Science of the Total Environment 574 (2017) 583–593

Contents lists available at ScienceDirect

Science of the Total Environment

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

The fate of selected pharmaceuticals in solar stills: Transfer, thermal degradation or photolysis?

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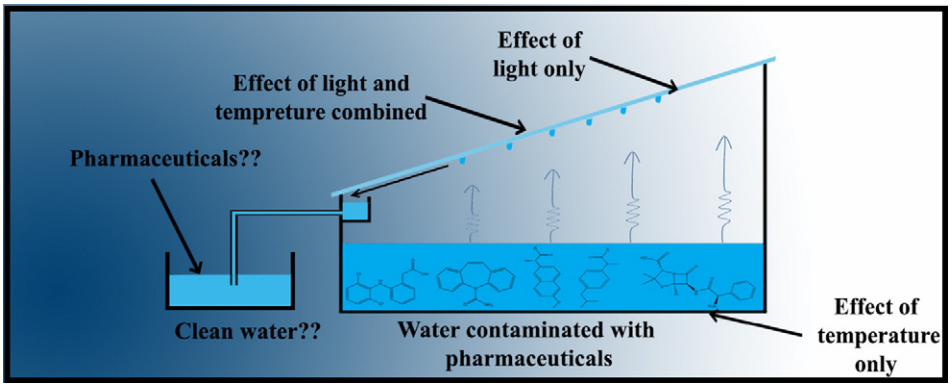
HIGHLIGHTS

- Solar stills are highly effective in removing several pharmaceuticals.
- Single pharmaceutical (Ibuprofen) transferred into the distillate and transfer percentage was very low.
- Naproxen, Ibuprofen and Carbamazepine require the effect of light and temperature combined to degrade significantly.
- Concentrated solar power showed promising results in the degradation of several pharmaceuticals.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 July 2016
Received in revised form 9 September 2016
Accepted 10 September 2016
Available online 14 October 2016

Editor: Jay Gan

Keywords:
Water contamination
Desalination
Pharmaceuticals
Photolysis
Solar degradation

ABSTRACT

The increase in demand for, and disposal of, pharmaceuticals, positively correlated with the growing human population, has led to the emergence of contaminants with high environmental and health impacts. Several developing countries that endure problems related to water sufficiency and/or quality resort to the use solar stills as an affordable water treatment method. This research is aimed at investigating the fate of five chemically distinct pharmaceuticals that might pervade solar stills; ibuprofen (IBU), diclofenac (DCF), carbamazepine (CBZ), ampicillin (AMP) and naproxen (NPX). The experiments were conducted under three conditions. The first condition studied the combined effect of temperature and light in simulated field-test-scale solar stills. The effect of temperature as a sole variable was investigated in the second while the third condition studied the effect of light only via concentrated solar power (CSP). Results show that distillates from solar stills did not contain the parent compounds for four out of the five pharmaceuticals. IBU was the only pharmaceutical that showed a transfer via vapor into the distillate with the highest recorded transfer percentage of 2.1% at 50 °C when subjected to temperature alone and 0.6% under the combined effect of temperature and light. In the case of NPX and DCF, the parent compounds did not undergo transfer into the distillate phase; however their degradation by-products did. In addition, the results also showed that in the case of NPX, IBU and CBZ both high temperatures and sunlight combined were required to attain noticeable degradation. CSP accelerated the degradation of DCF, NPX and IBU with a three-minutes-degradation percentage of 44%, 13% and 2% respectively.

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http://dx.doi.org/10.1016/j.scitotenv.2016.09.082
0048-9697/

1. Introduction

Fresh water resources are becoming increasingly critical in several regions around the world (Oelkers et al., 2011). More than a billion people, the vast majority of whom reside in Asia and Africa, do not have access to clean and reliable water supplies (Water, 2012).

Solar stills are a solar based desalination/water treatment technology and are considered as one of the simplest, cheapest and most sustainable processes. However they suffer from two disadvantages: their productivity is very low compared to other desalination methods and, they require relatively large areas of land which invariably increases their initial investment (Kannan et al., 2014; Kulkarni and Kulkarni, 2014; Velmurugan and Srithar, 2011).

Nevertheless, the simple construction of solar stills and their utility in removing various contaminants, lowering salinity, and disinfecting saline and contaminated water have enhanced their use in a number of developing countries as a primary source for domestic water supply (Bhattacharyya, 2013).

Pharmaceutically active compounds (and their metabolites) occur ubiquitously in all water bodies throughout the world (Hughes et al., 2012). Trace pharmaceutical compounds have been found in surface water (Petrie et al., 2015), ground water (Phillips et al., 2015) and coastal seawater (Gaw et al., 2014) ranging in magnitude from a few ng/L in seawater and potable water to high μg/L in sewage treatment plant (STP) effluents (Arnold et al., 2014; Fick et al., 2009; Giri et al., 2014; Cardoso et al., 2014). Pharmaceuticals are released to the aquatic environment via several pathways; these include emissions from manufacturing facilities, the discharge of treated sewage effluent from sewage treatment plants, from the application of sewage sludge, or animal manure, to land, leakage from sewage treatment plants, emissions from medical units and disposal of unwanted pharmaceuticals (Kookana et al., 2014).

The partial removal of pharmaceutical compounds by conventional wastewater treatment plants has, invariably, resulted in their accumulation in the water cycle (Fick et al., 2009; Triebskorn et al., 2014), and hence their continuous release into water bodies exerts a hazardous impact on both the environment and human health (Arnold et al., 2014; Giri et al., 2014; Cardoso et al., 2014; Triebskorn et al., 2014; Whitacre, 2010). Although several treatment methods, whether physical, chemical and/or biological, have been proposed for combatting pharmaceutical contamination (Kitsiou et al., 2014), photodegradation is one of the few available methods that could utilize renewable energy and may be deployed on a large scale. Sunlight may be directly absorbed by the pharmaceutical molecule or it can produce in-solution highly oxidative products such as reactive oxygen species (ROS) (Chong et al., 2010), which in turn would react with the molecule and break it into smaller ones, eventually mineralizing it into carbon dioxide, H_2O and mineral salts (Ikehata and El-Din, 2006). Considerable research investigated both indirect photolysis and photocatalysis as methods for elimination of pharmaceuticals in water (Doll and Frimmel, 2003; Dimitrakopoulou et al., 2012; Radjenović et al., 2009).

A study by Ayoub et al. (Ayoub et al., 2014; Ayoub et al., 2015) conducted to assess the efficiency of solar stills in removing contaminants and enhancing productivity reported the possibility of bacterial transfer from the solution via vapor to the distillate. This raises the possibility of the transfer of pharmaceuticals if present in the feed water to the distillate of solar stills and the possibility of degradation due to the effect of heat and light. Each of these two factors can have a separate effect or possibly have a combined synergistic effect. Indeed, most pharmaceuticals are designed to be thermally stable, however, they are known to be light sensitive (Doll and Frimmel, 2003) and will undergo photodegradation.

There are two types of photo-degradation: direct effect, where sunlight affects the molecule directly and is often referred to as direct photolysis, or when sunlight indirectly affects the molecule. Indirect photodegradation could occur either through indirect photolysis or through photo-catalysis (Doll and Frimmel, 2003). Considerable research effort has been expended on the utilization of indirect photolysis, photocatalysis and direct photolysis for the elimination of pharmaceuticals in water (Doll and Frimmel, 2003; Dimitrakopoulou et al., 2012; Fatta-Kassinos et al., 2011; Barnaby, 2009; Boreen et al., 2003; Mathon et al., 2016).

Experimental results reported in the literature on the recalcitrance of a particular pharmaceutical to photolytic degradation, on the number of photo degradation by products, on the mechanisms involved in the degradation process and on the toxicity of these photo degradation products for the same pharmaceutical are often contradictory. For example, Hanamoto et al., 2014 reported that photolysis of DCF did not appear to release degradation byproducts that were more toxic than the parent compound. On the other hand, Diniz et al., 2015 (Diniz et al., 2015), reported that the photolysis by-products of DCF were more toxic than the parent compound. More recently Kovacic et al., 2016 (Kovacic et al., 2016) has shown that direct photolysis of DCF resulted in the majority of the parent compound transforming into two degradation by-products and that the toxicity level of these by-products was rather low. Mathon et al., 2016 (Mathon et al., 2016) also reported on the number of photo degradation products where they reported the number to range from 1 by-product up to 13.

The main objectives of this study are to determine whether solar stills are capable of eliminating/mineralizing pharmaceuticals, whether pharmaceuticals and/or their degradation products are transferred to the distillate, thus rendering the distillate unsafe for use, and to establish which one of the mechanisms (thermal or direct photolysis) is prevalent/dominant in the degradation of pharamaceuticals or if the two mechanisms are synergistic in nature.

To achieve these objectives, the effects of light and heat, individually and in combination, on the transfer and degradation of pharmaceuticals, in the absence of mechanical disturbances, were evaluated under three different experimental modes: (a) solar still mode executed in a simulated solar still that was subjected to natural sunlight accompanied by a raise in temperature. In this mode, the synergetic effect of two independent variables, heat and ultraviolet radiation, was assessed. (b) Thermal-only mode performed in a heated container which was isolated from all light sources. This mode was set up in such a way so that heat would be the only effective variable. (c) Light-only mode implemented by a solar collector and a concentrator by which solar radiation was amplified. The duration of concentrated sunlight exposure was short in order to reduce heating of the samples.

2. Materials and methods

2.1. Pharmaceuticals used

The pharmaceuticals selected are ibuprofen (IBU), diclofenac (DCF), carbamazepine (CBZ), ampicillin (AMP), and naproxen (NPX). The selection of these five was based on their common usage, recalcitrance, potential detrimental environmental and health impacts and their identification as priority compounds in the developing world (Mansour et al., 2016).

IBU was supplied from Mediphar Laboratories (Lebanon), DCF, AMP and CBZ were acquired from Mephico S.A.L (Lebanon), while NPX sodium was obtained from Al-Hikma Pharmaceuticals (Jordan). All pharmaceuticals had a purity of 99%. Characteristics of the different pharmaceuticals used in this study are presented in Table 1.

Methanol and Acetonitrile of HPLC grade were obtained from Sigma-Aldrich (Germany). Double distilled as well as deionized (DI) water (Milli-Q purification system) were used in this study.

2.2. Chemical analysis

The concentration of pharmaceuticals in solution was determined using High Performance Liquid Chromatography (HPLC), Agilent 1100