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Development of functionalized nanostructured polymeric membranes for water purification

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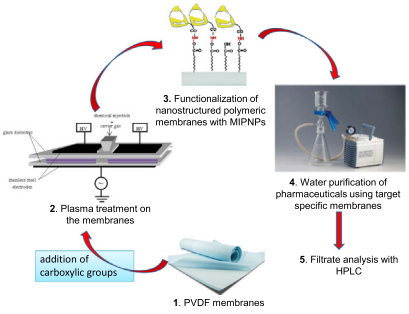
HIGHLIGHTS

- Target specific molecularly imprinted polymers nanoparticles (MIPNPs) were synthesized.
- MIPNPs were successfully incorporated into PVDF membrane and visualized with SEM.
- Capacity analyses of molecularly imprinted membranes (MIMs) were performed by HPLC.
- Nanostructured polymeric membrane is capable to capture targets from water.
- A pilot test was conducted indicating high potential of water purification using MIMs.

GRAPHICAL ABSTRACT



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ABSTRACT

Pharmaceuticals specific molecularly imprinted polymers nanoparticles (MIPNPs) were synthesized and applied onto the polyvinylidene fluoride (PVDF) membranes previously subjected to the plasma treatment. Diclofenac-, metoprolol- and vancomycin-MIPs were applied onto the membranes and scanning electron microscopy was employed to visualize MIPNPs on the membrane. After functionalization of the membranes with target-specific MIPs the molecularly imprinted membranes (MIMs) affinity against their targets was evaluated using solid phase extraction (SPE) technique coupled with high performance liquid chromatography (HPLC). MIMs were used as filters to load the target solutions through employing a vacuum pump to evaluate the amount of pharmaceuticals in filtrate. Moreover, a comparative study was performed by comparing the efficiency of MIMs functionalized either by adsorption or covalent immobilization. The capacity analysis of MIPNPs by SPE–HPLC revealed 100%, 96.3%, and 50.1% uptake of loaded solution of metoprolol, diclofenac and vancomycin, respectively. MIMs showed 99.6% uptake with a capacity of 60.39 ng cm^2 for metoprolol; 94.7% uptake with a capacity of 45.09 ng cm^2 for diclofenac; and 42.6% uptake with a capacity of 16.9 ng cm^2 for vancomycin. HPLC detection limits of targets were found as 3.7, 7.5 and 15 ng mL^{-1} for diclofenac, metoprolol and vancomycin respectively. A small scale pilot test was also conducted which indicates the promising future applications of the developed MIMs for high volume of filtrates especially in the case of the plasma-treated PVDF membranes prepared by covalent immobilization of the MIPs.

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1. Introduction

Pharmaceuticals are active compounds with biological effects and they are used in many applications for human and veterinary medicine. However, part of the administered dose is excreted as the active substance and/or as metabolite, essentially through the organisms' urine system and the biliary system leading to a release of drugs in the environment [1–3]. This problem has been recognized in the US in the 1970 s, and around ten years later in England. To date, the continuous advances in analytical techniques have raised concern about the levels of these compounds in wastewater. Sewage treatment is not efficient enough to eliminate most of these compounds which remain in the effluents and then get into the surface and groundwater. So far antibiotics, beta-blockers, antiphlogistics, vasodilators, antiepileptics, sympathomimetic, lipid regulators and anti-epileptics have been found in manure, sewage, wastewater, groundwater and drinking water [4,5].

Concentrations up to mg L^{-1} have been detected in effluents for single substances in Asian countries [6]. Pharmacodynamic and pharmacokinetic studies are largely carried out during the drug development process and environmental risk is also assessed. However, a risk assessment needs to be developed as well as assessment procedures within a case-by-case approach [6–7]. With the presence of trace level of pharmaceutical in drinking water supplies, the issue has become a public health concern. Further studies pointed out the adverse effects including endocrine disruption, genotoxicity, resistance in pathogenic bacteria and aquatic toxicity, nevertheless chronic health effects are not well known yet [8]. Constant development of analytical techniques is continuously improving pharmaceuticals detection in the aquatic environment and nowadays detections of residues at the amount of nanogram per liter are possible [9]. One of the main causes for the dispersion of pharmaceuticals after human treatment is the lack of efficiency of sewage treatment plants (STPs) in their mineralization, with evidences of the occurrence of more than 160 different pharmaceuticals in STP effluent, groundwater and surface water [6,10]. In wastewater treatment, two elimination procedures are important, biodegradation which occurs in the aerobic treatment and adsorption to suspended solids. If not removed in the waste water treatment plants (WWTPs), the drugs will spread into the ecosystem. Most WWTPs employ activated sludge operation in which microorganisms are used to mineralize the compounds to carbon dioxide and water, or reduce the pollutant to an acceptable structure. Another way to remove the substances is by stripping into air or by sorption onto sludge. Moreover, some residues may be subject to phototransformation. To summarize, the five mechanisms to remove pharmaceutical substances include phototransformation, sorption, air stripping, uptake by plants and biotransformation [9,11].

Since many years, researchers have been trying to develop membranes to detect or extract pharmaceuticals from water. Membrane filtration has been exploited to optimize the removal of pollutants such as pesticides and pharmaceuticals. In wastewaters treatment plants, membrane bioreactor (MBR) appears to be an interesting advanced technology. In fact, MBR encompasses organic matter degradation with membrane filtration more efficient than the conventional activated sludge (CAS) process with 56% elimination of diclofenac residues for MBR versus 26% for the CAS. MBR can be equipped with hollow-fiber ultrafiltration membranes, microfiltration-membrane or flat-sheet membrane [12]. Others studies characterized the removal of uncharged trace organics by nanofiltration (NF) membranes due to steric hindrance, whereas polar trace organics removal was influenced by electrostatic interaction with the charged membrane. Several studies compared the removal of pharmaceuticals with different kind of membrane systems. Reverse osmosis (RO) membranes with a molecular weight cut-off inferior to 200 Daltons provided a good removal with more than 90% removal of the tested compounds; largely more efficient than NF membranes. These significant results suggest that MBR–RO would provide efficient removal of the tested micropollutants [13].

Martínez and colleagues coupled membrane separation and photocatalytic oxidation processes for the degradation of pharmaceuticals [14]. They explored nanofiltration and reverse osmosis method and concluded that nanofiltration exhibits better conditions, in terms of power operation and time saving. They also suggested that the combination of photocatalytic oxidation with membrane separation would be a feasible alternative for pharmaceutical removal for wastewaters [14]. However, the occurrence of pharmaceuticals in environment and drinking water are still high in both developed and undeveloped countries. This emphasizes the lack of efficiency of WWTP and explains the large number of studies focusing on membrane development. Nanomaterials such as graphene and carbon nanotubes have also been used to develop efficient filtration systems for water purification due to their superior characteristics [15–19].

With the lack of efficiency of pharmaceuticals removal in water, researchers focused on improving the selectivity of membranes for toxins and drugs [20–22]. Therefore, the incorporation of selective ligands to the PVDF membrane for the selective removal of pharmaceuticals has been investigated in this work for the first time. Three commonly used drugs including diclofenac as a pain killer, metoprolol as a β-blocker and vancomycin as an antibiotic were selected. Molecular imprints of these molecules were created in the form of nanoparticles using a novel solid phase synthesis method [23–25]. After obtaining MIPs nanoparticles (MIPNPs) with high quality and uniform size, the capacity analysis was conducted by employing solid phase extraction (SPE) technique coupled with HPLC. The PVDF membranes were processed with plasma treatment for surface modification to add functional groups to the membranes prior to incorporating high capacity and affinity MIPs both by adsorption and covalent immobilization. The results provide a new and promising technology for the purification of water sources from pharmaceutical products by using nanostructured molecularly imprinted membranes (MIM). Scheme 1 illustrates the entire work with major steps.

2. Experimental section

2.1. Reagents and chemicals

Metoprolol, diclofenac, vancomycin hydrochloride, ethanol, 60 mL SPE tubes and 20 μm pore frits, acetonitrile (ACN), acrylic acid and sodium dihydrogen phosphate monohydrate were all obtained from Sigma–Aldrich (Poole, UK). 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and N-hydroxysuccinimide (NHS) were obtained from Fisher Scientific (Loughborough, UK). Glass beads (Spheriglass® 2429, 53 μm < diameter < 106 μm) were from Blagden Chemicals (UK). Nitrogen gas was obtained from BOC gases (Manchester, UK). All chemicals and solvents were analytical or HPLC grade with more than 95% purity and were used without further purification.

2.2. Apparatus and equipment

A Sartorius (Göttingen, Germany) analytical balance was used to weigh compounds and membranes. For MIPs and buffers productions a KNF LABOPORT® (KNF Neuberger, Inc., USA) pump