AMERICAN UNIVERSITY OF BEIRUT

TRANSFER OF SELECTED PHARMACEUTICALS VIA WATER VAPOR UNDER MODERATE TEMPERATURES IN SOLAR STILLS

By
ABBAS AKRAM BAALBAKI

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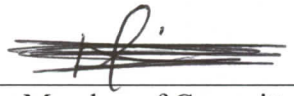
Approved by:

Dr. George M. Ayoub, Professor — Advisor
Department of Civil and Environmental Engineering



Dr. Antoine Ghauch, Associate Professor — Member of Committee
Department of Chemistry

Dr. Mahmoud Al Hindi, Assistant Professor — Member of Committee
Department of Chemical Engineering

Date of thesis defense: April 25, 2016

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AN ABSTRACT OF THE THESIS OF

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Title: Transfer of Selected Pharmaceuticals via Water Vapor under Moderate Temperatures in Solar Stills

The increase in demand and disposal of pharmaceuticals, positively correlated with the growing, developing human population led to the emergence of pharmaceuticals as a contaminant with high environmental impact. This impact is attributed to several factors: its numerous ways of entry to the environment, high stability, profound biological effects at low doses, and the incomplete removal of these contaminants by conventional water treatment methods. Moreover, very little is known about their effects on the ecosystem and human health.

Many developing countries that endure problems related to water sufficiency and/or quality use solar stills as an affordable water supply method. Very little research has been done on the effectiveness of solar stills in removing pharmaceuticals. This research was aimed at understanding the transfer and/or degradation of five chemically distinct pharmaceuticals in solar stills.

The studied pharmaceuticals were: Ibuprofen, Diclofenac, Carbamazepine, Ampicillin and Naproxen. Experiments were conducted under three conditions referred to as Conditions I, II and III. The first condition studied the combined effect of temperature and light in full-scale solar stills. The effect of temperature as a sole variable was investigated in condition II. The third condition covered the effect of light only via concentrated solar power (CSP) experiments. Results obtained show that solar stills are highly effective in preventing the transfer of the studied pharmaceuticals from feed solution into the distillate. Ibuprofen, having the highest Henry's law volatility constant among the tested pharmaceuticals, was the only pharmaceutical that transferred via vapor into the distillate with the highest transfer of 2.13% at 50°C in Condition II and 0.58% in Condition I. In the case of Naproxen and Diclofenac, the parent compounds did not undergo transfer into the distillate phase; however, their degradation byproducts did. In addition, the results also showed that in the case of Ampicillin, Naproxen and Carbamazepine, degradation is characterized by a temperature threshold after which high rate degradation of the compounds was induced. Naproxen, Ibuprofen and Carbamazepine required both high temperature and sunlight combined to degrade noticeably. Concentrated solar power accelerated the degradation of Diclofenac, Naproxen and Ibuprofen with a three-minutes-degradation percentage of 43.7%, 12.7% and 2.1% respectively.

Keywords: Water contamination, Water treatment, Desalination, Pharmaceuticals, Photolysis, Solar degradation, Ecological toxicity

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CHAPTER 1
INTRODUCTION

A. Environmental significance of pharmaceuticals

1. Increased demand and disposal of pharmaceuticals

The global demand for pharmaceuticals is on the rise for two major reasons. Firstly, the growth of the human population has been increasing at an unprecedented rate, and secondly, compared to previous years, the mean age of the human population is currently set at an older age (Arnold et al., 2014; Triebskorn et al., 2015). In addition, there has also been an increase in global food demand. A proportion of this food demand can be attributed to the increase in consumption of meat and dairy products which has led to the need for the expansion of livestock farm operations. Thus, in addition to human pharmaceutical demands, the need for pharmaceuticals for veterinary purposes is also increasing (Arnold et al., 2014; Triebskorn et al., 2015). Evidently, with this increase in pharmaceutical consumption comes an increased infiltration of this product into the environment.

2. Routes of contamination

Pharmaceuticals contaminate the environment through different routes. The most evident route is through human and animal wastes (fecal matter and urine).These pharmaceuticals can be discharged by animals or humans in either their metabolized or

original form. Therefore, these compounds can enter the natural environment in both forms (Giri & Pal, 2014).

Another way pharmaceuticals enter the environment is through direct or indirect disposal of expired and surplus medications. These medications enter either the sewer networks or landfills where the compounds eventually find their way to contaminate surface water, groundwater and soil (Giri & Pal, 2014; Triebskorn et al., 2015). An additional significant route of contamination is the effluent from pharmaceutical production facilities (Cardoso et al., 2014; Gaw et al., 2014; Triebskorn et al., 2015). For example, effluents from a pharmaceuticals factory in India contained 2.27 g L^{-1} of aspirin and 1.15 g. L^{-1} of salicylic acid (Cardoso et al., 2014). However, this finding dates back to 1993. In a more recent study, the effluent from a wastewater treatment plant that services 90 pharmaceutical production facilities in Patancheru, India was found to contain 24 different pharmaceuticals out of which 21 had concentrations greater than one μg L^{-1}. Additionally, three compounds showed concentrations higher than one mg. L^{-1} (Cardoso et al., 2014). Aquaculture and sludge are other means by which pharmaceuticals enter the environment. In the case of aquaculture, pharmaceuticals are directly released into surface water, however, in the case of sludge the contaminant is introduced via the constituents (human and/or animal wastes). This results in contaminating the soil which, in turn, indirectly contaminates both the surface and ground water in the presence of heavy rainfall (Giri & Pal, 2014).

Through these contamination routes, many other pharmaceuticals have been detected in the aquatic environment in magnitudes that range from nano to micro grams per liter (Arnold et al., 2014; Fick et al., 2009; Giri & Pal, 2014; Brain et al., 2008). For example, Ciprofloxacin was recorded at levels that ranged between 2.5 and 10 mg. L^{-1}

in rivers and 2.5 to 6.5 mg. L^{-1} in lakes. In addition, concentrations between 44 and 14000 ng. L^{-1} of ciprofloxacin were found in domestic water wells in Hyderabad, India (Cardoso et al., 2014; Fick et al., 2009).

The scientific community, at present, considers pharmaceuticals as an important emerging contaminant. As noted earlier, significant amounts and various types of these pharmaceuticals and their byproducts have been encountered in the environment. These exist at concentrations that were technically undetectable in the past, and would not have been detected had it not been for the recent advances in analytical chemistry techniques (Caldwell et al., 2014; Fick et al., 2009; Giri & Pal, 2014; Whitacre & Gunther, 2008).

3. Consequences of Contamination

a**.** Environmental hazards

Typically, pharmaceuticals are designed to have profound physiological effects on living organisms, even at low doses. As a result, pharmaceuticals have been classified as a major environmental concern (Arnold et al., 2014; Triebskorn et al., 2015; Whitacre & Gunther, 2008). In addition, pharmaceuticals are designed to be stable and resistant to change. Thus, they are not always completely removable by conventional or advanced water and wastewater treatment facilities. This has led to its higher occurrences and accumulations in the water cycle (Fick et al., 2009; Triebskorn et al., 2015). Moreover, their continuous release into the environment contributes to the chronic exposure of the aquatic and non-aquatic biota to these substances, which affects

them throughout their entire life cycle (Arnold et al., 2014; Triebskorn et al., 2015; Whitacre & Gunther, 2008).

Environmental effects additionally include consequences on reproduction, growth, behavior and feeding of fish and invertebrates (Giri & Pal, 2014). Testing of fish tissues found in nature also confirmed the presence of trace amounts of pharmaceuticals. Estrogenic effects on male fish living in certain rivers have been identified (Olsson & Forlin, 1999). Environmental exposure of vultures to Diclofenac and its biomagnification resulted in the near extinction of three of its major species (Arnold et al., 2014; Cardoso et al., 2014; Whitacre & Gunther, 2008). Another alerting factor is the discharge of many pharmaceuticals simultaneously into the environment which could lead to cocktail effect as a result of molecular interactions (Bound & Voulvoulis, 2004). Also, pharmaceuticals, especially those belonging to the antibiotics family, might contribute to the development of multi drug-resistant bacteria, which currently poses a major challenge for the medical community (Cardoso et al., 2014; Fick et al., 2009; Gaw et al., 2014; Whitacre & Gunther, 2008).

b. Human health hazards

In addition to ecological health effects, pharmaceuticals may cause human health hazards (Cardoso et al., 2014; Whitacre & Gunther, 2008). However, up to date, residual pharmaceutical quantities in drinking water are much lower than doses administered for therapeutic purposes, which is to say that their concentrations are very low in drinking water (Whitacre & Gunther, 2008). Additionally, the adverseness of long term exposure to low concentrations of pharmaceuticals is not well known (Giri &

Pal, 2014; Whitacre & Gunther, 2008). This fact makes it hard to confirm their potential human health hazards in drinking water. In fact, some researchers propose that they might be hazardless for human health (Fick et al., 2009; Whitacre & Gunther, 2008).

Multi-generational contact to multiple pharmaceuticals simultaneously, also known as the cocktail effect, grasped the attention of many researches. Cocktail effect is a more realistic scenario were toxicity concerns are much higher than those caused by the exposure to a single pharmaceutical (Barceló & Petrovic, 2007).

It is however undeniable that environmental concerns ensue from the presence of pharmaceuticals in water resources. These need to be addressed, even though their impact on human health is not established as of yet.

B. Solar desalination

1. Scarcity of water

During the last century the world population increased dramatically. This was a direct result of industrial advancement and improved medical care. Unfortunately, such advancement comes with higher demand on natural resources. However, this demand has yet to be met in many locations worldwide, especially in developing countries that lie in arid and semi-arid regions. More specifically, these regions experience critical shortages of potable water, to the extent that several political tensions have developed between countries that led to wars in some cases. (Barnaby, 2009; Starr, 1991).This may be counterintuitive, as two-thirds of the world's surface is covered with water. However most of the earth's water is unfit for direct use and requires extensive treatment to be

converted to safe potable water. Desalination is one method by which this water may be converted to a usable commodity. There exist several desalination methods with each having its advantages and limitations (Kannan et al., 2014; Kulkarni, 2014; Qiblawey & Banat, 2008; Velmurugan & Srithar, 2011).

2. Principal Desalination Technologies

The most common methods for desalination are membrane technologies, thermal distillation and electrodialysis. The majority of other methods are based on these technologies (Van der Bruggen, 2003). Worldwide, the most commonly used are multistage flash distillation (MSF), reverse osmosis (RO) and multiple-effect distillation (MED) (Kannan et al., 2014; Khawaji et al., 2008; Omara et al., 2013). MSF and MED are gradually being replaced by RO due to advances in membrane technologies except for the Arabian gulf countries. These methods are relatively efficient and practical in producing mass amounts of domestic water on the city or national levels. They additionally require smaller areas of land (low initial cost), yet higher energy and maintenance requirements (high operational costs). However, these methods are not technologically or financially accessible to developing countries (Bernat et al., 2010), where less technologically developed but more cost-sustainable methods are needed.

3. Advantages of Solar Desalination

Thermal desalination is generally an energy intensive process, where it is estimated that 10,000 tons of oil per year are needed to produce 1000 m^3 per day of potable water

(Tanaka, & Nakatake, 2004). Unlike oil rich countries, most third world countries are unable to afford such fossil fuel energy-intensive technologies. The only alternative energy sources these countries can resort to lies in renewable energy. Fortunately, most of these developing countries, located in arid and semi-arid regions, have plenty of sunlight. It is thus convenient for these countries to rely on solar power as the main energy source for desalination (Al-Hallaj et al., 2006). One main advantage of solar desalination is that it is an off-grid technology that could be installed anywhere, and does not depend on the presence of a nearby power plant. Rural developing communities can therefore conveniently use solar desalination (Bernat et al., 2010). These communities, who according to the World Health Organization (WHO) amount to more than one billion people, normally do not have access to electricity and suffer the most from potable water pollution (Onda et al., 2012). Accordingly, developing countries have the option to resort to solar desalination.

Solar stills are commonly used solar desalination technologies adopted in developing countries. Compared to other methods, in terms of design, solar stills are the simplest and most sturdy. That said, solar stills are mostly solid state, that is, they require low maintenance. However, productivity of solar stills is still considered very low compared to other methods. Additionally, it uses a lot of land space which, occasionally, increases the cost of the initial investment (Kannan et al., 2014; Kulkarni, 2014; Velmurugan & Srithar, 2011).Solar desalination, in the form of solar stills, has been used over the past ages and has been undergoing development to render it a more sustainable process.

4. Working mechanisms of a single basin solar still

In a single basin solar still, salty or brackish water is supplied into the basin which is usually painted black. This basin is covered by a transparent structure that will trap heat from sunlight (Fig. 1). The heat will induce evaporation where the vapor will be subjected to condensation at the roof surface.

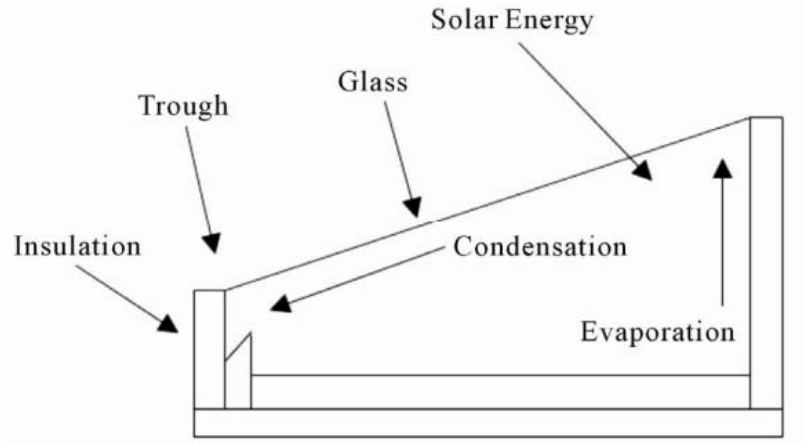


Figure 1: Diagram of a Solar Still (Gnanadason et al., 2011)

The surface of the container is exposed to a temperature gradient between the inside and the outside of the structure. The roof is usually shaped so that the condensate droplets move downstream and can be collected in a trough, leading the condensate to exit the still. As a result, the water in the basin will increase in salinity, to the extent that evaporation will be reduced. This liquid mixture is referred to as brine and is usually discarded (Velmurugan & Srithar, 2011).

Solar stills are used extensively in developing countries as a primary mean for the production of drinking water. It removes various contaminants, lowers salinity and disinfects water (Bhattacharyya, 2013). However, little research has been carried out on the possible transfer of pharmaceuticals 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. Most pharmaceuticals are designed to be thermally stable. However they are light sensitive. This is why they are stored in amber colored bottles (Doll & Frimmel, 2003). The process by which light-sensitive pharmaceuticals are modified or mineralized via light radiation is termed photodegradation (Aranami & Readman, 2007).

C. Photodegradation of Pharmaceuticals

Different methods have been proposed as a treatment for pharmaceutical contamination. These methods could be physical/chemical or biological. Physical/chemical methods include adsorption, hydrolysis, oxidation and reduction, while biological methods include destruction by fungal and microbial organisms (Kitsiou, Antoniadis, Mantzavinos, & Poulios, 2014). As for solar stills, water laden pharmaceuticals could be exposed to significant amounts of sunlight which could affect them. Indeed, sunlight might be directly absorbed by the pharmaceutical molecule or it could produce highly oxidative products such as reactive oxygen species (ROS) (Chong, Jin, Chow, & Saint, 2010). ROS would then react with the molecule and break it into smaller molecules, eventually mineralizing it into carbon dioxide, H_2O and mineral salts (Ikehata et al. 2006).

There exist two types of photodegradation. Where each type occurs depends on whether sunlight effects the molecule directly or indirectly. When sunlight directly affects the molecule this is called direct photolysis. However, when sunlight indirectly affects the molecule, it could occur either through indirect photolysis or through photocatalysis. Considerable amounts of research have investigated both indirect photolysis and

photocatalysis as method for elimination of pharmaceuticals in water (Doll & Frimmel, 2003). Dimitrakopoulou et al. (2012) studied the photocatalytic degradation of amoxicillin in ultrapure water and secondary effluents and they reported complete degradation of the antibiotic within 25 minutes of irradiation when ultrapure water was used. However, compared to pure water, amoxicillin degradation in secondary effluents (SE) is slower. Similarly, Radjenović, et al. (2009) reported lower degradation rates of acetaminophen and atenolol in the case of SE compared with distilled water, which was attributed to the detrimental effect of other organic compounds present in the effluent. However, limited research has investigated the effect of direct photolysis on pharmaceuticals, which is the type of photolysis that occurs most prominently in solar stills.

D. Research Objectives

This study aims to investigate whether pharmaceuticals, as contaminants, can transfer via vapor in moderate temperature distillation units in the absence of mechanical disturbances. Additionally, the study will examine whether the tested pharmaceuticals degrade or transform during this distillation process because of heat, UV/light or both. Not only does this study evaluate the pharmaceuticals in the distillate but also the remaining portion in the brine. Furthermore, degradation of pharmaceuticals under concentrated solar power will also be studied to check if they would disintegrate at a faster rate.

It should be noted that in the absence of appropriate instrumentation, the study will not cover any characterization of the byproducts resulting from any degradation or transformation.

E. Research Significance

Solar stills are used as a means of obtaining potable water from saline and contaminated sources. This is especially important in developing countries where solar stills are cost efficient and are easily accessible. Thus, it is necessary to assess the efficiency of such solar stills in removing contaminants as a study done by Ayoub et al. (2014) showed the possibility of bacterial transfer to the product water of a solar still (Ayoub et al., 2015). Pharmaceuticals, as a water contaminant, are an emerging concern, especially when considering that their consequences on the environment are proven to be harmful, while long-term consequences on humans, although not fully explored, are expected to be detrimental. Therefore, it is crucial to assess whether transfer of pharmaceuticals is induced into the distillate and if so, to what levels. Furthermore, the study will determine the state of the residual contaminant in the brine in the event that the product is disposed into the environment.

CHAPTER 2
MATERIALS AND METHODS

A. Introduction

Three different experimental modes were performed in this study with the objective of determining the effects of various variables on the transfer and degradation of pharmaceuticals in solar stills in the absence of mechanical disturbances. The first, solar still mode, was executed in a simulated solar still. The still was subjected to natural sunlight, which in turn heated the pharmaceutical solution. In this mode, the synergetic effect of two independent variables, heat and ultraviolet radiation was evaluated.

The second, thermal-only mode, was performed in a heated container which was isolated from all light sources. This mode was setup in such a way so that heat would be the only effective variable.

For the third, light-only mode, a solar collector and concentrator were used. In this setup, the independent variable was light. However, it is technically difficult to irradiate without heating unless using jacketed reactors. For this purpose, solar radiation, including ultraviolet radiation, were amplified several times. Additionally, compared to the two other experimental modes, exposure duration was much shorter in this mode so as to reduce heating of the samples. This partially eliminated the effect of temperature. For each mode, excluding the light-only mode, two duplicate experiments were run simultaneously under the same conditions for all experimental tests.

B. Materials

1. Materials for Solar Still Mode

Solar stills used in this experiment had three components. The first was a closed spherical glass flask (Fig. 2), encasing the two other components and working as the solar collector. The second was the feed plate containing the initial solution, positioned on a support at the bottom center of the glass flask. The final component was the plate-support.

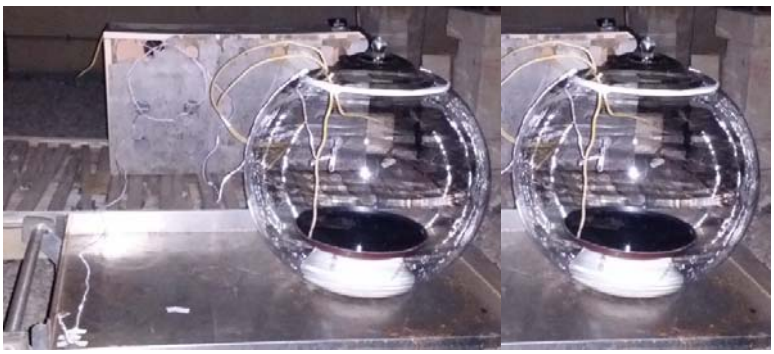


Figure 2: Full setup in solar still mode

The still used for this experiment was made of glass, so as to prevent any chemical interactions between the pharmaceuticals and the flask. The flask is composed of a 50L semi-spherical base with a flat bottom having an area of 0.13 m^2 and a maximum diameter of 50 cm at the center. The top opening of the flask was covered using a semi-spherical glass lid, thus completing the spherical shape of the flask (Fig. 3).

Figure 3: Glass Flask

The top cover was set to produce an air-tight flask and to isolate it from the external environment. The flask was obtained from Glass Contracting Co M.G.C.C, a local supplier, and customized at the AUB glass workshop. Using the method proposed by Noteboom and Will (1982), both parts were completely siliconized using Dichlorodimethylsilane solution purchased from Sigma-Aldrich, Missouri USA. Before each experiment, the flask was washed by using lab-grade detergent, followed by distilled water, and finally by acetone. After washing, the flask was either placed in an oven at 200 °C for two hours or left in the sunlight for 8 hours. This procedure was followed in order to remove any remaining organic residues.

The feed plate consisted of a shallow pan made from aluminum (Fig. 4). The upper side was coated with Teflon and the lower side was covered with ceramic enamel. The plate was obtained locally from Tefal™.

Figure 4: Feed plate

The plate has a diameter of 16 cm and a depth of 2 cm. It was filled with a maximum volume of 500 mL of feed solution. Before each experiment, the plate was washed; first with lab-grade detergent, then with distilled water, and finally with acetone. After washing, the plate was heated using a hot-plate. Again, this process was performed to remove any remaining organic residues. Prior to adding the solution and starting the experiment, the plate was properly leveled to prevent spilling of the pharmaceutical feed solution.

The plate-support (Fig. 5) is a porcelain platform that was siliconized using the same method as for the flask. The plate-support was also washed using the same procedure as that of the flask and the feed plate. After washing, it was placed in an oven at 200 °C for two hours.

Figure 5: Plate-support

2. Materials for Thermal-Only Mode

In this mode a deep semi-spherical pan was used (Fig. 6). This aluminum pan was supplied locally from Tefal™. Ceramic enamel and Teflon coatings were used to cover the lower side and the inside, respectively.

Figure 6: Full setup of thermal-only mode

The pan had a total volume of 4 L, a diameter of 34 cm and a total depth of 10 cm. One liter of the initial feed solution was filled directly into the pan. A siliconized porcelain plate was centered inside the pan to function as the distillate-collector. The pan's cover was a semi-spherical glass dome. It was siliconized using the same method adopted for the flask (Noteboom & Will, 1982). In this setup, the pan cover was placed upside down, in an inverted fashion so that the concavity of the cover would direct condensate droplets towards the inside of the porcelain collection plate.

The container was placed on 500 mL Electromantle Heating Mantle EM0500, OSA UK. The heater was connected to a programmable, temperature-controlled circuit-breaker. This ensured that the temperature would always remain within the preset range. For the heat only mode, the experiments were carried out at temperatures of 40, 50, and 60 °C.

For each experimental test, the temperatures of the feed solution and that of the air inside and outside the pan were continuously monitored and recorded. This was done to guarantee that the temperature, during the experiment, remained in the pre-determined desired range.

3. Materials for Light-Only Mode

In this mode, the feed solution was subjected to concentrated sunlight and ultraviolet radiation. The clarity and insignificant turbidity of the feed solution and its container (non-detectable at 0.001 NTU on a Hach 2100AN IS turbidimeter, Loveland USA) limited the amount of light absorbed and thus, as intended, water did not heat up as much as it did during the other experimental modes.

However, the feed solution was exposed to significantly higher amounts of ultraviolet radiation than during the other experimental modes. The initial feed solution was placed in a 12 mL screw-cap, clear borosilicate cylindrical vials. This vial had a radius of 1 cm, a length of 7 cm and glass-thickness of 1 mm. The vial was subjected to concentrated solar irradiation using a solar concentrator (Fig. 7).

Figure 7: Experimental work of light-only mode

The solar concentrator, made of a standard satellite dish, was covered with two layers of reflective chrome plated sticking tape. The double layer of chrome tape had a reflectiveness value of 80%. The satellite dish had a total area of 0.71 m^2, elliptical shape with major diameter of 100 cm, a minor diameter of 90 cm and a depth of 10 cm at the center. The focused image had an area of 0.0092 m^2 and the area ratio of dish to focused image was calculated to be 77/1; therefore, the light intensity at the focal point equaled 76×0.8 ~ 62 times the power of regular sunlight. The dish was mounted on a bi-axial mount that enabled it to be directed perpendicularly to incoming solar radiation. After aligning the dish, the focal point was identified using a black painted board. Both natural and concentrated solar flux as well as both natural and concentrated ultraviolet radiation A and B were measured and recorded, however readings for both parameters for concentrated sunlight were over range. The temperature of the feed solution was also measured and recorded before and after each experiment. The time of exposure in this

experiment was limited to 3 minutes under CSP and 2 hours in regular sunlight; this was done so that the tested solution's temperature will not rise more than 2 °C in both cases. The duration of exposure was varied between no exposure, regular sunlight for two hours and concentrated sunlight for periods of 30, 60, 90, and 180 seconds.

4. Sensors

Sensors included temperature sensors in the form of thermocouples and thermometers; light sensors were in form of lux and ultraviolet meters. These sensors were used to continuously monitor the experimental parameters and check if the conditions of the experiment were in the required range. Sensors were also used to record environmental factors that could have played an unforeseen role in the experiments.

The temperature sensors included type-K thermocouples (Fig. 8a). These were connected to 18200-00- Cole-Parmer data-acquisition system, Chicago USA, that was connected to a computer. Temperature logs were obtained using Cole-Parmer TracerDAQ software, Chicago USA. The sampling frequency was set to one measurement per second. Other temperature sensors included: Lutron SD Card real time data logger4 channels thermometer model: TM-947SD which follows ISO-9001 CE and IEC1010 standards, Taipei Taiwan (fig. 8b). An infrared thermometer and a digital hand-held thermometer (Fig 8c).

Figure 8 a: Type-K thermocouple and data acquisition unit
b: Hand-held thermometers
c: Data logging thermometer

The light sensor (Fig. 9) included a real time data logger hand-held lux meter model: LX-1128SD with the maximum reading limit of 100,000 LUX supplied by Lutron, Taipei Taiwan. This sensor was used to measure the intensity of natural sunlight during each experimental run.

Figure 9: Lux meter

It additionally measured the intensity of light absorbed by the glass in the still and the intensity of concentrated sunlight. The meter had data-logging properties and, during each test of the solar still mode, was set to record light flux at a frequency of one measurement per second.

Two different instruments were used to measure ultraviolet radiation. The first instrument was a hand-held UV meter with two sensors; one for UVA and the other for UVB (Fig. 10).

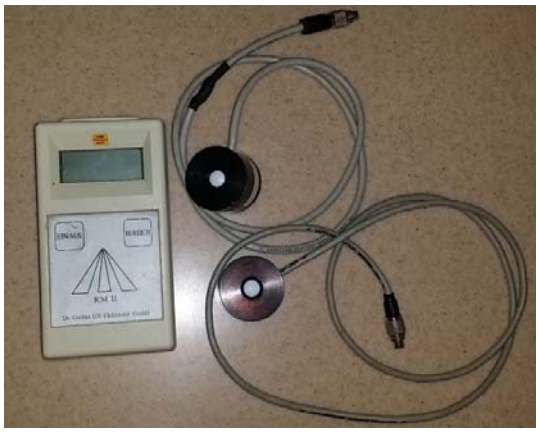


Figure 10: Hand-held UVA/UVB meter

The meter, model RM-11, was supplied by Opsytec Dr. Gröbel GmbH, Germany, and had a measurement range between 0 to 20 $mW.cm^{-2}$ for both UVA and UVB. The second instrument consisted of two UV-sensor chips (Fig. 11).

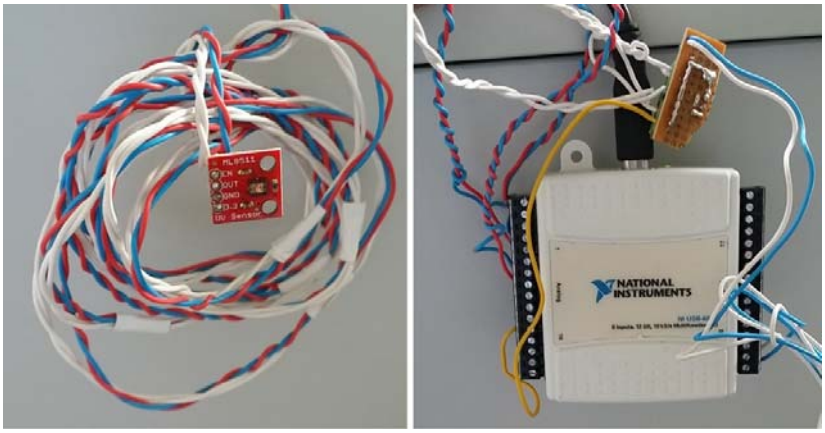


Figure 11: UV sensor chip and data acquisition unit

These chips (model number ML8511) were supplied by SparkFun, Colorado USA, and have a measurement spectrum as shown in Fig. 12

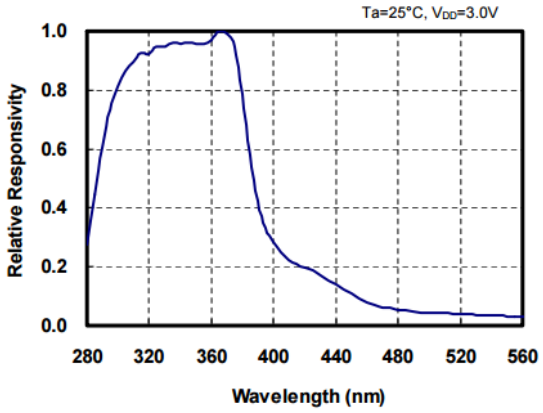


Figure 12: Measurement spectrum of ML8511 (Lapis, 2013)

The function of the chips was to convert UVA and UVB into electrical potential proportional to UV intensity. The chips were connected to a NI USB-6008 a bus-powered multifunction DAQ USB device supplied by National Instruments (NI), Austin USA. The data-acquisition unit measured the electrical potential supplied by the chips and logged it as raw data into a computer. Data was integrated and converted into UV-intensity values using a custom programmed software. NI labview was used as a

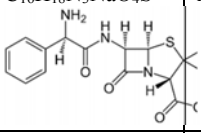
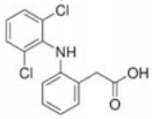
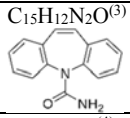
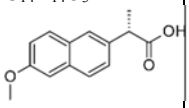
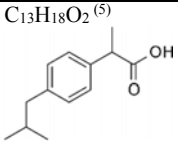
program platform. Of the two sensors, one was mounted inside the still, parallel to the feed plate and the second outside the still, parallel to the flat-base of the still.

5. Pharmaceuticals

The pharmaceuticals used in the experimental study were Ibuprofen, Diclofenac, Carbamazepin, Ampicillin and Naproxen. These pharmaceuticals were either purchased in their pure form or as capsules. When supplied in their pure form, they were used directly in the preparation of the feed solution. However, when supplied in capsule form, they were passed through a purification process to extract the active ingredient and get rid of the insoluble excipients. The purification process consisted of weighing the dry medicine inside the capsule and dissolving the required amount of medicine in deionized water. The solution was mixed overnight at room temperature 20±2 °C using a magnetic bar stirrer. The aim was to generally achieve saturation concentration levels for each pharmaceutical. Following that, the solution was filtered through a Whatman 934-AH, ashless, glass microfiber filter with a pore size of 1.2 µm. The excipient was then dried and weighed to ensure that the active ingredient in the pharmaceuticals was completely dissolved in the DI water.

Characterization of the different pharmaceuticals obtained from different manufacturing sources for the experiments is shown in table 1.

Table 1: Pharmaceuticals tested and their characterization

Name and Structure	Chemical Formula	Class	Function	Toxicity Level	Henry's Constant	Solubility in water at 21 °C and 1 Atmosphere (mg .L^{-1})	CAS ID
Ampicillin	$C_{16}H_{18}N_3NaO_4S$[1] 	Antibiotic[7]	Treats bacterial infections[7]	Hazardous upon inhalation and ingestion[1]	2.39×10^{-17}[9]	10100 [12]	69-53-4
Diclofenac	$C_{14}H_{10}Cl_2NO_2$[2] 	Nonsteroidal anti-inflammatory drug (NSAID) [10]	Has inflammation, pain and fever reduction properties[10]	Its oral lethal dose (LD(50)) is 53 mg/kg in rats and 157 mg/kg in rabbits[2]	4.73×10^{-12} [11]	18700[6]	15307-86-5
Carbamazepine	$C_{15}H_{12}N_2O$[3] 	Anticonvulsant[8]	Used to treat seizures[8]	Hazardous upon ingestion[3]	1.08×10^{-10} [11]	111 [12]	298-46-4
Naproxen	$C_{14}H_{14}O_3$ [4] 	NSAID[10]	Alleviation of mild to moderate pain, fever, and inflammation[10]	Oral LD(50) is 248 mg/kg in rats and 360 mg/kg in mice[4]	3.39×10^{-10} [11]	16 [12]	22204-53-1
Ibuprofen	$C_{13}H_{18}O_2$ [5] 	NSAID[10]	Reduces moderate pain, fever, and inflammation[10]	Oral lethal dose 50 (LD (50)) = 636 mg/kg in rats and 495 mg/kg in guinea pigs. Considered very hazardous[5]	1.52×10^{-7} [11]	30.12 [12]	15687-27-1

[1] [2] [3] [4] [5] *for Sciencelab, 2013a, b, c, d, and e, respectively*
[6] *Burke, 2007*
[7] *United States National Library of Medicine, 2015a*
[8] *United States National Library of Medicine, 2015b*
[9] *US EPA, 2012*
[10] *Cleauvers, 2004*
[11] *Tixier et al., 2003*
[12] *Samuel H. Yalkowsky, Yan He, 2010*

6. Analytical techniques

The concentration of pharmaceuticals in solution was determined using High Performance Liquid Chromatography (HPLC), Agilent 1100 Series LC system, equipped with a quaternary pump, autosampler, diode array detector (DAD) and supported by an analytical work station supplied by Agilent Technologies, California USA. The separation was achieved on an analytical column Discovery C18 (5 mm, 25 cm long × 4.6 mm ID) connected to a security guard column Discovery HS C18 (5 mm, 2 cm long × 4.0 mm ID), both supplied by Supelco Sigma-Aldrich, Missouri USA.

Each pharmaceutical was to be tested following a specific method summarized in table 2. Most of these methods, though taken from outside sources, were optimized to give best results.

Table 2: HPLC methods used for each pharmaceutical

Name of Pharmaceutical	Method reference	Eluent	Elution mode	Flow rate ($mL.min^{-1}$)	Injection volume (µL)	Column temperature (°C)	Detection wavelength (nm)	Retention time (minutes)
Ampicillin	(Ghauch et al. 2009)	(Methanol) MeOH/water (30:70, v/v)	isocratic mode	0.8	50	30	210	7.7
Diclofenac	(Ghauch et al. 2010)	mixture of MeOH/0.1% formic acid in water (80:20, v/v)	isocratic mode	1	25	30	275	7.24
Ibuprofen	(Ghauch et al., 2012)	(Acetonitrile) ACN/0.1% formic acid in water (65:35, v/v)	isocratic mode	1	50	30	196	8.3
Naproxen	(Ghauch,& Tuqan, 2014)	ACN/water (55:45, v/v)	isocratic mode	1	10	30	230	6.78
Carbamazepine	(Ghauch et al., 2011)	MeOH/0.1% formic acid water (70:30, v/v)	isocratic mode	0.8	30	30	235	5.98

C. Methodology

The research aimed to study each pharmaceutical compound in distinct experimental runs. These were all performed in the first half of the year 2015. First, a stock solution of the pharmaceutical was prepared. This stock solution was tested using HPLC and a known standard to confirm the purity and the concentration of the solution and was stored in a refrigerator at 4 °C for a maximum period of one week. In case storage exceeded a week, the old solution would be discarded and a new solution would be prepared. Prior to using this solution as a feed in any experiment, a sample was taken and labeled 'initial sample', to ensure that the solution did not degrade while in storage. Generally, the initial sample was taken on the same day during which the experiment was to be performed. This process of solution preparation was common to all experimental runs.

For the thermal-only mode, each pan was filled with one liter of the stock solution. After filling the pan, the distillate collector plate was positioned at the center of the pan. The pan was then sealed with a glass cover with the top sheathed in aluminum foil on the exterior. The glass cover had a hole through which two thermocouples were inserted. One of the thermocouples was dipped into the solution while the other remained in the air space of the pan. The heater was turned on, and the connected temperature regulator was programed to the desired temperature. At each distinct test, the temperature was kept constant at 40, 50 or 60 °C. The temperature logging software was set to begin logging. Additionally, a third thermocouple was placed 1.5 m above ground level, in the room where the experiment took place. This thermocouple measured the ambient room temperature. The temperature log from the thermocouples was used to ensure that the temperature remained within the desired range. This

experiment was done in two pans and was timed to end at t = 24 hours. At the end of the experiment, two samples of 2 ml were collected. One from the distillate and the other from the brine of each pan. In addition to these samples, the volumes of the distillate and the brine were measured and recorted.

For the solar-still mode, the experiment was performed on the roof of CCC-Scientific Research Building at the American University of Beirut (Latitude: N33°54'; Longitude: 35°29'; Altitude: 29 m). The glass flask was positioned and leveled on a stainless steel platform. The feed plate and the plate support were also positioned and leveled in the center of the bottom of the glass flask. The feed plate filled with 500 mL of the stock solution. After filling the plate, time was set to $t_0 = 0$, which was always after sunset. Similar to the thermal-only mode, the container was closed with a glass cover pierced through for the installation of two thermocouples for measuring temperature at the solution and the air inside the flask. A third thermocouple placed in the shade was used to measure the ambient temperature. The temperature log from the thermocouples is important for determining the maximum temperatures reached, and to determine for how long the pharmaceuticals were exposed to different temperatures. In addition to the thermocouples, two UV sensors were installed, with one located inside the still, parallel to the feed plate while the second was placed outside the still, parallel to the experimental setup. Monitoring UV was necessary to determine the effect of UV intensity on degradation. Another important variable, light intensity, was monitored using a data logging lux meter. The experiment ended at t = 24 hours. Three 2 ml samples were taken. One from the distillate a second from the brine, and the third from the condensed water droplets which accumulated on the glass cover. The final sample

was taken to ascertain that no cross contamination took place. After taking the samples, the volumes of the distillate and the brine were measured and recorded.

As for the light-only mode, the solar concentrator was first directed towards the sun, and its focal point determined using a long holder and a black sheet. Each of the six pharmaceuticals used in this study were poured in a set of vials. Each set contained six vials with every vial subjected to five different sets of conditions. These conditions were regular sunlight for two hours, concentrated sunlight for 30, 60, 90 and 180 s. UVA, UVB and solar flux of regular and concentrated sunlight was measured and recorded. These variables were also measured behind empty vials and vials filled with deionized water. Temperature of each vial was taken at both the beginning and end of the experiment to make sure that the tested solution's temperature did not rise above 2°C.

Preliminary experiments showed that the maximum ratio of brine to initial sample was always less 1/3 V/V therefore initial pharmaceutical solutions used in this study had chosen concentrations that would ensure no super-saturation in case the pharmaceutical solution was concentrated up to three times at 20 °C. Solubility tests were conducted prior to any experiment. These concentrations are summarized in table 3.

Water used for preparing the pharmaceutical solutions was obtained from a double distillator and a Milli-Q purification system, it had the properties mentioned in table 4.

Table 3: Initial concentrations of pharmaceuticals tested

Pharmaceutical	Initial Concentration mg. L^{-1}
Ampicillin	50
Diclofenac	50
Carbamazepine	50
Naproxen	5
Ibuprofen	10

Table 4: Physiochemical properties of solvent used

Solvent tested at 25 °C	pH	Total Dissolved Solids (mg $.L^{-1}$)	Conductivity ($\mu S.cm^{-1}$)	Total Organic Carbon (ppb)	Dissolved oxygen (mg $.L^{-1}$)	Turbidity (NTU)
Milli-Q® water	6.5	0.47	0.73	2	8	0

CHAPTER 3
RESULTS AND DISCUSSION

A. Introduction

Variations in the data are chiefly attributed to the type of pharmaceutical used. Indeed, molecular weight and structure, which differ according to the pharmaceutical, play a significant role in temperature and light sensitivity and volatility which translates into a difference in the transfer rate from liquid to vapor. However, the pharmaceuticals were chosen to cover a broad spectrum of properties, such as volatility and gas liquid equilibrium concentration. As seen in the table 5, the ratios of Henry's Constant of the pharmaceuticals as compared to that of Ampicillin (lowest Henry's Law constant) differ greatly.

Table 5: Henry's Law Volatility Constant K_H for pharmaceuticals used (defined via concentration) (US EPA, 2012)

Pharmaceutical	Henry's Law Volatility Constant K_H ($atm.m^3.mole^{-1}$)
Ampicillin	2.39×10^{-17}
Diclofenac	4.73×10^{-12}
Carbamazepine	1.08×10^{-10}
Naproxen	3.39×10^{-10}
Ibuprofen	1.52×10^{-7}

1. Preliminary Experimentation

A total of eighteen experimental tests were performed between July 2014 and May 2015. Initially, Diclofenac was the only pharmaceutical tested at a very low concentration (1 mg. L^{-1}) to mimic concentrations of pharmaceuticals in the environment. These tests didn't show any transfer of Diclofenac into the distillate. Yet degradation of Diclofenac occurred in the brine of the solar still mode, no degradation was observed in the thermal only mode, conducted always at 50 °C. However, these tests alone were not conclusive in determining whether transfer occurred. This is because the initial concentration of Diclofenac used was very low, and thus the amount of pharmaceutical transferred could possibly be too low to be detected using the analytical machines having 50 µg. L^{-1} as a limit of quantification. Table 6 summarizes findings from these early Diclofenac experiments.

Table 6: Preliminary Experimentation

	Concentration (mg. L^{-1})										
Date	1-Jun	15-Jun	1-Jul	10-Jul	22-Jul	5-Aug	15-Aug	25-Aug	3-Sep	5-Oct	10-Oct
Test number	One	two	three	Four	Five	Six	Seven	Eight	Nine	ten	eleven
Initial	1.00	1.01	0.98	1.02	0.97	1.01	0.95	0.99	1.00	1.03	1.00
Still A Distillate	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Still B Distillate	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Still A Brine	0.54	0.45	0.56	0.28	0.45	0.60	0.50	0.52	0.35	0.40	0.32
Still B Brine	0.46	0.38	0.51	0.21	0.42	0.50	0.40	0.45	0.33	0.45	0.21
Pan A Distillate	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Pan B Distillate	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Pan A Brine	1.21	1.24	1.18	1.01	1.10	1.06	1.04	1.16	1.08	1.03	1.10
Pan B Brine	1.23	1.19	1.20	1.12	1.19	1.08	1.04	1.19	1.05	1.04	1.16

For practical purposes, the experiments were then performed for several pharmaceuticals with varying properties at higher concentrations. It was assumed that if

transfer does not occur or is not detectable at high concentrations then it will not occur at lower concentrations encountered in the environment.

B. Experimental Conditions

During this study three experimental conditions/variables were monitored: temperature, solar radiation and ultraviolet radiation.

The solar still mode experiments were only conducted during sunny and clear days, this resulted in minimal variability in experimental conditions. This fact made it unreasonable to study the effects of these conditions on transfer or degradation. However, this was essential to mimic optimal transfer conditions in a regular solar still by targeting highest temperatures possible which will increase evaporation of water and the volatilization of the pharmaceuticals. Figure 13 shows averaged temperature variations in solar still for all experiments conducted.

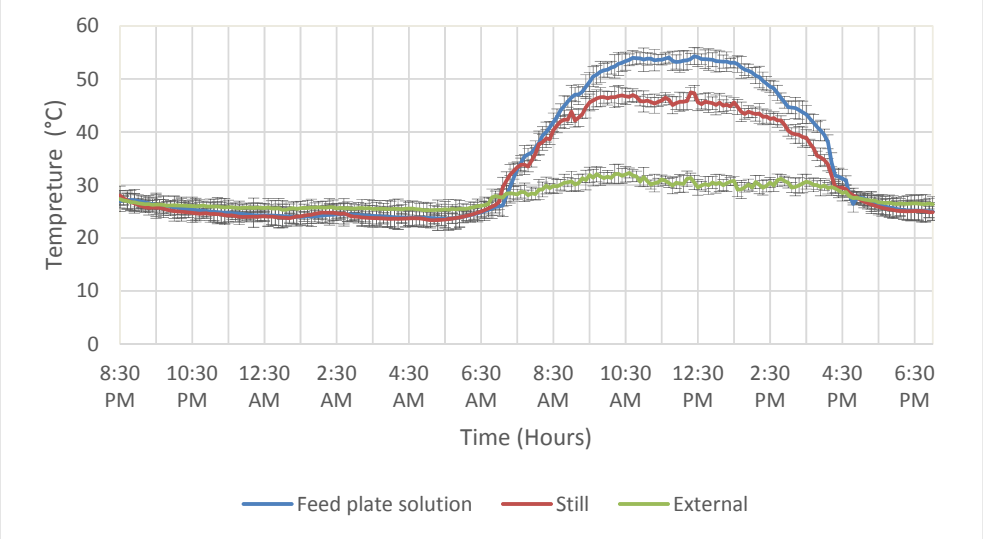


Figure 13: Averaged temperature variation in solar still mode

Figure 13 was obtained from temperature records of the eighteen different duplicated experimental tests, it shows that the entire system was subjected to the external

temperature having a value of 26±1.0 °C during night hours. During the day external temperature increased slightly to the level of about 30±1.0 °C while the temperature of the air inside the still increased to become steady at about 45±2.0 °C for a period of five hours. This trend was also followed by the pharmaceutical solution in the feed plate where the temperature increased to over 40 °C for a period of 8 hours during which a temperature in the range of 52±2.0 °C was recorded for a period of 5 hours.

UV records for the different experimental tests also showed low variability; figures 14 and 16 show averaged UV levels recorded for each pharmaceutical inside and outside the still respectively. The averaged UV variation which is the general trend is shown in figures 15 and 17. It is clearly noticed that the same general trend is observed in the different tests except for some short but sharp fluctuations caused by intermittent clouds. The tested solutions were subjected to UV levels rising from 0 to 3.8 mW/cm² for a period of 2 hours, then UV intensity remained constant around 3.8 mW/cm² for another 3 hours, after that UV intensity decreased rapidly over a period of 40 minutes to reach a level of 0.8 mW/cm² finally a slow descent to zero extended over a period of 5 hours and 20 minutes.

It is worth noting that UV inside the solar still reached higher levels than UV outside the solar still during early morning, despite of the presence of UV-absorbing glass, due to the diffraction of sunlight caused by the spherical shape of the glass still.

Figures 18 and 19 show the intensity of light outside the solar still, the thin glass of the still had negligible effect on the intensity of sunlight, the sensor was positioned outside the solar still only because it is affected by the presence of humidity inside the still. The Lux meter used had a maximum measuring capacity of 100000 Lux, this explains the static sunlight intensity shown on the curve. Sunlight intensity showed little variation

during different experiments, the trend observed was a sharp increase in the intensity up to 100000 Lux for a period of 2 hours, then the sunlight intensity reached an unknown value above 100000 Lux for a period of six hours, finally the intensity decreased over a period of two hours to reach a value of zero Lux.

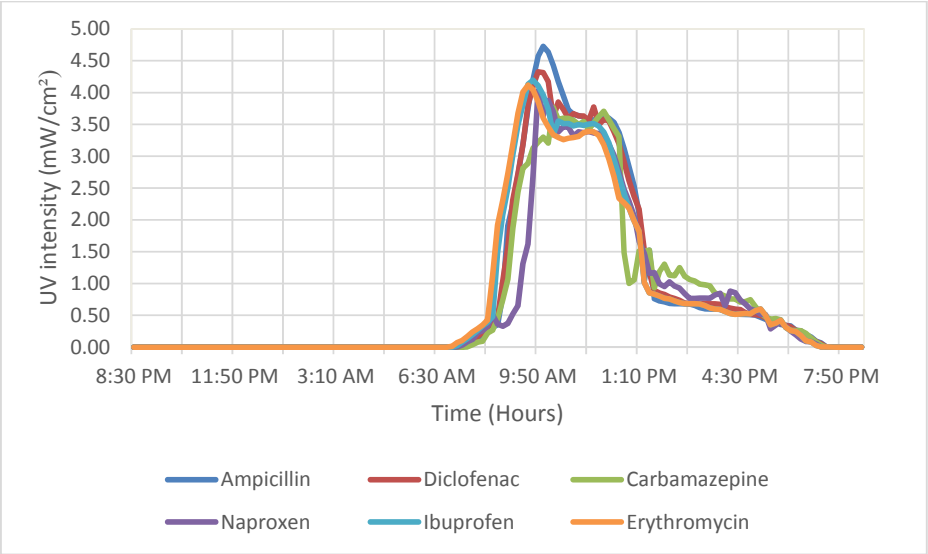


Figure 14: Averaged UV variation inside the solar still for each pharamcautical

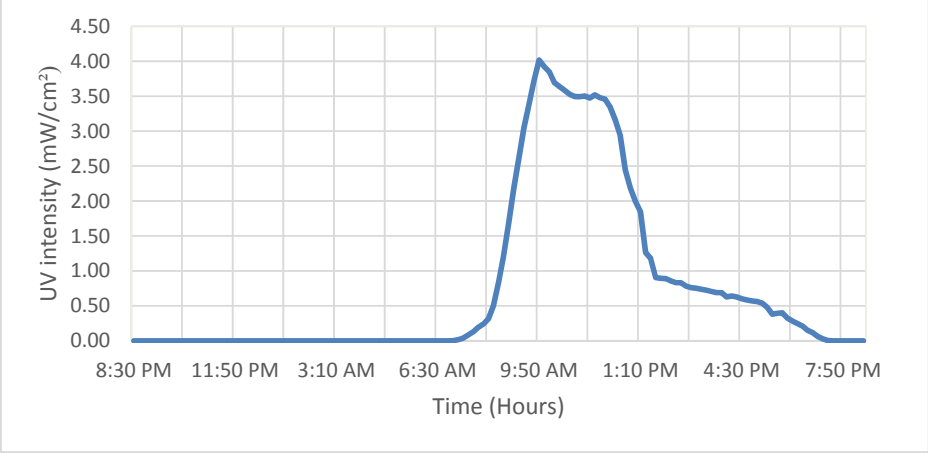


Figure 15: Averaged UV variation inside solar still

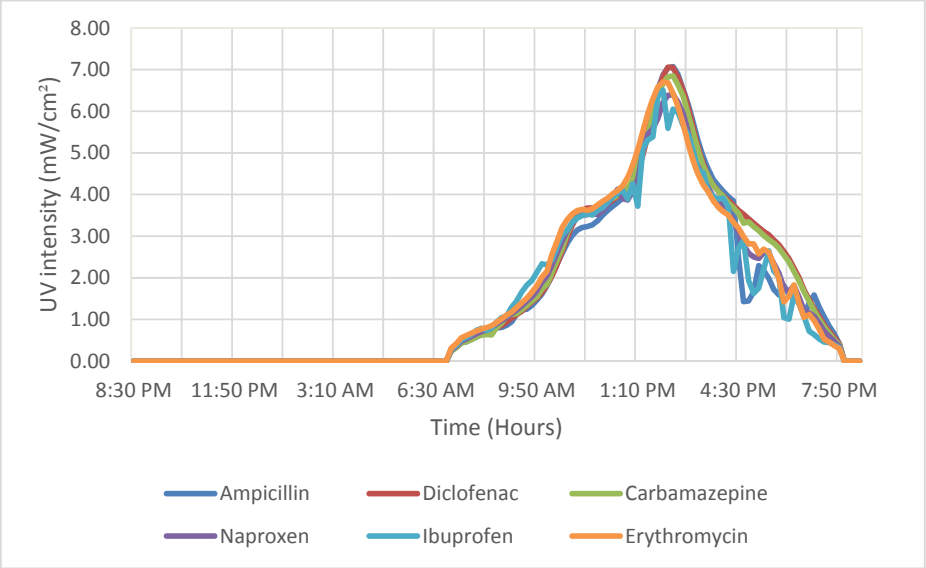


Figure 16: Averaged UV variation outside the solar still for each pharamcautical

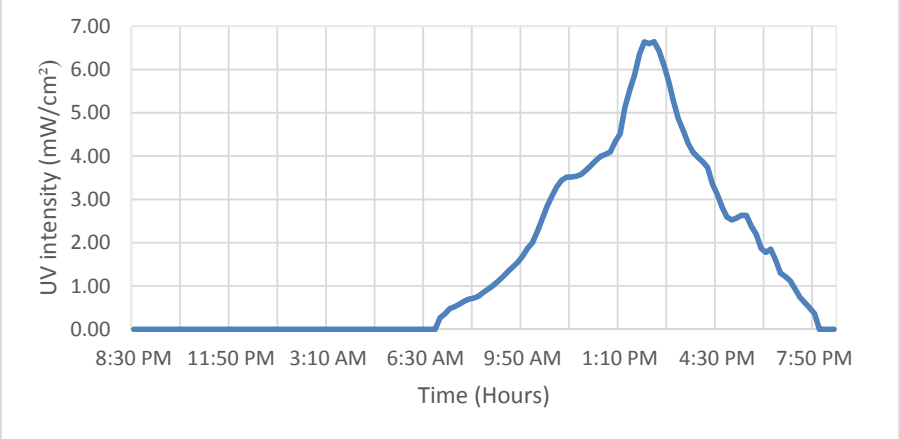


Figure 17: Averaged UV variation outside the solar still

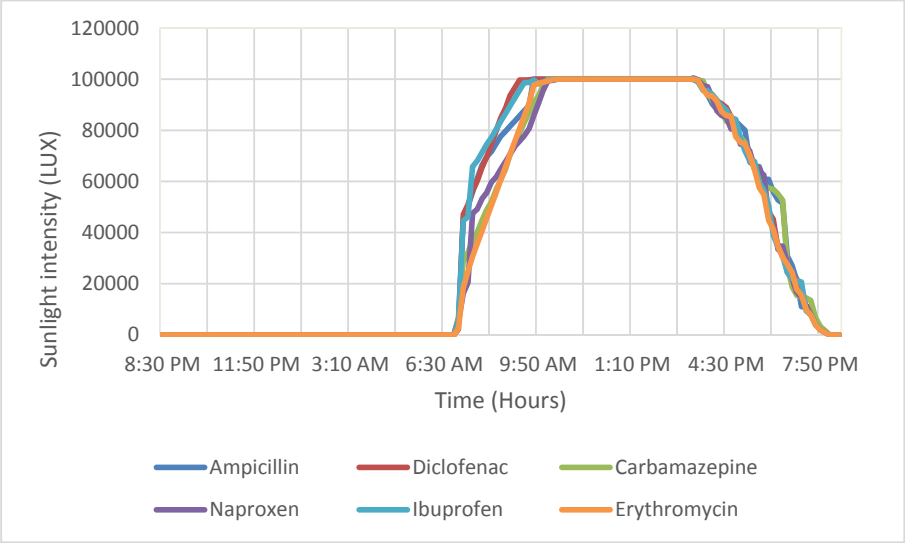


Figure 18: Averaged sunlight intensity outside the solar still for each pharmaceutical

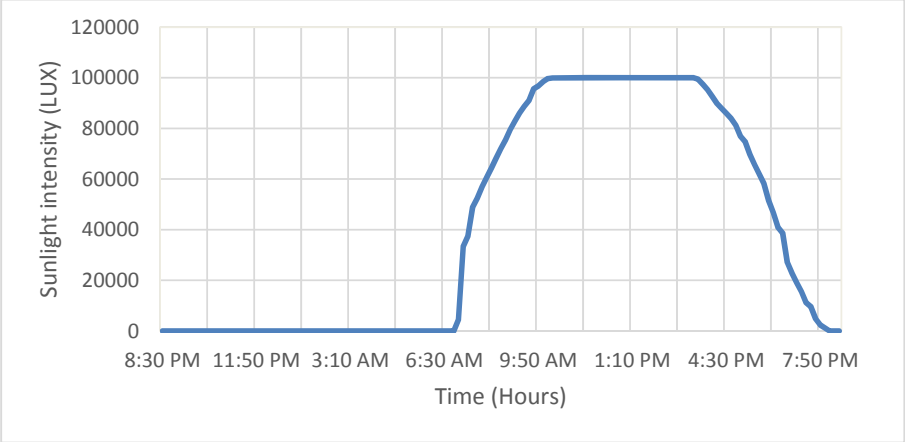


Figure 19: Averaged sunlight intensity outside the solar still

C. Data Analysis

For each pharmaceutical, the percentage transferred and degraded were calculated. This was done by carrying out a mass balance analysis and converting concentrations and volumes into quantities, masses, of pharmaceuticals. HPLC chromatographs gave the absorbance area of each sample at a specific wavelength. These values were

transformed into concentrations using calibration curves prepared from standards with known concentration. The volume of the distillate and the brine of each sample was measured at the end of the experiment, volume values measured were multiplied to their corresponding concentrations to obtain a mass value. The mass values obtained were named as: $m_{initial}$, m_{final}, $m_{distillate}$, and m_{brine}. $m_{initial}$ is the mass of pharmaceutical that was deposited at the beginning of the experiment in the solar still mode and the thermal only mode. At the end of the experiment the mass of the pharmaceuticals measured in both the distillate ($m_{distillate}$) and the brine (m_{brine}) equals the final mass (m_{final}) so $m_{final} = m_{distillate} + m_{brine}$.

During transfer degradation occurred, however, from our findings the percentage of pharmaceuticals transferred is negligible compared to the amount that was degraded. Thus, variations in concentration during degradation did not significantly interfere with the amount transferred. For the sake of practicality, when calculating percentage transferred, it was assumed that m_{final} at the end of the experiment is equal to $m_{brine} + m_{distillate}$.

Thus, percent of pharmaceutical degraded (%deg) was calculated as:

$$\%deg = \frac{m_{initial} - m_{final}}{m_{initial}} \times 100$$

The percentage of pharmaceutical transferred (%tran) was calculated as:

$$\%tran = \frac{m_{distillate}}{m_{final}} \times 100$$

In the solar still mode, parameters were not under control. The experiments were conducted to study the synergetic relationship between UV, solar radiation and temperature under uncontrolled conditions. Only %deg and %tran were calculated in the

solar still mode. These percentages were compared to the monitored values of UV, solar radiation and temperature.

Table 7: General experimental conditions

Name of Pharmaceutical	Form of Pharmaceutical Used	Tested solubility in DI water at 20 °C (mg. L^{-1})	HPLC limit of quantification (µg. L^{-1})	Initial concentration (mg. L^{-1})
Ampicillin	Capsules, anhydrous pure	150	50	50
Diclofenac	Powder, Sodium salt	150	50	50
Carbamazepine	Pills, pure	150	50	50
Naproxen	Powder, Sodium salt	15	20	5
Ibuprofen	Capsules, pure	30	25	10

1. Ampicillin

Ampicillin didn't show significant absorbance above 290 nm, hence low direct solar degradation was expected.

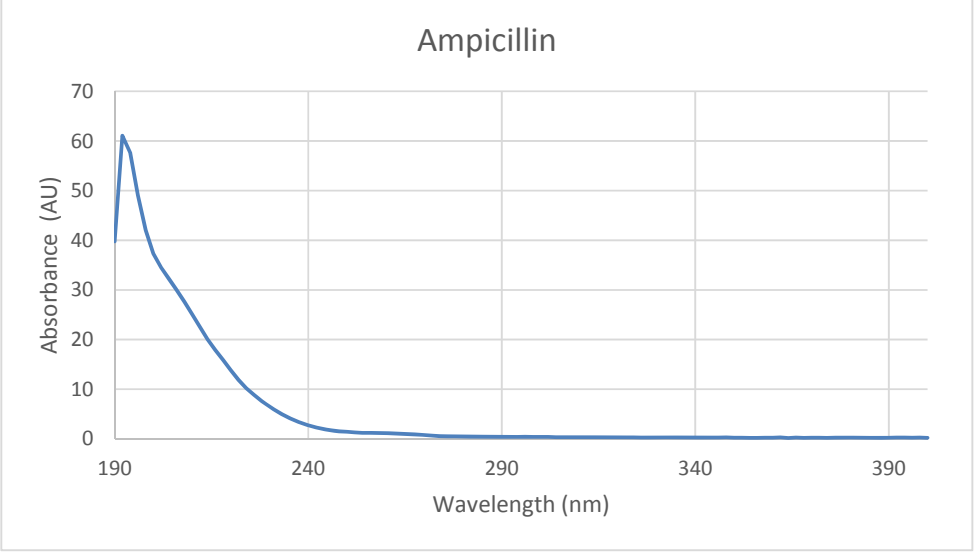


Figure 20: UV absorption spectrum of Ampicillin

a. Solar Still Mode

In the solar still mode, contrary to what was expected, Ampicillin showed moderate degradation of about 39.05 % (SD = 2.26). This observation could be attributed to the effect of temperature on the rate of degradation. No study up to date has tested Ampicillin's fate under sunlight. However, two studies tested photolysis of Ampicillin solutions exposed to artificial UV. In the first study, Lunn et al. (1994) obtained full degradation using a medium pressure Hg lamp with emission in the region of 200 – 1400 nm. While Elmolla & Chaudhuri (2009), using UV lamp that emits at 365 nm, reported insignificant degradation of Ampicillin. In the present study no Ampicillin Transfer to the distillate was detected and its photoproducts were not detectable.

b. Thermal Only Mode

At 40 °C Ampicillin showed only 1.05 % degradation, however at 50 and 60 °C degradation increased to 30.15 % and 37.84 %, respectively. Compared with the solar still degradation results (39.05 %), it could be assumed that Ampicillin mainly undergoes thermal degradation. A study done by Oliyai and Lindenbaum (1991) showed that Ampicillin could be thermally decomposed and the observed degradation rate constant increased from 74 h^{-1} at 25 °C to 500 h^{-1} at 50 °C. Also in thermal only mode no transfer was encountered in this study.

c. Light Only Mode

Ampicillin didn't show any degradation neither under concentrated sunlight nor under regular sunlight. This warrants that it is a very stable compound under light even when

intensified. Hence, it could be presumed that degradation in the solar still is predominantly due to the thermal effect.

d. Obtained Data

Table 8: Processed chromatographic data and averaged duplicates for Ampicillin

	Day 1		Day 2		Day 3	
	Concentration (mg. L^{-1})	Volume (mL)	Concentration (mg. L^{-1})	Volume (mL)	Concentration (mg. L^{-1})	Volume (mL)
Solar still						
Initial	50.3	500	48.18	500	49.46	500
Condensate	0.00	Droplets	0.00	Droplets	0.00	Droplets
Distillate	0.00	350	0.00	335	0.00	270
Brine	134.01	119	112.15	130	69.38	210
Thermal						
Temperature	40 °C		50 °C		60 °C	
Initial	50.3	1000	48.18	1000	49.46	1000
Distillate	0.00	65	0.00	205	0.00	360
Brine	55	905	46.1	730	54.9	560

During processing, samples were tested using HPLC-DAD. This measured the absorbance of light of certain wavelength specific to each pharmaceutical after separation on an analytical column. Samples of known concentrations were also tested during each HPLC run to create a calibration curve. The equation obtained from the calibration curve was used to determine the concentration of each sample. As mentioned earlier all tests except for the concentrated solar power tests were performed in duplicates. Results shown here are the average values for the purpose of analysis simplification.

Table 9: Mass balance data for Ampicillin

	Day 1	Day 2	Day 3
Solar still			
Mass initial (mg)	25.15	24.09	24.73
Mass final in distillate (mg)	0.00	0.00	0.00
Mass final in brine (mg)	15.94	14.58	14.57
Thermal			
Temperature	40 °C	50 °C	60 °C
Mass initial (mg)	50.3	48.18	49.46
Mass final in distillate (mg)	0.00	0.00	0.00
Mass final in brine (mg)	49.77	33.65	30.74

To obtain the masses shown each concentration was multiplied with the corresponding volume
Volume of the solution in the thermal only mode was half the volume of the solar still mode and thus the mass

Table 10: Percentage of degradation and percentage of transfer for Ampicillin

Solar still					
	Day 1	Day 2	Day 3	Average	SD
%deg	36.59	39.47	41.05	39.05	2.26
%tran	0.00	0.00	0.00	0.00	0.00
Thermal					
Temperature	40 °C	50 °C	60 °C		
%deg	1.05	30.15	37.84		
%tran	0.00	0.00	0.00		

This table was obtained through the following equations:

$$m_{final} = m_{distillate} + m_{brine}$$

$$\%deg = \frac{m_{initial} - m_{final}}{m_{initial}} \times 100$$

$$\%tran = \frac{m_{distillate}}{m_{final}} \times 100$$

Table 11: Percentage of degradation in the Light-only mode (CSP) for Ampicillin

62X CSP	Concentration (mg. L^{-1})	%deg
0 seconds (initial)	50	0
30 seconds	50	0
60 seconds	50	0
90 seconds	50	0
180 seconds	50	0
2 hours*	49	0

*: Under regular sunlight

2. Diclofenac

The absorption spectrum of Diclofenac (Figure 21) showed a maximum at 202 nm, tailing over and overlapping with the UV radiation of sunlight in the region of 300-330 nm.

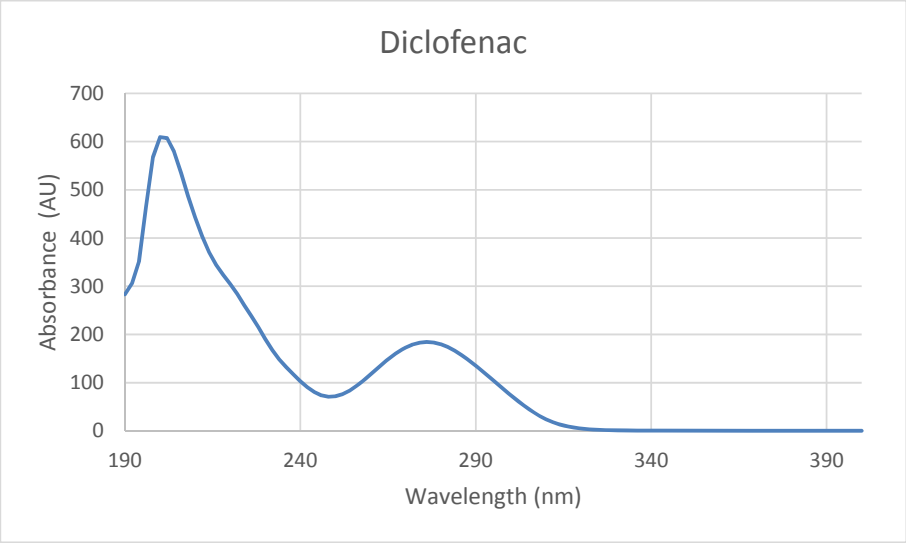


Figure 21: UV absorption spectrum of Diclofenac

a. Solar Still Mode

Six tests in the solar still mode showed an average of 50.48 % (SD = 2.63) degradation percentage in the brine accompanied by the formation of a byproduct (Rt = 6.1 minutes) that was retained in the brine without transferring. Another byproduct (Rt = 8.8 minutes) was detected only in the transferred solution and not in the brine indicating its affinity to vaporize directly after its formation. However, the parental compound 'Diclofenac' didn't show any transfer.

The observed rate of degradation of Diclofenac was relatively less than what was reported in literature depending on different experimental conditions.

For example, a study on surface water of a lake in Switzerland showed 90 % less concentration of Diclofenac in its outflow. This was accounted mainly to the effect of photolytic degradation (Buser et al., 1998). However, in the present study only deionized water (DI) was utilized in order to avoid any interference.

Another study employed a simulated sunlight irradiation source (350 W xenon lamp) instead of natural sunlight. Results showed more than 90 % of Diclofenac degradation in only 15 minutes (Zhang et al., 2011).

Moreover, a variation in Diclofenac degradation rate under sunlight was reported on a 5 days study done by Bartels et al. (2007). The rate was less than 30 % in two days, and greater than 70 % in the other three days. This discrepancy was attributed to differences in light intensity.

In addition, Agüera et al. (2005) reported more than 70 % decay of Diclofenac in DI water under natural sunlight over 30 hours.

Three main types of transformation products are formed as a result of Diclofenac photodecomposition: UV-stable products, UV-metastable products, and UV-sensible products (Bartels et al., 2007). UV-sensible products could compete with Diclofenac in the photodegradation process. The other products are recalcitrant. Hence, their formation and persistence under sunlight is the reason why the solution changed into clear brownish color at time of exposure (Figure 22).

Figure 22: Diclofenac solution color change after exposure to sunlight

These stable products could act as 'inner' filter and deprive sunlight to reach Diclofenac (Agüera et al., 2005). Therefore, the accumulation of phototransformation products inside the solar still prevented the degradation of Diclofenac from reaching completion.

b. Thermal Only Mode

Six tests (two duplicate tests for each temperature) showed low degradation of Diclofenac at 40 °C (6.76 %), this increased to reach 23.30 % at 50 °C and slightly increased to 25.65 % at 60 °C. Similarly, as in the solar mode, transfer of Diclofenac was insignificant. However, byproducts were not detected in the brine or in the distillate. In this conducted experiment, Diclofenac showed a slight thermal stability; however, it showed much greater thermal stability under buffering and complexation in other studies (Backensfeldet al., 1991; Chen et al., 2015).

The temperature gradient effect played a role in improving thermal degradation. In the present setup, the solution was heated using a heating mantle, and not an oven. This was necessary to ensure the condensation process on the cover and thus distillation; however, this could have created very slow convection currents (Figure 23).

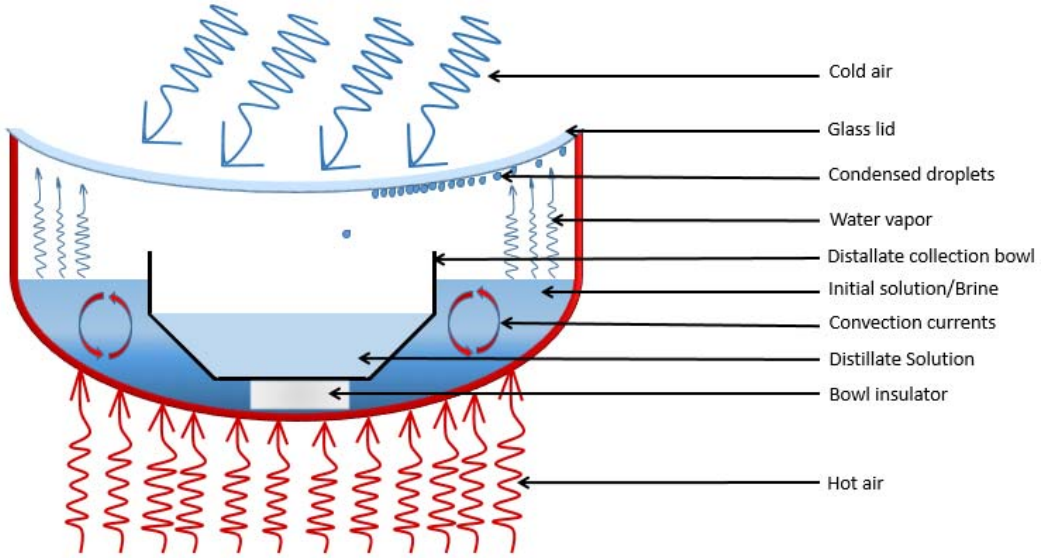


Figure 23: Diagram of thermal only mode showing convection currents

Convection currents might have played a role in increasing the rate of degradation by playing the role of slow mixing not present in stationary systems.

c. Light Only Mode

Diclofenac under light only mode showed the highest degradation rate compared to other selected pharmaceutical (Figure 24).

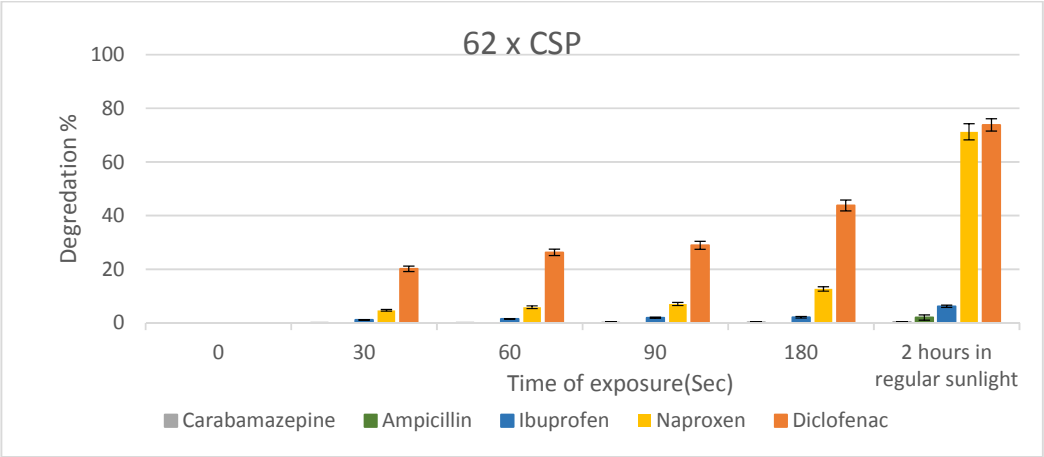


Figure 24: CSP degradation percentages

It showed 43.77 % and 73.78 % degradation over 180 seconds of concentrated sunlight and over 2 hours of regular sunlight, respectively. This observation confirmed the photosensitivity of Diclofenac. However, in the solar still setup, the photolysis of Diclofenac was impaired by an inner sunlight barrier of accumulated brown transformation products shown in figure 22.

d. Obtained Data

Data obtained from tests on Diclofenac are shown in tables 12, 13, 14 and 15.

Table 12: Processed chromatographic data and averaged duplicates for Diclofenac

	Day 1		Day 2		Day 3	
	Concentration (mg. L^{-1})	Volume (mL)	Concentration (mg. L^{-1})	Volume (mL)	Concentration (mg. L^{-1})	Volume (mL)
Solar still						
Initial	48.78	500	48.19	500	49.19	500
Condensate	0.00	Droplets	0.00	Droplets	0.00	Droplets
Distillate	0.00	210	0.00	230	0.00	225
Brine	45.65	260	54.96	230	48.60	240
Thermal						
Temperature	40 °C		50 °C		60 °C	
Initial	48.78	1000	48.19	1000	49.19	1000
Distillate	0.00	60	0.00	190	0.00	345
Brine	49.44	920	49.94	740	63.04	580

Table 13: Mass balance data for Diclofenac

	Day 1	Day 2	Day 3
Solar still			
Mass initial (mg)	24.39	24.09	24.59
Mass final in distillate (mg)	0.00	0.00	0.00
Mass final in brine (mg)	11.87	12.64	11.66
Thermal			
Temperature	40 °C	50 °C	60 °C
Mass initial (mg)	48.78	48.19	49.19
Mass final in distillate (mg)	0.00	0.00	0.00

Mass final in brine (mg)	45.48	36.95	36.57

Table 14: Percentage of degradation and percentage of transfer for Diclofenac

Solar still					
	Day 1	Day 2	Day 3	Average	SD
%deg	51.33	47.53	52.58	50.48	2.63
%tran	0.00	0.00	0.00	0.00	0.00
Thermal					
Temperature	40 °C	50 °C	60 °C		
%deg	6.76	23.30	25.65		
%tran	0.00	0.00	0.00		

Table 15: Percentage of degradation in the light-only mode (CSP) for Diclofenac

62X CSP	Concentration (mg/L)	%deg
0 seconds (initial)	50.35	0.00
30 seconds	40.21	20.15
60 seconds	37.12	26.27
90 seconds	35.78	28.93
180 seconds	28.31	43.77
2 hours*	13.20	73.78

*: Under regular sunlight

3. Carbamazepine

The absorbance spectrum of Carbamazepine showed an extension to 320 nm (Figure 25). Despite of its capability of absorbing sunlight UV radiation, its photodegradation is relatively slow (Tixier et al., 2003; Doll & Frimmel, 2003).

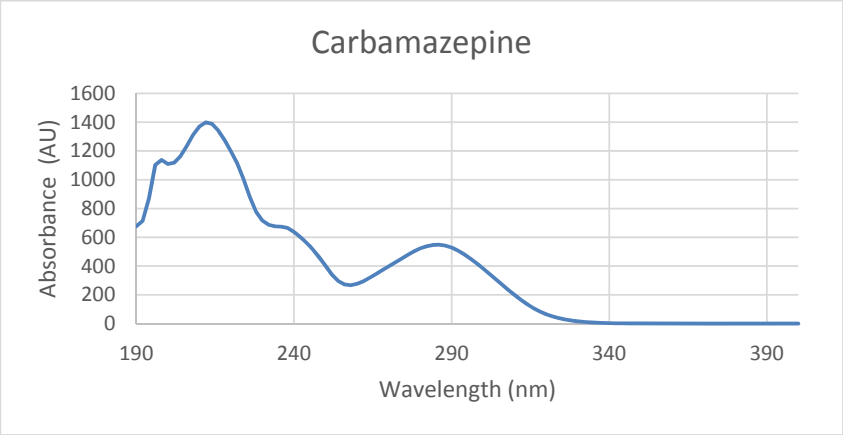


Figure 25: UV absorption spectrum of Carbamazepine

a. Solar Still Mode

In this study about half of Carbamazepine was degraded (52.16 % SD 4.65) in the brine of the solar still over a 12 hours period of sunlight exposure. However, it is reported in the literature that a longer exposure time is required to attain such degradation levels. For example, Andereozzi et al (2002) reported that the half-life of Carbamazepine under sunlight was about 122 hours in double distilled water using cooled glass reactors that were maintained at 25 °C.A lower half-life of Carbamazepine under sunlight (72 hours) was obtained by Matamoros et.al (2009) using UV transparent quartz vessels. Both solar degradation studies showed that Carbamazepine was more persistent when using the glass or quartz reactors compared to solar still.

Furthermore, artificial UV lamps which are primary used for disinfection, such as Low Pressure Hg lamps (emission: 254 nm) and Medium Pressure Hg lamps (emission: 205nm - 500nm), showed insignificant Carbamazepine removal in surface water with slightly higher rates using Medium Pressure Hg lamps (Pereira et al., 2007). However, sunlight-simulator Xe lamps had successfully induced Carbamazepine degradation showing a half-life of 115 hours, close to what was reported under natural sunlight by Andereozzi et al. (2002) and Lam & Mabury (2005).

The synergetic effect of sunlight and elevated temperatures could explain the reason why the degradation rate of Carbamazepine was higher in the present tests in comparison to these reported in the literature. A study by Yamamoto et al. (2008) showed a relation between photodegradation and external temperature. Results indicated that Carbamazepine was stable in May (T = 25 °C) over 70 hours of sunlight exposure. However, about 40 % degradation percentage over 50 hours of sunlight exposure was recorded in August (T = 39 °C). Half-life was reduced intensely from 2100 hours in May to 86 hours in August. Beside the effect of light intensity, the temperature influence is inevitable and should be taken into consideration.

The transformation products of Carbamazepine were undetectable in this study. However, it was repeatedly predicted that 10,11-epoxycarbamazepine is the major product of Carbamazepine photolysis (Lam & Mabury, 2005). Moreover, no transfer of Carbamazepine into the distillate was detected over the whole sunlight exposure period.

b. Thermal Only Mode

Carbamazepine in the thermal-only mode showed limited degradation of 4.02% and 7.55% at temperatures 40 and 50 °C, respectively. However, thermal degradation of Carbamazepine reached 57.97% at 60 °C. By comparison with the solar still mode

where a similar degradation percentage (52.16 %) was achieved, it could be assumed that the temperature had a major impact on the degradation process of Carbamazepine.

c. Light Only Mode

Insignificant degradation of Carbamazepine was obtained under both concentrated sunlight and regular sunlight with only 0.24 % and 0.4 % degradation, respectively. This indicates that Carbamazepine is slightly photosensitive, but rather its degradation in the solar still was predominately thermal.

d. Obtained Data

Carbamazepine experimental results are shown in tables 16, 17, 18 and 19.

Table 16: Processed chromatographic data and averaged duplicates for Carbamazepine

	Day 1		Day 2		Day 3	
	Concentration (mg. L^{-1})	Volume (mL)	Concentration (mg. L^{-1})	Volume (mL)	Concentration (mg. L^{-1})	Volume (mL)
Solar still						
Initial	49.99	500	49.91	500	49.34	500
Condensate	0.00	Droplets	0.00	Droplets	0.00	Droplets
Distillate	0.00	290	0.00	315	0.00	280
Brine	67.72	170	71.34	155	72.80	180
Thermal						
Temperature	40 °C		50 °C		60 °C	
Initial	49.99	1000	49.91	1000	49.34	1000
Distillate	0.00	70	0.00	200	0.00	350
Brine	52.73	910	62.78	735	36.11	575

Table 17: Mass balance data for Carbamazepine

	Day 1	Day 2	Day 3
Solar still			
Mass initial (mg)	24.99	24.95	24.67
Mass final in distillate (mg)	0.00	0.00	0.00
Mass final in brine (mg)	11.51	11.06	13.10
Thermal			
Temperature	40 °C	50 °C	60 °C
Mass initial (mg)	49.99	49.91	49.34
Mass final in distillate (mg)	0.00	0.00	0.00
Mass final in brine (mg)	47.98	46.14	20.76

Table 18: Percentage of degradation and percentage of transfer for Carbamazepine

Solar still					
	Day 1	Day 2	Day 3	Average	SD
%deg	53.94	55.67	46.89	52.16	4.65
%tran	0.00	0.00	0.00	0.00	0.00
Thermal					
Temperature	40 °C	50 °C	60 °C		
%deg	4.02	7.55	57.92		
%tran	0.00	0.00	0.00		

Table 19: Percentage of degradation in the light-only mode (CSP) for Carbamazepine

62X CSP	Concentration (mg. L^{-1})	%deg
0 seconds	50.00	0.00
30 seconds	49.97	0.06
60 seconds	49.97	0.06
90 seconds	49.91	0.10
180 seconds	49.88	0.24
2 hours*	49.78	0.40

*: Under regular sunlight

4. Naproxen

The absorption spectrum of Naproxen (Figure 26) showed a maximum at 230 nm, and extends into the solar UV spectrum of absorption wavelengths greater than 290 nm up to 340 nm indicating its possibility of direct photolysis.

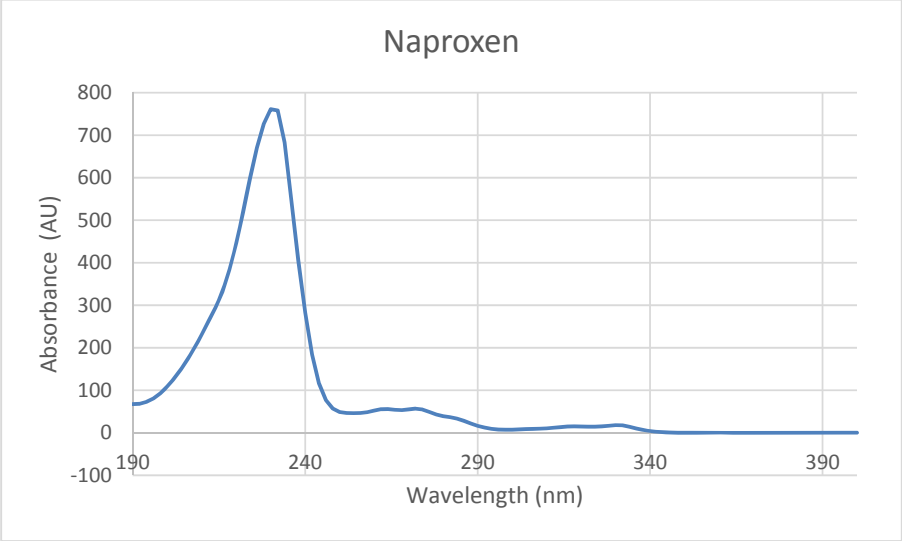


Figure 26: UV absorption spectrum of Naproxen

a. Solar Still Mode

All of the six tests in the solar still mode showed full degradation of Naproxen in the brine. This is consistent with previous studies. For instance, Kanakaraju (2013) reported that 100% of Naproxen is degraded in distilled water after 6 hours of sunlight exposure using an immersion-well reactor. Packer et al. (2003) demonstrated that Naproxen is readily photodegradable under solar radiation in both Milli-Q water and in river water over short periods of time using quartz tubes as reactor vessels. Furthermore, the employment of artificial UV light attributed to a higher degradation rate than natural

sunlight (Felis et al., 2007; Ma et al., 2014) due to the fact that only about 4 % of the solar radiation is in the UV region (Oppenländer, 2003).

As a result of Naproxen photolysis, two transformation products were detected in the brine. One of the byproducts showed Rt of 6.2 minutes and the other showed Rt of 9.5 minutes with respect to the HPLC method described in Table 2. Both byproducts were also detected in the distillate, indicating that they had higher potential of transferring compared to the mother compound "Naproxen" that didn't show any transfer at all. Naproxen is reported to be predominately susceptible to decarboxylation under direct photolysis in aqueous systems (Boscá et al., 2001). The decarboxylated intermediate readily undergoes hydroxylation and oxygenation in the presence of oxygen and two main photoproducts were predicted: ketone adduct and alcoholic adduct, as a result of the formation of a carbonyl group and a hydroxyl group at the position of decarboxylation, respectively (Arany et al., 2013; Boscá et al., 2001; Marotta et al.1, 2013). Similarly, in this study, it was assumed that these two photoproducts were formed. The photoproduct that appeared at Rt of 9.5 minutes could be the alcoholic adduct (higher polarity), and the one that appeared at Rt of 6.2 minutes could be the ketone adduct (lower polarity).

b. Thermal Only Mode

Naproxen showed insignificant thermal degradation at 40 °C and 50 °C, about 0.1 % and 1.2 %, respectively; however, this has increased intensively to reach 88.11 % at 60 °C. It could be hypothesized that a fragile bond was cleaved, most probably the carboxyl group bond, when the temperature was maintained high at 60 °C, but this suggestion was not confirmed due to insufficient data relative to the byproducts. Moreover, no transfer was encountered for Naproxen at all selected temperatures.

c. Light Only Mode

Naproxen showed the second highest degradation under light – only mode of about 12.67 % and 71.22 % over 180 seconds of concentrated sunlight and 2 hours of regular sunlight, respectively. Although Naproxen reached full degradation in the solar still, however, when the light factor contribution was over a short period it showed less degradation. This indicates that Naproxen degradation could be both light and temperature dependent.

d. Obtained Data

Experimental outcomes from tests on Naproxen are represented in tables 20, 21, 22 and 23

Table 20: Processed chromatographic data and averaged duplicates for Naproxen

	Day 1		Day 2		Day 3	
	Concentration (mg. L^{-1})	Volume (mL)	Concentration (mg. L^{-1})	Volume (mL)	Concentration (mg. L^{-1})	Volume (mL)
Solar still						
Initial	4.99	500	5.00	500	4.94	500
Condensate	0.00	Droplets	0.00	Droplets	0.00	Droplets
Distillate	0.00	280	0.00	290	0.00	295
Brine	0.00	175	0.00	170	0.00	165
Thermal						
Temperature	40 °C		50 °C		60 °C	
Initial	4.99	1000	5.00	1000	4.94	1000
Distillate	0.00	80	0.00	205	0.00	355
Brine	5.53	895	6.78	730	0.92	565

Table 21: Mass balance data for Naproxen

	Day 1	Day 2	Day 3
Solar still			
Mass initial (mg)	2.49	2.50	2.47
Mass final in distillate (mg)	0.00	0.00	0.00
Mass final in brine (mg)	0.00	0.00	0.00
Thermal			
Temperature	40 °C	50 °C	60 °C
Mass initial (mg)	4.99	5.00	4.94
Mass final in distillate (mg)	0.00	0.00	0.00
Mass final in brine (mg)	4.95	4.94	0.52

Table 22: Percentage of degradation and percentage of transfer for Naproxen

Solar still					
	Day 1	Day 2	Day 3	Average	SD
%deg	100.00	100.00	100.00	100.00	0.00
%tran	0.00	0.00	0.00	0.00	0.00
Thermal					
Temperature	40 °C	50 °C	60 °C		
%deg	0.80	1.20	89.47		
%tran	0.00	0.00	0.00		

Table 23: Percentage of degradation in the light-only mode (CSP) for Naproxen

62X CSP	Concentration	%deg
0 seconds	4.97	0.00
30 seconds	4.74	4.68
60 seconds	4.68	5.83
90 seconds	4.62	7.04
180 seconds	4.34	12.67
2 hours*	1.43	71.22

*: Under regular sunlight

5. Ibuprofen

The absorption spectrum of Ibuprofen (Figure 27) showed a maximum at 194 nm and an insignificant absorbance at wavelengths greater than 240 nm.

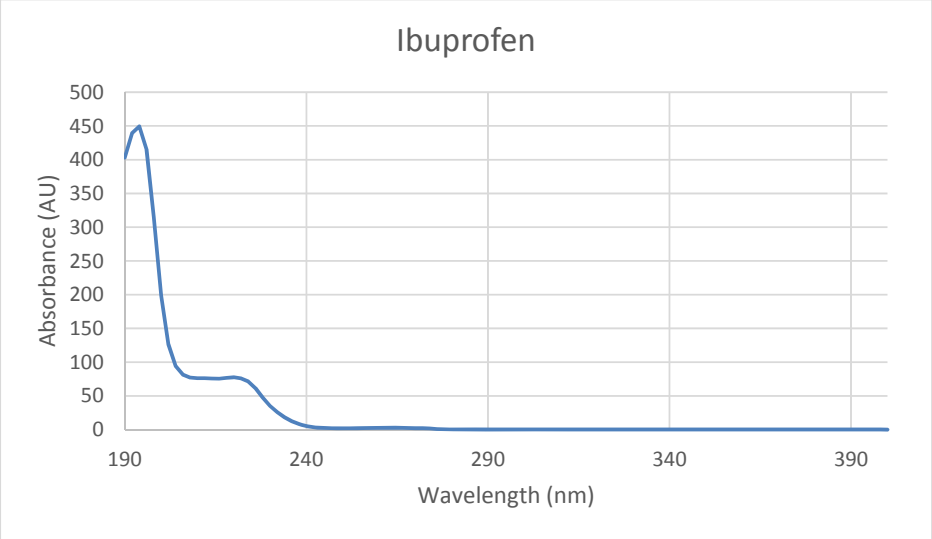


Figure 27: UV absorption spectrum of Ibuprofen

a. Solar Still Mode

Six tests in the solar still mode showed an average of 38.48 % (SD = 1.8) degradation percentage of Ibuprofen in the brine. As pharmaceuticals with chromophores that absorb at wavelengths greater than 290 nm are expected to undergo direct photolysis under sunlight (Kanakaraju, 2013), Ibuprofen showed no absorbance beyond 290 nm was therefore deemed to be relatively stable. However, it indicated instead a fair degradation. This observation could be attributed to the synergetic effect of sunlight and temperature.

In aquatic environments, the loss of Ibuprofen is predominately referred to as biotransformation rather than direct photolysis (Tixier et al., 2003).

In some laboratory experiments, direct photolysis of Ibuprofen obtained negligible results in Milli-Q water after 20 hours of exposure to Xe arc lamp that was equipped with filters to remove all wavelengths below 290 nm (Lin et al., 2005). Under these conditions, Ibuprofen was reasonably stable, since it does not absorb light with wavelength above 290 nm. However, other studies conducted on Ibuprofen in river water reported that degradation accelerated with Ibuprofen showing a half-life of 15 hours. This was attributed to the indirect photolysis that was promoted by dissolved organic matter present in the river (Lin et al., 2005).

Other laboratory studies indicated that Ibuprofen was vulnerable to photodegradation when exposed to low pressure mercury lamp emitting at 254 nm. One study showed that Ibuprofen at a high concentration (e.g. 100 mg. L^{-1}) had a 90% conversion in 4.5 hours (Epold et al., 2012), while another study reported that Ibuprofen at a low concentration (e.g. 1.0 mg. L^{-1}) resulted in about 60 % degradation in 1 hour (Giri et al., 2010).

In addition to the effect of the type of lamp used for irradiation, the effect of concentration of Ibuprofen is another influential factor. As the concentration of Ibuprofen increases, the rate of photodegradation decreases, due to reduction in the photon quantum per unit molecule (Li et al., 2015).

Yamamoto et al. (2009) conducted a study under natural sunlight using river water. The reactor vessels were 30 mL quartz tubes that are UV transparent and are not expected to highly elevate the internal temperature of the solution with respect to the external temperature. The initial concentration of Ibuprofen was 0.1 mg. L^{-1}. Although Ibuprofen didn't show any significant degradation over 50 hours of exposure, its half-life was reduced 16.5 times in August (T = 39 °C) compared to May (T = 25 °C). This implies that the temperature factor has an influence on the photolytic activity.

No study up to date has tested the synergetic effect of light and temperature on the pharmaceutical degradation, particularly for Ibuprofen. Most studies that used artificial lamps had supplied their reactor with a cooling setup to maintain temperature below 25 °C (Epold et al., 2012; Giri et al., 2010; Li et al., 2015). In addition, others who focused on the effect of natural sunlight had either studied Ibuprofen in surface water under environmental temperature variations (Tixier et al., 2003), or used transparent reactor vessels that do not warm up intensively under sunlight (Yamamoto et al., 2009), so the temperature was maintained at room level. However, in this study, the black Teflon plate placed inside the solar still is capable of increasing the temperature to a maximum level between 50 °C and 60 °C (Figure 4).

Both the high temperature values reached in the presence of sunlight and the use of a relatively low concentration of Ibuprofen (10 mg. L^{-1}), gave a clear evidence why such degradation of Ibuprofen was encountered.

Furthermore, Ibuprofen was the only pharmaceutical that showed transfer by vapor. This is because it has the highest K_H value among the other selected pharmaceuticals (K_H Ibuprofen = 6359832636 K_H Ampicillin) (Table 5). About 0.58 % (SD = 0.32) of the initial amount of Ibuprofen was transferred to the solar still distillate.

b. Thermal Only Mode

Six tests (two duplicate of each temperature) in the dark showed low degradation of Ibuprofen, around 1 %, at T = 40, 50 and 60 °C. This indicates that temperature alone, even at high values, is not enough to induce Ibuprofen degradation without the aid of sunlight. In addition, transfer was also obtained in the thermal mode at all studied temperatures with a maximum of 2.13 % transfer at T = 50 °C (Table 25).

The stability of Ibuprofen at high temperatures (T = 20, 40, 60 and 80 °C) was also reported in a thermodegradation study by Mendez-Arriaga et al. (2008). However, in the study samples were taken when the set point was reached and they were not left for long durations at a particular temperature.

c. Light Only Mode

The degradation of Ibuprofen under light without temperature interference was very minor confirming that Ibuprofen is relatively stable under light. For example, only 2.1 % were degraded over 180 seconds under concentrated light and 6.2 % over 2 hours of exposure to regular sunlight.

This implies that neither light factor alone nor temperature factor alone is sufficient for inducing significant decomposition of Ibuprofen, but rather the synergetic effect of both factors is crucial for achieving better Ibuprofen degradation as in the case of the solar still.

d. Obtained Data

Experimental results for Ibuprofen Experiments are presented in tables 24, 25, 26 and 27.

Table 24: Processed chromatographic data and averaged duplicates for Ibuprofen

	Day 1		Day 2		Day 3	
	Concentration (mg. L^{-1})	Volume (mL)	Concentration (mg. L^{-1})	Volume (mL)	Concentration (mg. L^{-1})	Volume (mL)
Solar still						
Initial	10.07	500	10.30	500	10.40	500
Condensate	0.29	Droplets	0.20	Droplets	0.50	Droplets
Distillate	0.32	76.5	0.18	94.4	0.54	100
Brine	8.13	391	8.53	359.9	8.69	370
Thermal						
Temperature	40 °C		50 °C		60 °C	
Initial	10.07	1000	10.30	1000	10.40	1000
Distillate	0.96	85	1.04	210	0.52	350
Brine	11.00	905	14.15	720	17.89	575

Table 25: Mass balance data for Ibuprofen

	Day 1	Day 2	Day 3
Solar still			
Mass initial (mg)	5.03	5.15	5.2
Mass final in distillate (mg)	0.02	0.02	0.05
Mass final in brine (mg)	3.18	3.07	3.21
Thermal			
Temperature	40 °C	50 °C	60 °C
Mass initial (mg)	10.07	10.30	10.40
Mass final in distillate (mg)	0.08	0.22	0.18
Mass final in brine (mg)	9.95	10.19	10.29

Table 26: Percentage of degradation and percentage of transfer for Ibuprofen

Solar still					
	Day 1	Day 2	Day 3	Average	SD
%deg	36.78	40.38	38.27	38.48	1.80
%tran	0.39	0.39	0.96	0.58	0.32
Thermal					
Temperature	40 °C	50 °C	60 °C		
%deg	1.19	1.06	1.06		
%tran	0.79	2.13	1.73		

Table 27: Percentage of degradation in the light-only mode (CSP) for Ibuprofen

62X CSP	Concentration	%deg
0 seconds (initial)	10.00	0.00
30 seconds	9.89	1.10
60 seconds	9.85	1.50
90 seconds	9.81	1.90
180 seconds	9.79	2.10
2 hours*	9.38	6.20

*: Under regular sunlight

CHAPTER 4
CONCLUSION, LIMITATIONS AND RECOMMENDATIONS

A. Conclusion

This study demonstrated that transfer and degradation of pharmaceuticals are most dependent on the pharmaceutical type. However, transfer percentage remains very low compared to initial concentration with the maximum value obtained being 2.13% in the case of Ibuprofen which was the only pharmaceutical that showed transfer in its initial form. What is to be noted is that Naproxen and Diclofenac did not transfer in their initial form, however after exposure to sunlight, their byproducts of degradation transferred. In the case of Naproxen, high intensity solar radiation resulted in an array of up to 10 different unidentified byproducts, where some of these might be more toxic than their parent compound.

In addition, the research also showed that in the case of Ampicillin, Naproxen and Carbamazepine, degradation is characterized by a temperature threshold beyond which a high rate degradation of the compounds is induced. Naproxen, Ibuprofen and Carbamazepine required both high temperature and sunlight combined to degrade effectively. Concentrated solar power accelerated the degradation of Diclofenac, Naproxen and Ibuprofen with a three-minutes-degradation percentage of 43.7%, 12.7% and 2.1% respectively.

B. Limitations and Recommendations

Limitations were faced during the chemical analysis and identification of the degradation product compounds. This was mainly due to the absence of a reliable mass spectrometer. Indeed, to define the degradation pathways, a mass spectrometer equipped

with a library is necessary to identify product compounds. Therefore identification of the compound would allow us to obtain their corresponding standards to determine their concentrations. In turn, kinetics of the degradation reactions could be determined.

The light-only experimental mode, done using concentrated solar power, would have benefited from more consistent results if it had been automated. The solar concentrator we used was manually directed towards sunlight. Automation could have been achieved by equipping the solar concentrator with the heliostat and two-axis rotors. This would have enabled a larger number of experimental tests. In addition, this would allow for a continuous flow process instead of a batch process. A continuous flow design is more practical and is more akin to a commercial setup.

The rate of degradation observed in some pharmaceuticals during the light-only experiment would be much higher if a catalyst was used. Additionally, the rate of photocatalysis as well as photolysis both depend on the solution's temperature, where the solution temperature increases with prolonged exposure time. A higher exposure time therefore might lead to more effective degradation process.

Studying a mixture of pharmaceuticals and investigating the cocktail effect is highly recommended for future research.

Concentrated solar power, feasibly affordable and low tech, might be used along with an appropriate catalyst to treat effluents of contaminated sources such as wastewater originating from pharmaceutical production and medical facilities.

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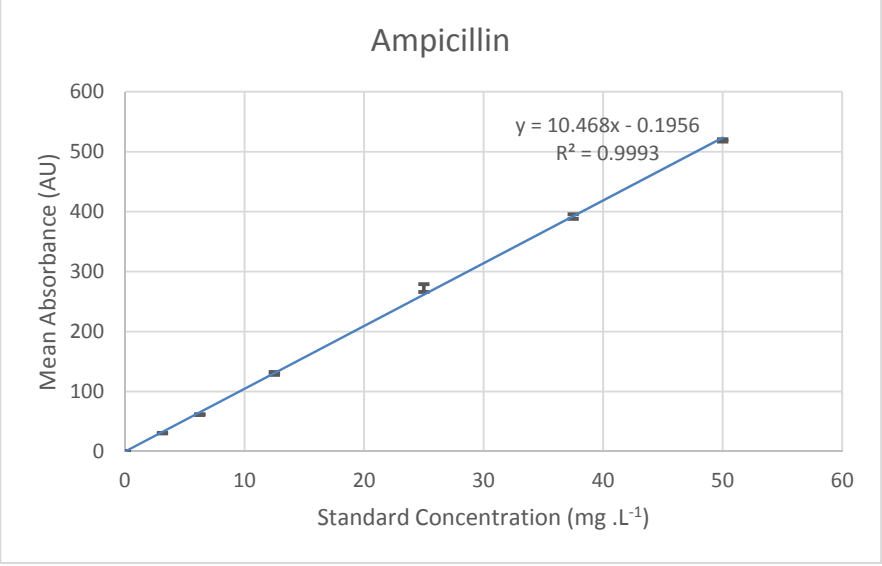
APPENDIX I
STANDARDS DATA AND CURVES

Ampicillin

Ampicillin						
Concentration (mg. L^{-1})	Peak Area 1 (AU)	Peak Area 2 (AU)	Peak Area 3 (AU)	Mean Peak Area (AU)	Standard Deviation (AU)	Error at 95% confidence interval (AU)
0	0	0	0	0	0	0
3.125	30.5	30.2	30.5	30.4	0.173205	0.4303
6.25	61.7	61.7	61.5	61.63333	0.115470	0.286866667
12.5	130.5	131	129	130.1666	1.040833	2.58578119
25	275.2	270	272	272.4	2.622975	6.51635803
37.5	392.3	390	393	391.7666	1.569500	3.899171258
50	519.7	518	519	518.9	0.854400	2.122619496

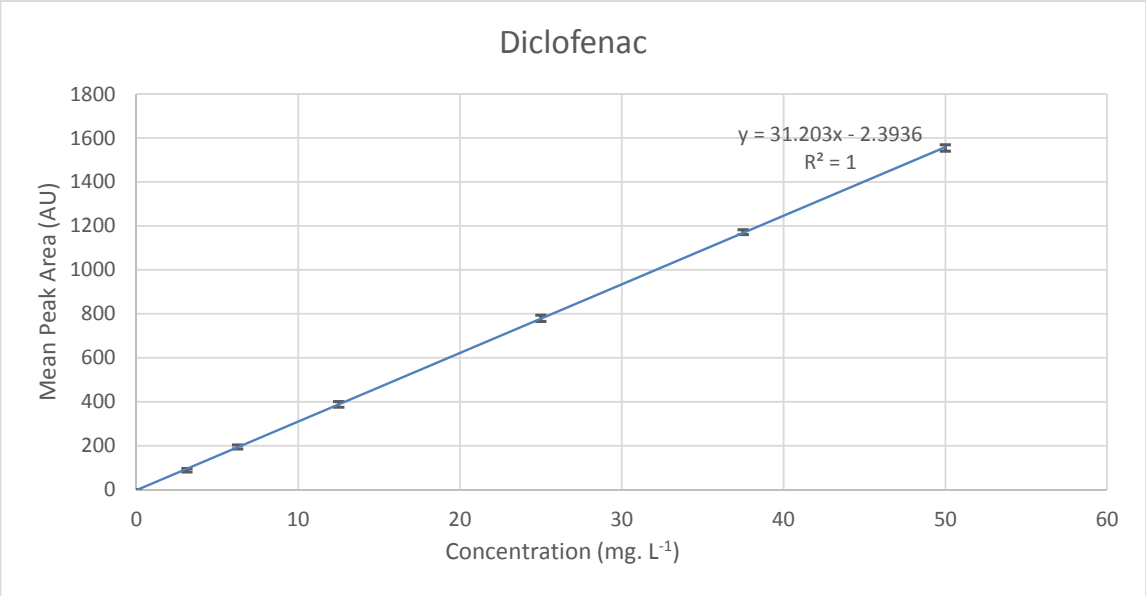
Slope	10.46798793	-0.195601552	Y intercept
Slope uncertainty	0.119994712	3.121288979	Y intercept uncertainty
Correlation coefficient (R^2)	0.999343428	5.572728106	Standard error for Y estimate



Diclofenac

Diclofenac						
Concentration (mg. L^{-1})	Peak Area 1 (AU)	Peak Area 2 (AU)	Peak Area 3 (AU)	Mean Peak Area (AU)	Standard Deviation (AU)	Error at 95% confidence interval (AU)
0	0	0	0	0	0	0
3.125	88.88	87.33	89.3	88.50333333	1.037609432	2.577772757
6.25	194.86	193.3	195.7	194.62	1.217866988	3.02559349
12.5	389.82	388.2	386.3	388.1066667	1.761855083	4.3770439
25	780.66	777.2	780.4	779.42	1.926966528	4.787236572
37.5	1170.83	1169.83	1172.7	1171.12	1.456811587	3.619212688
50	1556.7	1553.2	1553.3	1554.4	1.992485885	4.950008812

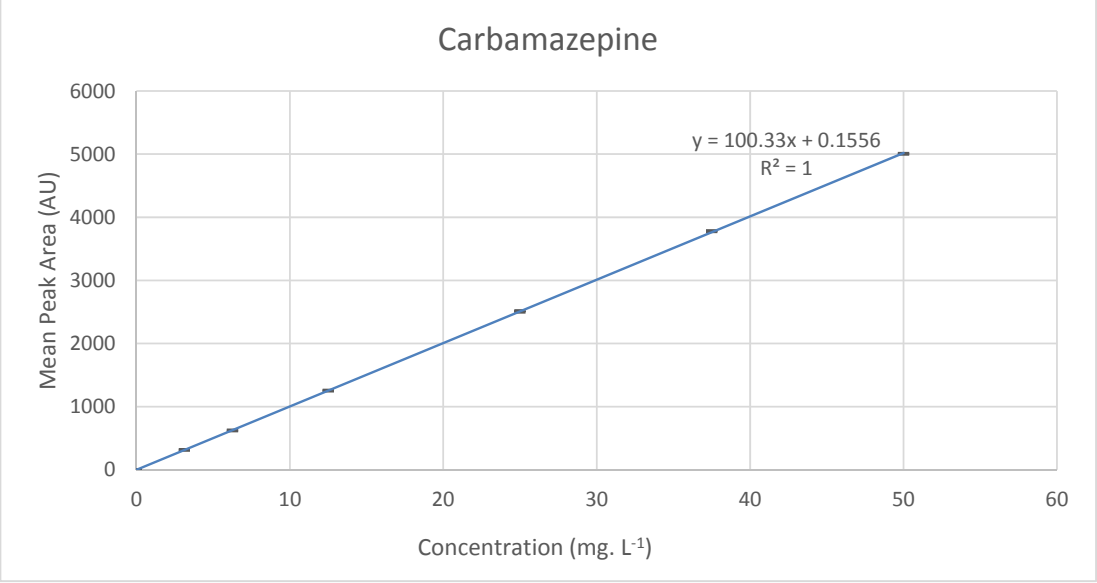
Slope	31.20316274	-2.393570505	Y intercept
Slope uncertainty	0.085861889	2.233429813	Y intercept uncertainty
Correlation coefficient (R^2)	0.999962142	3.987550392	Standard error for Y estimate



Carbamazepine

Carbamazepine						
Concentration (mg. L^{-1})	Peak Area 1 (AU)	Peak Area 2 (AU)	Peak Area 3 (AU)	Mean Peak Area (AU)	Standard Deviation Standard Deviation (AU)	Error at 95% confidence interval (AU)
0	0	0	0	0	0	0
3.13	315.5	314.4	314	314.6333333	0.776745347	1.929698142
6.25	622.32	623	621.12	622.1466667	0.95191036	2.364867278
12.50	1255.01	1253	1254	1254.003333	1.005004146	2.496770199
25.00	2508.64	2506	2509	2507.88	1.638047618	4.069464285
37.50	3779.04	3780	3778	3779.013333	1.000266631	2.48500061
50.00	5005.2	5004	5006	5005.066667	1.006644591	2.500845621

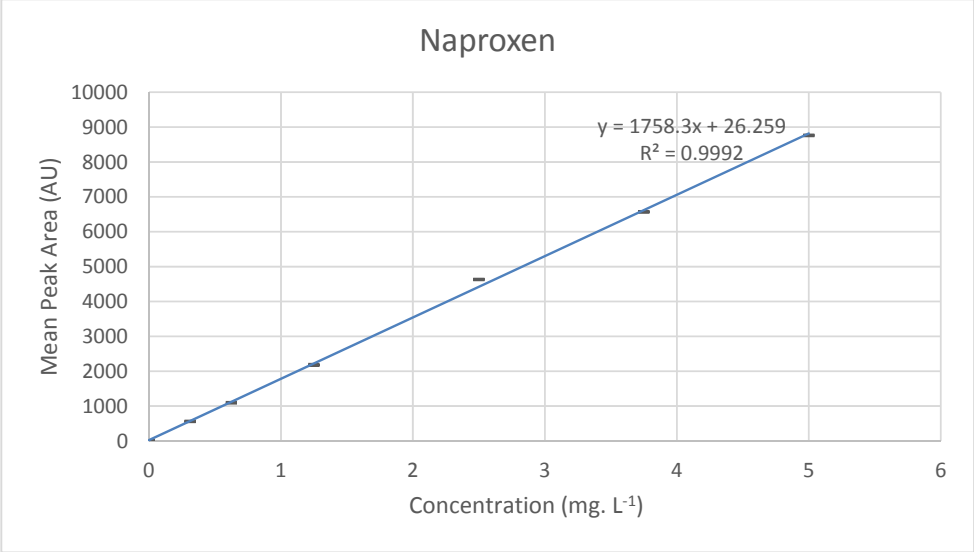
Slope	100.3285865	0.155646831	Y intercept
Slope uncertainty	0.200371832	5.212049598	Y intercept uncertainty
Correlation coefficient (R^2)	0.999980057	9.305557891	Standard error for Y estimate



Naproxen

Naproxen						
Concentration (mg. L^{-1})	Peak Area 1 (AU)	Peak Area 2 (AU)	Peak Area 3 (AU)	Mean Peak Area (AU)	Standard Deviation (AU)	Error at 95% confidence interval (AU)
0	0	0	0	0	0	0
0.3125	562.19	561.3	563.4	562.2967	1.054056	2.833489106
0.625	1097.95	1096	1098	1097.317	1.140541	8.500467318
1.25	2184	2182	2186	2184	2	4.968676417
2.5	4632.6	4632	4634	4632.867	1.02632	2.549726705
3.75	6570.68	6572	6570	6570.893	1.016923	2.526381819
5	8764.11	8762	8763	8763.037	1.055478	2.622163764

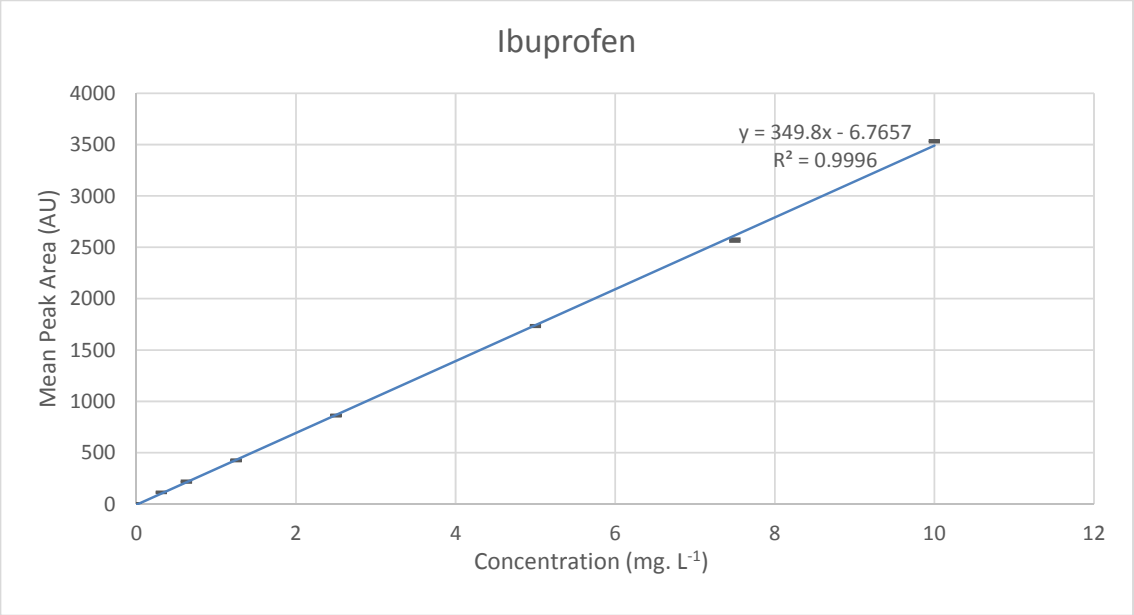
Slope	1758.258	26.25908	Y intercept
Slope uncertainty	22.19277	57.72758	Y intercept uncertainty
Correlation coefficient (R^2)	0.999204	103.0664	Standard error for Y estimate



Ibuprofen

Ibuprofen						
Concentration (mg. L^{-1})	Peak Area 1 (AU)	Peak Area 2 (AU)	Peak Area 3 (AU)	Mean Peak Area (AU)	Standard Deviation (AU)	Error at 95% confidence interval (AU)
0	0	0	0	0	0	0
0.3125	113.65	113	114	113.55	0.507444578	1.260663954
0.625	219	218	219.5	218.8333333	0.763762616	1.897444649
1.25	426.66	425.7	427	426.4533333	0.674190873	1.674918146
2.5	862	861.5	862.5	862	0.5	1.242169104
5	1733.62	1732.7	1734	1733.44	0.668430999	1.66060867
7.5	2570.41	2571	2568	2569.803333	1.589349972	3.948482862
10	3532	3531	3533	3532	1	2.484338208

Slope	349.8006644	-6.765695439	Y intercept
Slope uncertainty	2.68621499	13.0755078	Y intercept uncertainty
Correlation coefficient (R^2)	0.999646298	26.47738247	Standard error for Y estimate



Appendix II
Supplementary tables and figures

Table 1: Summary of results for solar still and thermal only modes

		Solar still	40 °C	50 °C	60 °C
Ampicillin	%deg	39.05±2.26	1.05	30.15	37.84
	%tran	0.00	0.00	0.00	0.00
Diclofenac	%deg	50.48±2.63	6.76	23.30	25.65
	%tran	0.00	0.00	0.00	0.00
Carbamazepine	%deg	52.16±4.65	4.02	7.55	57.97
	%tran	0.00	0.00	0.00	0.00
Naproxen	%deg	100.00±0.00	0.10	1.2	88.11
	%tran	0.00	0.00	0.00	0.00
Ibuprofen	%deg	38.48±1.8	1.19	1.06	1.06
	%tran	0.58±0.32	0.79	2.13	1.73

Table 2: Summary of results for solar only mode

CSP 62X	% degradation				
	Ampicillin	Diclofenac	Carbamazepine	Naproxen	Ibuprofen
0 seconds (initial)	0.00	0.00	0.00	0.00	0.00
30seconds	0.00	20.15	0.06	4.68	1.10
60seconds	0.00	26.27	0.06	5.83	1.50
90seconds	0.00	28.93	0.10	7.04	1.90
180seconds	0.00	43.77	0.24	12.67	2.10
2 hours*	0.00	73.78	0.40	71.22	6.20

***: Under regular sunlight**

Table 3: Presence and properties of byproducts

	Byproduct	Ampicillin	Diclofenac	Carbamazepine	Naproxen	Ibuprofen
Solar Distillate	Presence	No	Yes	No	yes	No
	Number, Retention time	n/a	1@8.85min	n/a	2@6.2 and 9.5 minutes	n/a
Solar Brine	Presence	No	Yes	No	Yes	No
	Number, Retention time	n/a	1@6.11min	n/a	2@6.2 and 9.5 minutes	n/a
Thermal Distillate	Presence	No	No	No	No	No
	Number, Retention time	n/a	n/a	n/a	n/a	n/a
Thermal Brine	Presence	No	No	No	No	No
	Number, Retention time	n/a	n/a	n/a	n/a	n/a
CSP	Presence	No	Yes	No	Yes	No
	Number, Retention time	n/a	numerous	n/a	numerous	n/a

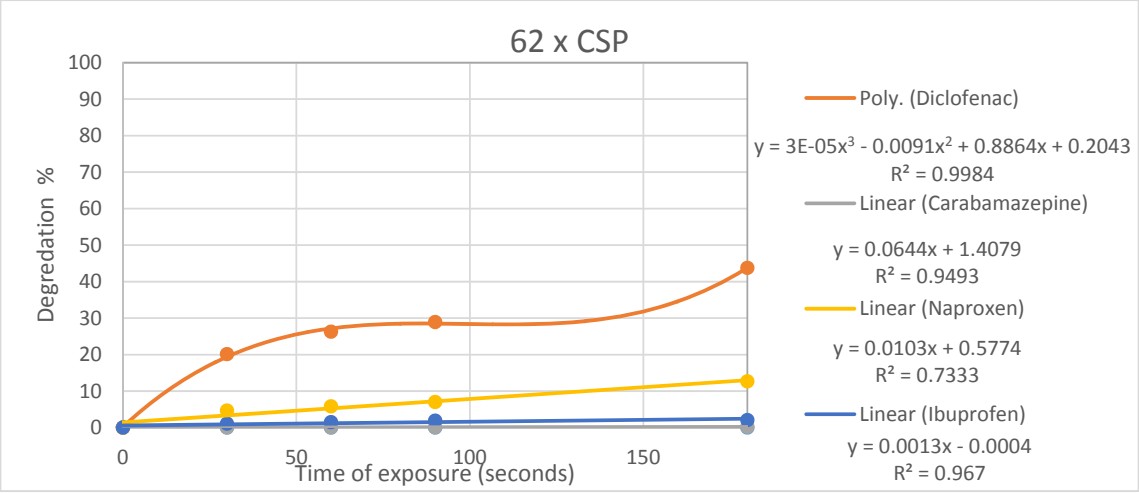


Figure 1: CSP degradation percentages

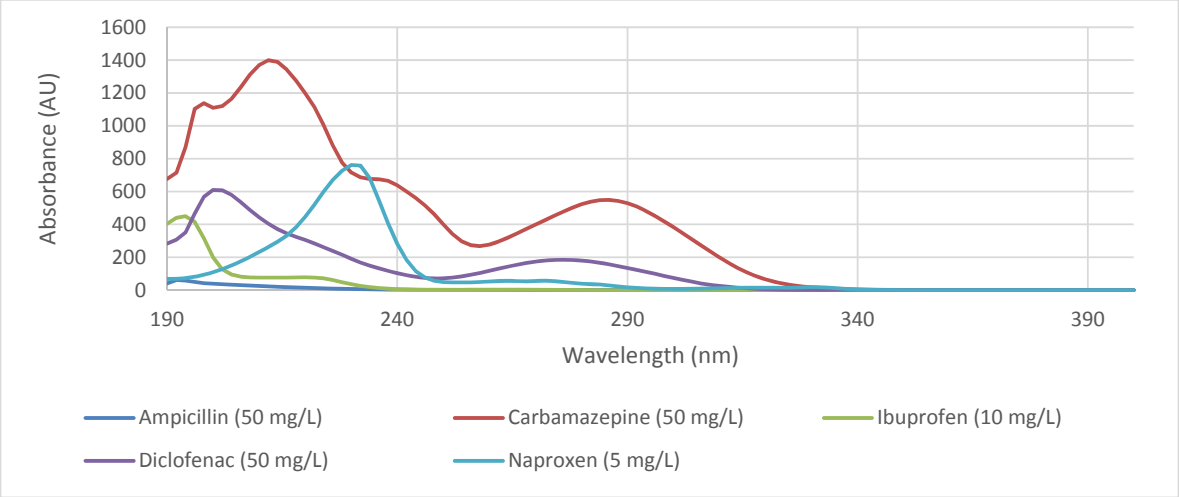


Figure 2: Absorbance spectrums of initial samples used