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Ion-exchange molecularly imprinted polymer for the extraction of negatively charged acesulfame from wastewater samples

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ABSTRACT

Acesulfame is a known indicator that is used to identify the introduction of domestic wastewater into water systems. It is negatively charged and highly water-soluble at environmental pH values. In this study, a molecularly imprinted polymer (MIP) was synthesized for negatively charged acesulfame and successfully applied for the selective solid phase extraction (SPE) of acesulfame from influent and effluent wastewater samples. (Vinylbenzyl)trimethylammonium chloride (VBTA) was used as a novel phase transfer reagent, which enhanced the solubility of negatively charged acesulfame in the organic solvent (porogen) and served as a functional monomer in MIP synthesis. Different molecularly imprinted polymers were synthesized to optimize the extraction capability of acesulfame. The different materials were evaluated using equilibrium rebinding experiments, selectivity experiments and scanning electron microscopy (SEM). The most efficient MIP was used in a molecularly imprinted-solid phase extraction (MISPE) protocol to extract acesulfame from wastewater samples. Using high-performance liquid chromatography–tandem mass spectrometry (HPLC–MS–MS) analysis, detection and quantification limits were achieved at 0.12 $\mu g\,L^{-1}$ and 0.35 $\mu g\,L^{-1}$, respectively. Certain cross selectivity for the chemical compounds containing negatively charged sulfonamide functional group was observed during selectivity experiments.

1. Introduction

Acesulfame is an artificial low-calorie sweetener that is consumed in substantial quantities and can be found in various foods and beverages. After undergoing human metabolism, it passes through the system largely unaffected and as a result, is ubiquitously present in aquatic environments [1]. It may also enter soils via irrigation with wastewater-polluted surface water, fertilization with sewage sludge, or through leaky sewers [2]. Due to its large consumption levels and persistency toward molecular transformation in treatment processes, acesulfame has been accepted as an ideal indicator to identify the impact of wastewater on e.g. groundwater [3]. This is particularly the case in urban settings with complex hydrology, where indicator substances can be used to locate pollution sources and to discover aquifer pathways [4,5]. A systematic study has shown that even multi-barrier treatment systems cannot remove acesulfame completely from surface water, thus this compound was the only artificial sweetener detected in fully processed drinking water [4]. In many studies, acesulfame has been reported as a marker which can be used to identify wastewater-related contaminations in surface water [6–8], sewage sludge [9], leachate [10], groundwater samples [8,11–13] and hyporheic and riparian zones [14,15]. In these kinds of studies, a targeted analysis of the marker substance can help facilitate the investigation of complex systems and simplify the associated data processing. In order to determine a specific target compound like acesulfame, a selective separation from accompanying substances is required. A review of existing analytical methods for determining the presence of artificial sweeteners (including acesulfame) in aqueous environmental samples has been previously reported [16]. Liquid chromatography–electrospray ionization tandem mass spectrometry and liquid chromatography–electrospray ionization high-resolution mass spectrometry are the most widely applied methods [16]. Although these methods are commonly used for trace analysis of acesulfame, either directly or after solid-phase extraction, their selectivity is very poor and the retained chemicals can interfere with the detection of the compounds of interest.

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A new class of selective sorbent materials is molecularly imprinted polymers (MIPs) which are based on molecular recognition. MIPs operate as artificial specific receptors that can be used as a powerful tool in the development of highly selective analytical methods [17–20]. MIPs are tailor-made polymers in which template-complementary binding sites are imprinted in the polymer matrix by stabilizing the appropriate functional monomers around the target molecule. Template-functional monomers complex can be formed using three main approaches, including: covalent, semi-covalent or non-covalent interactions. To date, the non-covalent interaction technique (hydrogen bond, ionic or hydrophobic interaction) is the most commonly used approach for the synthesis of MIPs. In non-covalent imprinting processes, the affinity of the binding sites in the resulting synthesized polymer is directly influenced by stable binding interactions during the complex formation between template and functional monomers [21]. The main challenge for this approach is to find an appropriate strategy for the synthesis of an actual valid and proper MIP for water-soluble compounds, such as acesulfame. In order to solve this problem, some methodologies have already been devised. To prepare 2,4,5-trichlorophenoxyacetic acid, bisphenol A, tratarzine and antibiotics/oligopeptides imprinted polymers in water and methanol–water systems, 4-vinylpyridine [22], 3-acrylamido-N,N,N-trimethylpropan-1-aminium chloride (AMTC) [23], 1-(α-methyl acrylate)-3-methylimidazolium bromide (1-MA-3MI-Br) [24] and acryloyl-cyclodextrins [25] were used as functional monomers, respectively. An ionic template-functional monomer complex and a water-soluble crosslinking reagent were used for the synthesis of (4-tributylammoniummethyl)-benzyl tributylammonium chloride (TBTA)-imprinted polymer in water as a porogenic solvent [26]. For preparation of the pyridoxine-imprinted polymer, dodecyl sulfate ion (DS^-) was used to transfer pyridoxine ion (Py^+) from water to chloroform via ion-pair complex formation [27]. Recently, a sol–gel approach was developed for the preparation of molecularly imprinted polymer nanofiber [28] and nanomembrane [29] for non-ionic acesulfame.

In this study, a selective imprinted polymer was synthesized for the negatively charged acesulfame. (Vinylbenzyl)trimethylammonium chloride (VBTA) was used as a phase-transfer catalyst and a functional monomer. After the phase transfer process, methacrylic acid was used as an extra functional monomer to enhance the selectivity of the synthesized polymer. After polymerization evaluations, a solid phase extraction (SPE) protocol was devised, optimized and applied for the selective extraction of acesulfame from different wastewater samples.

2. Materials and methods

2.1. Reagents and apparatus

The chemicals used for polymer synthesis and the extraction experiments were acetic acid, ammonium hydroxide solution (25%) (NH_4OH 25%), methanol and chloroform of GC grade purity provided by MERCK (Darmstadt, Germany). Ethylene glycol dimethacrylate (EGDMA), methacrylic acid (MAA), 2,2′-azobisisobutyronitrile (AIBN), (Vinylbenzyl)trimethylammonium chloride (VBTA), saccharin (CAS No. 81-07-2), bentazon (CAS No. 25057-89-0), ibuprofen sodium salt (CAS No. 31121-93-4), naproxen sodium (CAS No. 26159-34-2), caffeine (CAS No. 58-08-2) and potassium hydroxide (KOH) were obtained from Sigma–Aldrich (Steinheim, Germany). Acesulfame potassium salt (Acesulfame-K) (6-Methyl-3,4-dihydro-1,2,3-oxathiazin-4-on-2,2-dioxid, CAS No. 55589-62-3) with 99% purity level was supplied by Fluka (Seelze, Germany).

A KDS100 syringe pump from KD Scientific (Holliston, USA) was used to generate defined flows through the prepared cartridges. A VL-6LM UV-lamp (6W, 312 nm) was used for the synthesis of the imprinted polymers. 8 mL BAKERBOND SPE glass columns, polytetrafluoroethylene (PTFE) frits and SDB cartridge (200 mg/3 mL) were purchased from J.T. Baker (Deventer, Holland).

2.2. Polymer preparation

2.2.1. Solubility evaluation of acesulfame

Acesulfame is freely soluble in water, while its solubility in chloroform is negligible when used as a porogen (Table S3). Due to the serious drawbacks of polar solvents, non-polar solvents such as chloroform are commonly used for MIP synthesis [27]. In order to increase acesulfame solubility in chloroform, two procedures were tested and evaluated. Both methods are based on ion-pair formation between acesulfame and VBTA. In the first experiment, VBTA was used to enhance the solubility of acesulfame in chloroform. 201 mg (1 mmoL) of acesulfame-K and 211 mg (1 mmoL) of VBTA were weighted together in a glass vial and 10 mL of chloroform was added. The mixture was sonicated for 15 min and subsequently shaken at 300 min^{-1} for 1 h. In comparison, the same procedures were applied to dissolve 201 mg acesulfame-K in 10 mL chloroform.

In the second series of experiments, VBTA was used as a phase transfer reagent to facilitate the extraction of acesulfame from water into chloroform. 201 mg of acesulfame-K and 211 mg of VBTA were weighted together and dissolved in 3 mL water. 10 mL chloroform was added to the prepared mixture and stirred vigorously for 1 h. The two phases were separated and the concentration of acesulfame in chloroform was analyzed. As a comparison, 201 mg of acesulfame-K was dissolved in 3 mL water. The mixture had 10 mL of chloroform added to it, as before, and was also stirred vigorously for 1 h. The two phases were separated in the same way and the concentration of acesulfame in chloroform was analyzed.

In order to evaluate the transfer efficiency of acesulfame into the chloroform phase, the ratio between acesulfame and VBTA was changed in a series of experiments. The amount of acesulfame was kept constant at 1 mmoL and the amount of VBTA was increased from 0.5 to 1 and 1.5 mmoL. For each experiment, the whole extraction process was repeated 3 times (E1, E2 and E3). The concentration of acesulfame in chloroform for each of the extracted fractions was analyzed.

2.2.2. MIP synthesis

In order to evaluate the efficiency of VBTA and MAA as functional monomers, 4 different polymers were prepared. Table 1 outlines the composition of reagents for MIP synthesis using the precipitation method. All polymer mixtures were deaerated with helium for 15 min and photochemically polymerized at 15 °C for 3 h using a UV-lamp at 312 nm. For all of the MIPs mentioned above, the corresponding non-imprinted polymers (NIPs) were prepared in the same way without the target molecule. Following polymerization, the materials were washed with methanol/NH_4OH 25% (80:20, v/v) and the supernatant was separated by centrifugation. Washing processes were checked and verified using a high-performance liquid chromatography–tandem mass spectrometry (HPLC–MS–MS) instrument and were continued until target molecules were no longer detectable. Afterwards, the materials were activated (the reason for activation is explained in Section 3.3) and very fine particles were removed using Soxhlet extraction. The upper edge of an extraction thimble was cut so that it was lower than the siphon-top of the extractor. Methanol/acetic acid (99:1, v/v) was used as the extraction solvent. Finally, the polymer particles were dried under vacuum conditions and stored in a desiccator at room temperature until use.