"Extractability of Drug Traces and Metabolites from Water Media by Polyurethane Foam and Block Copolymer Membranes"

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Recent studies indicate the ubiquitous and widespread occurrence of low-level concentrations of pharmaceuticals in the aquatic environment, the active drugs and their metabolites as well. It is an urgent need to improve the techniques of water purification and to employ analytical methods in order to monitor the input of drugs and their metabolites into the aquatic environment. The analytical technique usually used is HPLC, which still affords an efficient sample pretreatment.

The aim of this study was to investigate the applicability of certain types of open cell solid membranes to extract efficiently selected drugs of environmental concern from water such as sulfamethoxazole (SFM), carbamazepine (CBZ), diclofenac (DCF), ibuprofen (IBU), tetracycline (TC), and chlortetracycline (CTC). The metabolites investigated in this study were iso-chlortetracycline (iso-CTC) and N-4-acetylsulfamethoxazole (ASFM). The latter compound was synthesized and its structure confirmed by common spectroscopic methods.

Polyurethane foams (PUF) and novel block copolymer membranes (BM) were used to carry out membrane-batch experiments. Polyether-based PUF- membranes (type a, b and c) with different pores sizes (100, 50 and 10 µm) were tested and type d, a polyester-based PUF (10 µm). In case of the extractability of metabolite ASFM the following order was found: a (48%) > b (34%) ≥ c (33%). Obviously, membrane a with the largest pores has the highest extraction efficiency. For comparison, 30% of ASFM were extracted by PUF-polyester type d. It is assumed, that the PUF-polyether extracts comparatively more strongly than PUF-polyester due to easier formation of hydrogen bonds with the amino groups in ASFM molecules.

The drug permeability through the membranes strongly depends on the composition of the aqueous medium: e.g. the ability of sorption of CBZ, SFM and ASFM generally increased in the order:

pH3 > pH 9 >> pH 7. Between 73 % (CBZ) and 80% (ASFM) were extracted at pH 3. Under these conditions the extraction yields for tetracyclines were about 60%. In 0.1M NaCl the results increased up to 94% CBZ and 98% for SFM and ASFM. The effect of individual cations on the sorption of drugs increased in the following order: $Na^+ \approx NH_4^+ > K^+ > Mg^{2+}$. By use of acetone 52-60% of the loaded drug amounts can be eluted and even to a lesser extent by acetonitrile.

Novel types of open cell block copolymer membranes (BM) efficiently separate certain drugs from aqueous solutions (1mg/L), as demonstrated by membrane BM42 (43% SFM, 44% CBZ) and BM43 (89% DCF, 93% IBU) and in particular in the case of TC (98%). BM32 and BM34 extract also CTC and iso-CTC to some extent (~60%). In acidic solution (pH 3) the extractability is remarkably increased: After 4 hours BM43 separates 99% of TC, 73% of TC, 50% of iso-CTC, 62% of SFM, 70% of CBZ and 97% of IBU. BM34 also shows a sufficient behaviour, since the extraction percentage for TC and IBU exceed 97%. Recovery studies with drug loaded polymer cubes reveal, that acetone eluates 100% of IBU, 81 % of TC, 69% of CBZ and 32% of SFM from BM34. Acetonitrile recoveres TC completely and the other drugs in the range of 60%. A quantitative recovery of TC and IBU was achieved by means of BM43 and acetone, whereas SFM and CBZ were eluted to a less extent (~ 60%). Acetonitrile acts less efficient, as only 34% of SFM and 86% of TC could be recovered.

The different types of polymeric membranes, polyurethane foams and the novel block-copolymers investigated in this work reveal different profiles of extraction and elution behaviour. Due to their distinct selectivity towards various classes of active drugs and metabolites, they offer some potential for certain applications in the fields of water treatment and analytical chemistry.