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Synthesis and application of a molecularly imprinted polymer in the solid-phase extraction of ketoprofen from wastewater

Silindile Senamile Zunngu [a], Lawrence Mzukisi Madikizela [a, *], Luke Chimuka [b], Phumlane Selby Mdluli [a]

[a] Department of Chemistry, Durban University of Technology, P O Box 1334, Durban, 4000, South Africa
[b] Molecular Sciences Institute, School of Chemistry, University of Witwatersrand, Private Bag x3, Johannesburg, 2050, South Africa

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ABSTRACT

Ketoprofen is a nonsteroidal anti-inflammatory drug widely consumed by humans as it possesses analgesic activities. A selective molecularly imprinted polymer (MIP) for ketoprofen was synthesized and applied as a solid-phase extraction sorbent. MIP was synthesized using 2-vinylpyridine, ethylene glycol dimethacrylate, 1,1′-azobis(cyclohexanecarbonitrile), toluene/acetonitrile (9:1, v/v), and ketoprofen as a functional monomer, cross-linker, initiator, porogenic mixture, and template, respectively. The polymerization was performed at 60 °C for 16 h, and thereafter the temperature was increased to 80 °C for 24 h to achieve a solid monolith polymer. Nonimprinted polymer was synthesized in a similar manner with the omission of ketoprofen. Characterization with thermogravimetric analysis and X-ray diffraction showed that the synthesized polymers were thermally stable and amorphous. Solid-phase extraction cartridges packed with MIP were used with high-performance liquid chromatography for quantitative analysis of ketoprofen in wastewater. The analytical method gave detection limits of 0.23, 0.17, and 0.09 μg/L in wastewater influent, effluent, and deionized water, respectively. The recovery for the wastewater influent and effluent spiked with 5 μg/L of ketoprofen was 68%, whereas 114% was obtained for deionized water. The concentrations of ketoprofen in the influent and effluent samples were in the ranges of 22.5–34.0 and 1.14–5.33 μg/L, respectively. Overall, the analytical method for the analysis of ketoprofen in wastewater was rapid, affordable, accurate, precise, sensitive, and selective.

1. Introduction

Ketoprofen, also known as [(*RS*)-2-(3-benzoylphenyl)-propionic acid], is a commonly used pharmaceutical drug which possesses anti-inflammatory and analgesic activities because of its ability to inhibit cyclooxygenase enzymes that promote inflammation [1]. Ketoprofen is widely used in medical care because it is able to treat inflammatory diseases and musculoskeletal injury [2]. Because of the large quantity of ketoprofen consumed by humans, the compound is widely detected with other nonsteroidal anti-inflammatory drugs (NSAIDs) in wastewater and surface water [3–5]. Once consumed, 80% of ketoprofen is eliminated as unchanged drug and its degradation in wastewater treatment plants (WWTPs) depends on the biological treatment efficiency [6]. It has been previously reported that WWTPs are the primary source of pharmaceuticals in river water [5].

To date, many reports have emerged on the occurrence of NSAIDs such as ibuprofen, naproxen, and diclofenac in South African environment [7–13]. However, there are

* Corresponding author.
E-mail address: lawrencem2@dut.ac.za (L.M. Madikizela).

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currently few studies that have reported on the presence of ketoprofen in South African aquatic conditions [11–13]. With the view of preserving the precious resource such as water, there is a need to understand the extent of all widely used pharmaceuticals in the environment. South Africa has a large number of WWTPs that are mainly used for domestic wastewater treatment and their potential for removal of pharmaceuticals such as ketoprofen is not known. There is currently a lack of data on the toxicity of ketoprofen in aquatic life. To understand the risk of aquatic life and water consumers from suffering the health effects caused by pollutant levels, it is necessary to fully evaluate the occurrence of ketoprofen in water resources.

To address this problem, the development of highly sensitive and selective methods for trace determination of compounds such as ketoprofen in complex wastewater matrix is required. One of the most suitable methods of ketoprofen analysis is the use of chromatographic methods that are equipped with a very sensitive mass spectrometry detector [14,15]. However, the operation, maintenance and cost, of mass spectrometry detector is expensive. Therefore, some laboratories had opted for the use of a cheap and readily available UV–visible detector. The sensitivity of UV–visible detector is usually improved by the use of solid-phase extraction (SPE) for cleanup and preconcentration of target compounds [16].

In SPE, the most widely used extraction media for ketoprofen are Strata X, C_{18}, and Oasis hydrophilic lipophilic balanced (HLB) sorbents [17,18]. Although the application of these sorbents leads to the improvement of sensitivity, they often lack selectivity and their single use results in massive generation of solid waste. Nowadays, molecularly imprinted polymers (MIPs) are developed for SPE applications because of their properties that include high selectivity, reusability, mechanical strength, and resistance against acids, bases, and organic solvents [19]. The development and application of MIPs for the selective analysis of single NSAID such as ibuprofen and diclofenac is well documented [20,21]. The use of multitemplate MIPs for ketoprofen and several NSAIDs in wastewater analysis has been explored [22]. MIPs synthesized using the multitemplate approach are usually selective toward a group of compounds. However, these may not be useful in the analysis of a single analyte as it is important to obtain cleaner chromatograms which subsequently lead to more accurate measurements. Currently, there is a lack of available information for the synthesis of MIP that can selectively extract ketoprofen from aqueous samples.

Ketoprofen has been identified as one of the pharmaceutical drugs that contaminate Umgeni River which is found in the northern part of Durban city in South Africa [11,13]. With the exception of the work published by Madikizela et al. [12], there are currently no reports on the occurrence of ketoprofen in the southern region of Durban. Apart from these studies [11–13], there is currently no other South African study that has focused on the analysis of ketoprofen in water resources. Therefore, the aims of this study were to evaluate the occurrence and removal efficiency of ketoprofen in WWTPs located in the southern part of Durban city, South Africa. To achieve these aims, an MIP was synthesized, characterized, and applied in selective SPE of ketoprofen from wastewater before high-performance liquid chromatographic quantification.

2. Experimental section

2.1. Materials

Ketoprofen (≥98%), triclosan (≥97%), 2-vinylpyridine (97%), high-performance liquid chromatography (HPLC) grade methanol (≥99.9%), 1,1′-azobis-(cyclohexanecarbonitrile) (98%), ethylene glycol dimethacrylate (98%), and toluene (99.7%) were purchased from Sigma-Aldrich (Steinheim, Germany). HPLC grade acetonitrile (≥99.9%) and glacial acetic acid (100%) were purchased from Merck (Darmstadt, Germany). Formic acid (approximately 98%), fenoprofen (≥97%), and HPLC grade triethylamine (≥99%) were purchased from Fluka (Steinheim, Germany).

2.2. Synthesis of MIP

Published work was adopted with slight modifications for the synthesis of MIP for ketoprofen [23,24]. Synthesis was carried out by mixing 25 mg of ketoprofen with 54 μL of 2-vinylpyridine. The mixture was stirred at room temperature in a 250 mL round-bottomed flask containing 10 mL of a acetonitrile/toluene (1:9, v/v) porogenic mixture for 30 min. Thereafter, the reaction vessel was placed on ice to prevent unwanted polymerization. Ethylene glycol dimethacrylate (4.77 mL) and 100 mg of 1,1′-azobis-(cyclohexanecarbonitrile) were added. The mixture was purged with nitrogen gas for 10 min, sealed, and stirred in an oil bath at 60 °C for 16 h to initiate polymerization. After 16 h, the temperature was increased to 80 °C and maintained for 24 h to achieve a solid monolith polymer. The polymer was dried to constant mass at 80 °C followed by grinding and sieving. Particles ranging from 25 to 90 μm were collected and washed repeatedly with a mixture of acetic acid/acetonitrile (1:9; v/v) until ketoprofen could not be detected in high-performance liquid chromatographic system. Nonimprinted polymer (NIP) was synthesized and treated likewise with the omission of ketoprofen in the reaction mixture.

2.3. Apparatus

HPLC system consisting of an online mobile phase degasser unit (model DGU-20A5), 20 μL sample loop, pump (model LC-20AT), and UV–visible detector (model SPD-20A) obtained from Shimadzu Corporation (Kyoto, Japan) was used. The mobile phase conditions consisted of a mixture of acetonitrile and 0.2 formic acid in water (60:40, v/v) at a flow rate of 1 mL/min. Separation was performed on a Gemini C_{18} HPLC column of 150 × 4.6 mm × 5 μm obtained from Phenominex (California, USA). Shimadzu liquid chromatography (LC) solutions software was used for data collection and processing. Detector wavelength was set at 255 nm.

For characterization, thermal analysis was performed using thermogravimetric analysis/differential scanning