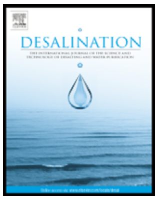
Desalination 249 (2009) 398–402

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal



Freeze concentration for removal of pharmaceutically active compounds in water

W. Gao *, Y. Shao

Department of Civil Engineering, Lakehead University, 955 Oliver Road, Thunder Bay, ON, Canada P7B 5E1

ARTICLE INFO

Article history:
Accepted 13 December 2008
Available online 4 October 2009

Keywords:
Pharmaceutically active compounds (PhACs)
Progressive freeze concentration
Municipal wastewater treatment
Impurity rejection

ABSTRACT

A progressive freeze concentration process, unidirectional downward freezing (UDF), was investigated for removal of five commonly used pharmaceuticals (ibuprofen, gemfibrozil, acetylsalicylic acid, metoprolol and sulfamethoxazole) in water. The feed water with the pharmaceutically active compounds (PhACs) at concentrations from ng/L to mg/L range was frozen at −7 and −15 °C. The separation efficiency of PhACs in the single stage and two-stage UDF was examined. By freezing only 80% (volume) of the feed water and without washing of the ice, about 84–92% reduction of the drug content in ice was achieved in the single stage UDF and about 99% reduction in the two-stage UDF. The partitioning behavior of the PhACs in the ice and liquid phases seems different from the solutes in glucose solutions or liquid foods reported in the literature. A strong linear relationship between the PhACs concentration and their TOC concentration was established, suggesting that TOC, a parameter commonly used to measure WWTP effluent quality might be used to monitor the level of PhACs in WWTP effluent.

1. Introduction

Numerous studies have been conducted recently to investigate the occurrence, transport, and the fate of pharmaceutically active compounds (PhACs) in the environment. Municipal wastewater treatment plant (WWTP) effluent has been identified as the main source for releasing PhACs into the aquatic environment as conventional treatment systems cannot effectively eliminate PhACs from the effluent [1–4]. Meanwhile, the amount of PhACs discharged is expected to increase, including a wide variety of new drugs with unknown fates and effects on the environment produced each year, due to the rapid development of the pharmaceutical industry and the general aging population [5] As treatment plants are faced with the challenge to remove PhACs from effluent streams in anticipation of stricter regulations, the demand for the development of efficient systems for removing these compounds from water has thus assumed [6]. Research of advanced treatment technologies such as membrane filtration, membrane bioreactor, advanced oxidation processes, UV irradiation, photocatalysis, etc. for PhACs removal has been undertaken [6–10], however, numerous uncertainties and knowledge gaps persist [11].

Freeze concentration is a physical process and it involves the fractional crystallization of water and subsequent removal of ice. The process was effective to remove various contaminants from industrial wastewater/liquid waste [12–14]. When freeze concentration is used to purify water or liquid waste, impurities are separated from water during the formation of ice crystals. The theories of impurity separation by freeze concentration have been discussed by various researchers [15–17]. The current paper presents the first study of using a progressive freeze concentration process, unidirectional downward freezing (UDF), to remove PhACs in water. Laboratory experiments were carried out to investigate: the efficacy of the single and two-stage UDF for separation of the selected pharmaceuticals (individual or mixed) in water, and the effect of initial impurity (drug) concentration and freezing temperature on the removal efficiency. The behavior of the selected PhACs during freezing was also discussed. Furthermore, considering that the hundred or even thousand different PhACs and their metabolites may present in municipal wastewater, it is impractical, if not possible, for WWTPs to monitor all of the PhACs during routine operations. For organic contaminants, the effluent quality is usually measured using gross parameters such as BOD, COD and TOC. Effluent quality control in terms of the organic contaminants is thus accomplished by controlling the concentrations of TOC, BOD, and/or COD causing materials. In order to evaluate the capacity of the UDF process for general PhAC removal and provide information that may be useful for treatment plants in effluent PhAC control, feed water with high concentrations of individual or mixed pharmaceuticals was tested in this study and the association of the concentration of the selected PhACs with TOC concentration was examined.

2. Materials and methods

2.1. Materials

Five commonly used prescription and nonprescription drugs were selected for this study: ibuprofen, gemfibrozil, acetylsalicylic acid,

---

* Corresponding author. Tel.: +1 807 3438538; fax: +1 807 3438928.
E-mail address: wagao@lakeheadu.ca (W. Gao).

0011-9164/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.desal.2008.12.065

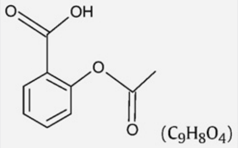
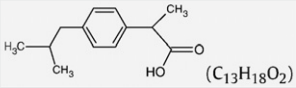
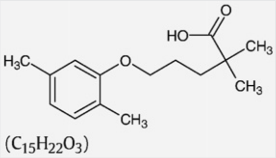
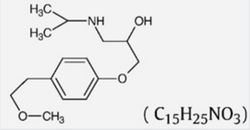
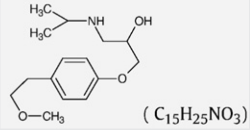
metoprolol and sulfamethoxazole. Ibuprofen, gemfibrozil, and acetylsalicylic acid are acid drugs while metoprolol is a beta blocker, and sulfamethoxazole, an antibiotic. The chemical standards of all pharmaceuticals were of high-purity grade (>95%) and purchased from Sigma-Aldrich (Mississauga, ON). Table 1 shows the chemical structures of the selected PhACs. For sample derivatization for GC-MS analysis, the silylating agent, N,O-*bis*(trimethylsilyl) trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS), in 0.1-mL ampoules and a solvent, *iso*-octane were used and they were also obtained from Sigma-Aldrich (Mississauga, ON).

Stock solutions and calibration solutions were prepared in acetonitrile for individual drugs and in acetone for the mixture of the five drugs. The feed water for the freeze concentration test was obtained by diluting the stock solutions with distilled water. The feed water with different initial drug concentrations was used to examine the effect of the impurity concentration on freeze concentration efficiency.

2.2. Sample analysis

Sample pH and conductivity were measured using a Thermo Orion Model 710A+ pH meter and a Thermo Orion 162A conductivity meter, respectively. GC-MS was used to determine ibuprofen and gemfibrozil concentrations when the drug concentration of the initial feed water was <100 ng/L. The GC-MS included a CP 3800 gas chromatograph equipped with a VARIAN CP-8400 automatic liquid sampler and a VARIAN 1200 mass selective detector (Varian, Mississauga, ON). The sample preparation (extraction and derivatization) procedures and GC-MS analytical method developed by Lee et al. [18] for the acidic drug measurement was followed. Oasis® HLB cartridges (6-mL, 200-mg, Waters, U.S.) were used for the solid phase extraction of the samples. Both calibration (external) standards and an internal standard (2,3-ichlorophenoxyacetic acid, 2– 3 D) were used during GC-MS analysis. The characteristic ions chosen for ibuprofen are 263 and 278, and 201, 194, 322 for gemfibrozil. For the feed water with initial drug concentration >100 µg/L, sample TOC concentration was measured. A Thermo Electron TOC analyzer was used for TOC determination. *Standard Methods* [19] were followed for sample pH, conductivity and TOC analysis.

Table 1
Pharmaceuticals used in this study.

Pharmaceuticals	Chemical structure	Application/ Class
Acetylsalicylic acid (A.S.A.)		Analgesic
Ibuprofen (IBP)		Anti-inflammatory
Gemfibrozil (GFB)		Lipid regulator
Metoprolol		Beta blocker
Sulfamethoxazole		Antibiotic

2.3. Freezing experiment

A unidirectional downward freezing (UDF) method was used for separation of the PhACs from the water. The UDF was used because of its similarity with the natural freezing occurring in a storage pond during winter and might be modified as a natural freezing method for treatment of municipal wastewater containing PhACs and other contaminants in the regions where natural freezing is available. The ice produced from the UDF process was therefore not washed. Fig. 1 is the schematic of the freezing tests and the samples collected for GC-MS or TOC analysis. Blank (distilled water) samples were used during the experiment to monitor the possible contamination. The feed water with various initial drug concentrations was placed in 1000-mL beakers and frozen in an environmentally controlled test room (a walk-in freezer) (Climatic Testing Systems Incorporated, Warminster, PA, USA) at −7 °C and −15 °C. The temperature fluctuation of the freezer was at ±0.5 °C. Samples were precooled to near 0 °C before the freezing test. The beakers were insulated and freezing took place from top to bottom. After the samples were placed in the freezer, the freezing proceeded progressively until approximately 80% of the original volume was frozen; the unfrozen liquid was then separated from the ice. The ice was melted at room temperature. The samples were stirred with magnetic bars during the freezing by placing the beakers on magnetic stirrers.

Single and two-stage freezing were carried out. For the feed water with low initial concentration of ibuprofen or gemfibrozil (<100 ng/L), the unfrozen liquid (the concentrate) collected from the first stage freezing was used as the feed water for the second stage freezing. GC-MS was used to measure the drug concentration in the feed water and the unfrozen liquid samples. Ice samples were collected but were not analyzed considering the much lower ibuprofen and gemfibrozil content in the ice, the complex procedures associated with sample preparation and the cost. For the feed water with higher initial drug concentrations,

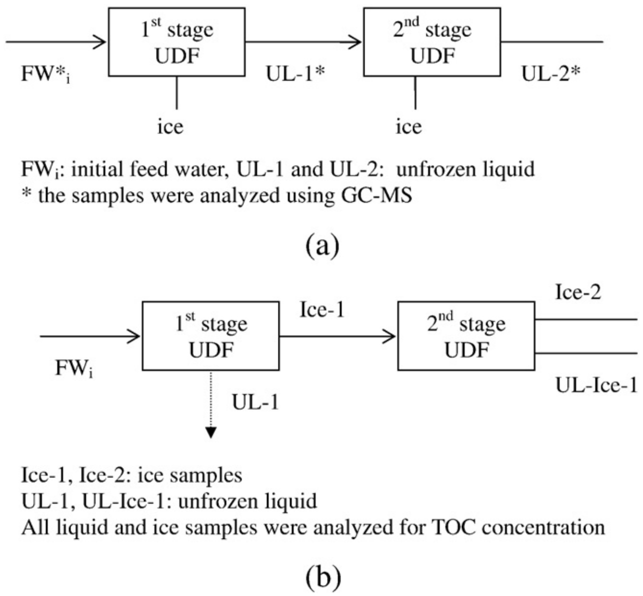


Fig. 1. The schematic of the freeze concentration tests.