Gábor Németh, Henrietta Hampel, Raul Vazquez, Ildikó Galambos, “Global clean water problem: deteriorating surface water quality in the light of growing human needs- monitoring of emerging contaminants in the River Tomebamba, Ecuador.“ : X. Soós Ernő International Scientific Conference, 2024. Poster presentation, Zalakaros, 2024.10.17-18.

Z. Zrinyi, **N. Kovács**, R. Gerencsér-Berta, I. Galambos, B. Kovács, T. Kucserka, I. Hatvani, A. Vancsik, L. Bauer, L. Szabó, Z. Szalai, G. Maász, and Ac. Kondor, “Organic micropollutants in the lower section of River Mur and its tributaries,” 40th Informal Meeting on Mass Spectrometry, 2024. Poster presentation, Budapest, 2024.05.12-15.

K. Nikoletta, M. Gábor, G.-B. Renáta, G. Ildikó, and T. Etelka, “Hydrophobized magnetite nanoparticles for water remediation: removal of endocrine disrupting bisphenol A,” Water and wastewater treatment in the industry 2023 : IX. Soós Ernő International Scientific Conference, 2023. Oral presentation, Zalakaros, 2023.10.19-20.

K. Nikoletta, M. Gábor, G. Ildikó, G.-B. Renáta, and E. Tombácz, “Removal of endocrine disrupting pesticide glyphosate from water by magnetic nanoparticles,” Water and wastewater treatment in the industry 2022: 8th Soós Ernő International Scientific Conference, 2022. Oral presentation, Zalakaros, 2022.10.13.

K. Nikoletta, M. Gábor, G. Ildikó, G.-B. Renáta, and T. Etelka, “Glyphosate/AMPA adsorption on magnetite: measure the trace amounts and separate simply,” in Chemistry, Physics and Biology of Colloids and Interfaces 2022. Oral presentation, Eger, 2022.06.06-10.

K. Nikoletta, M. Gábor, G. Ildikó, and G.-B. Renáta, “High-sensitivity analytical methods supporting the evaluation of adsorption studies,” Chemistry, Physics and Biology of Colloids and Interfaces 2022. Poster presentation, Eger, 2022.06.06-10.

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