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Synthesis, adsorption and selectivity studies of a polymer imprinted with naproxen, ibuprofen and diclofenac

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ABSTRACT

In this study, selective removal of acidic pharmaceutical from aqueous media was investigated. The purpose of this work was to use the multi template molecularly imprinted polymer (MIP) for the selective extraction of naproxen, ibuprofen and diclofenac from aqueous samples. A multi template MIP was synthesized using a bulk polymerization method. The performance of the MIP in aqueous solutions was evaluated by optimizing several adsorption parameters. The optimized adsorption conditions were 50 mg of MIP, extraction time of 10 min and a sample pH of 4.6. The imprinting factors obtained for naproxen, ibuprofen and diclofenac were 1.25, 1.42, and 2.01, respectively, which corresponded to the selectivity order of diclofenac > ibuprofen > naproxen. Furthermore, the synthesized MIP showed great selectivity to the target compounds in the presence of gemfibrozil and fenoprofen. The data was modelled best by pseudo 2nd order which implied a chemisorption of pharmaceuticals onto MIP particles. Based on R^2 values, it was determined that the adsorption data fitted Langmuir isotherm which meant that the binding occurred on the homogeneous sites. The recovery in wastewater influent for naproxen, ibuprofen and diclofenac was 38%, 69% and 87%, respectively.

1. Introduction

Naproxen, ibuprofen and diclofenac are acidic pharmaceuticals that belong to the class of non-steroidal anti-inflammatory drugs (NSAIDs) [1]. NSAIDs are analgesics that are used to treat inflammation and fever in humans. NSAIDs can lead to side effects if overdosed [2]. The presence of pharmaceuticals in the environment is a result of direct disposal to aquatic systems and incomplete removal during wastewater treatment. Occurrence of such compounds in the environment have raised serious concerns for the scientific community and general public at large [3]. There are presently no regulatory standards for these pharmaceuticals although they are considered to have potential for adverse human and environmental effects with increased risk potential on exposure [3].

Wastewater treatment plants (WWTPs) receive high concentration of pharmaceuticals through human urinary, fecal excretion and from pharmaceutical manufacturing effluents [4]. WWTPs have been reported to be the major source of pharmaceuticals in the aquatic environment [5–8]. NSAIDs as shown in Table 1 are polar compounds that are soluble in water [9–12], therefore they escape the wastewater treatment process easily. Recently, more work on the determination of NSAIDs in aqueous systems have been reported [13–15]. NSAIDs have been detected globally in wastewater [13], surface water [14] and drinking water [15].

Quantification of NSAIDs is usually carried out with chromatographic techniques after their extraction from aqueous matrices with a suitable sample preparation method. Gas chromatographic analysis employs derivatization procedures for the conversion of NSAIDs into volatile forms [16]. Compounds selected in this study are not volatile, therefore they are best separated in a high performance liquid chromatographic column prior to their detection. Solid-phase extraction (SPE) and solid phase micro-extraction (SPME) are the established techniques that are widely used as sample clean-up steps prior to chromatographic separation [12–15]. Both techniques are based on adsorption of compounds onto packing materials. The adsorbents used in both SPE and SPME techniques provide limited selectivity towards target compound(s). Selectivity is improved in SPE when molecularly imprinted polymer (MIP) is employed as the adsorbent [17].

MIP is a stable synthetic polymer that contains highly specific sites having an affinity for a target molecule [17]. Over the years,

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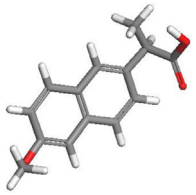
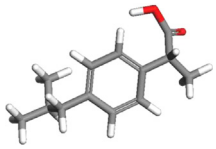
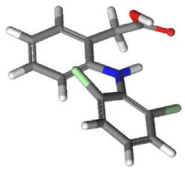
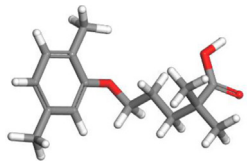
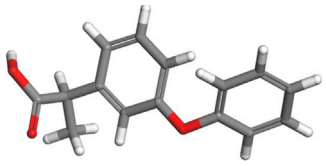
Table 1
Chemical structures and physicochemical properties of acidic pharmaceuticals [9–12].

Compound	Chemical Structure	Water Solubility ($mg\,L^{-1}$)	pK_a	Log K_{ow}
Naproxen		44	4.2	3.10
Ibuprofen		58	4.9	3.71
Diclofenac		10	4.2	4.02
Gemfibrozil		8.4	4.7	4.51
Fenoprofen		30	4.5	4.05

Hydrogen, carbon, oxygen, chlorine and nitrogen atoms are represented by white, grey, red, green and blue, respectively.

MIPs have been synthesized in the presence of one target molecule [18–20]. Different classes of pharmaceuticals are being detected in the environmental samples, hence MIPs are being designed for the removal or isolation and pre-concentration of such pollutants. Recent work in this aspect involves the development of MIPs for selective removal of antiviral and antidiabetic drugs in aqueous media [21,22]. Recent work also demonstrate the potential for MIPs in the removal of specific group of pharmaceuticals [21–23]. MIPs are useful adsorbents for acidic pharmaceuticals in water, hence their characterization such as thermal stability is highly required for their correct utilization. The removal of acidic pharmaceuticals from lake water using multi-template MIPs have been reported [23], however, the performance of such polymers in more complicated sample matrix such as wastewater influent and effluent have not been fully evaluated. This is important because although MIPs are selective to particular functional groups, they are not specific to certain molecule(s). The backbone polymer of molecularly imprinted sorbent can adsorb some compounds based on functional groups present especially for aqueous samples. Selective elution in this case is performed.

Owing to the recent studies that have reported the occurrence of pharmaceuticals in South African water bodies that includes wastewater and river water [3,6], there is a strong need to develop and evaluate the performance of selective adsorbents for accurate analysis using HPLC systems with simple detectors such as UV–vis. Besides the gain in selectivity for these materials, they can also be re-used. Smart adsorbents such as MIPs have been well developed and applied in the removal of pharmaceutical pollutants from water resources of well developed countries [17,20–23], however there are no reports on the selective removal of pharmaceuticals from South African aqueous matrix. Therefore, the aim of this work was to give a detailed report on the evaluation of the adsorption, selective washing and elution of naproxen, ibuprofen and diclofenac by MIP sorbent that was synthesized using a multi-template approach from wastewater.

2. Experimental

2.1. Chemicals

Naproxen (98%), ibuprofen (≥98%), diclofenac sodium salt, 2-vinylpyridine (97%), 1,1′-azobis-(cyclohexanecarbonitrile) (98%), ethylene glycol dimethacrylate (98%), HPLC grade methanol (≥99.9%) and toluene (99.7%) were purchased from Sigma-Aldrich