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Rozprawa doktorska

Ultrafiltracyjne membrany polimerowe modyfikowane nanomateriałami w usuwaniu ze strumieni wodnych wybranych mikrozanieczyszczeń organicznych

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Abstract

In this dissertation, an attempt was made to determine the possibility of effective removal of selected substances belonging to the three basic groups of micropollutants: bisphenol A (xenoestrogen), caffeine (pharmaceutical), carbamazepine (pharmaceutical) and α-endosulfan (pesticide). Ultrafiltration based on polymer membranes comprising carbon nanotubes embedded in polymer matrix or membrane surface. Until now, high-pressure processes such as nanofiltration (NF) or reverse osmosis (RO) were necessary to remove micropollutants. In this research, a preparation method of ultrafiltration membranes capable of removing micropollutants from aqueous solutions was developed.

Firstly, two types of modified ultrafiltration membranes were prepared, such as integral asymmetric membranes and thin film composite/nanocomposite membranes. To ensure the most effective transport and retention results, it was necessary to select appropriate polyethersulfone and modifier concentration in casting solution. Integral asymmetric membranes were prepared by phase inversion method. For thin film composite (TFC) membrane, interfacial polymerization in situ method was used. Preparation of TFC membranes was innovative due to the fact, that thin polymer layer was synthesised on surface of ultrafiltration membrane. Due to this process membrane properties were changed. It should be emphasized that in the experiments conducted so far in Poland and around the world, the supports used were mostly high-pressure polymer membranes (NF and RO).

Moreover, both types of membranes were modified by carbon nanotubes – single-walled carbon nanotubes functionalized by carboxyl groups (SWCNT-COOH) and high-purity large surface area single-walled carbon nanotubes (HPLSA-SWCNT). Modification by SWCNT-COOH increased membrane hydrophilicity. On the other hand, modification by HPLSA-SWCNT increased total surface area of membrane and therefore membrane sorption capacity.

The most beneficial membranes was: integral asymmetric PES 15 HP 0.02 and thin film nanocomposite (TFN) PES 12 TFN 0.02, both modified by high-purity large surface area single-walled carbon nanotubes. These membranes were characterized by high permeate fluxes: for asymmetric membrane was 47.16 $dm^3/m^2 \cdot h$, for TFN membrane was 38.28 $dm^3/m^2 \cdot h$. Micropollutants removal degree were between 24.7% and 100%, and could be arranged in the following order: END > BPA > CBZ > CAF.

Prepared polymer membranes were characterized by their structure and surface properties (contact angle and zeta potential) as well as intensity of fouling phenomenon.

Obtained results led to determination of irreversible and reversible membrane fouling values. Modification by carbon nanotubes was beneficial for antifouling properties of membranes. Unmodified membranes had higher resistance values than the membranes with the modifier.

Finally, membranes with the most beneficial transport and separation properties were regenerated. The most effective method of regeneration for integral asymmetric membrane was regeneration by ultrasounds. As a result, it was possible to obtain 50% larger permeate flux and 10% higher removal degree in comparison to unregenerated membrane. For TFN membrane the most effective method of regeneration was soaking in the mixture of ozone and deionised water. Permeate flux was restored in 81% and removal of caffeine and bisphenol A was 4% higher in comparison to results achieved by unregenerated membrane.