Abstract

Recently, the level of pollution of water sources by various micropollutants has been increasing, of which substances considered to be endocrine disruptors have become of particular interest. Endocrine disrupting compounds such as some pesticides, surfactants, plasticizers and natural/synthetic estrogens or benzophenones (UV-filters) are widely distributed in the environment, food, consumer products and pharmaceuticals. Endocrine dysfunction associated with exposure to these substances includes effects on biosynthesis, metabolism and/or hormone action with consequent disruption of homeostasis and reproductive processes. Primarily natural estrogens, estrone, estradiol and estriol, or synthetic estrogens, e.g. ethinylestradiol, which are widely excreted by humans and animals and/or used in hormonal and contraceptive products. Another group of hazardous substances are benzophenones (widely used as UV filters in sunscreens and other cosmetic products), which are of particular concern due to their genotoxicity, neurotoxicity, and potential to act as endocrine disruptors. Both of these groups have a high estrogenic potency on a variety of organisms (i.e. they are physiologically active at very low concentrations in the order of picograms to nanograms per litre) and due to their lipophilic nature have the ability to bioaccumulate in their tissues, this is a risk primarily for aquatic communities where there is a continuous exposure to these substances. Pollution of water sources and surfaces is caused by intensive human activities (e.g. crop, livestock and industrial production) and by the lack of elimination of these substances in the wastewater treatment system, where even advanced wastewater treatment processes achieve 90-99 % efficiency. Hydrophobic eutectic solvents may be one option to improve the elimination of endocrine disruptors from water sources. These are unique liquids that are most often formed by mixing two or more solids to lower the melting point and form a liquid. To test the feasibility of using hydrophobic eutectic solvents for the extraction of selected estrogens and benzophenones from various water samples, a series of these solvents based on organic compounds, specifically terpenes in combination with aliphatic carboxylic acids, were prepared. The extraction efficiency of the different eutectic solvents was studied in terms of their composition, molar ratio of the starting materials used, extraction time and rate, and the possibility of their reuse after several extraction cycles. The extraction efficiency of each eutectic solvent was expressed as the loss of a known amount of pollutants in the aqueous sample. Determination of the residual concentration of pollutants in aqueous samples after purification with eutectic solvents was performed by liquid chromatography with tandem mass detection. For both tested groups of endocrine disruptors (estrogens and benzophenones), the

eutectic solvent based on menthol and octanoic acid (in a molar ratio of 1:1) showed the highest extraction efficiency and under the optimal setting of experimental parameters directly affecting the extraction efficiency (shaking frequency, shaking time, reuse). For laboratory-prepared water samples, the extraction efficiency was at least 99.6 % and for real surface water samples the extraction efficiency was more than 94.1 % for the least polar analyte. The extraction efficiencies of the individual eutectic solvents were compared with reference organic solvents with at least the same but in most cases better results. Since the eutectic solvents are non-toxic, biodegradable, they are good candidates for implementation in wastewater treatment processes.