Chapter 1: Introduction

Since the appearance of man's chemical abilities, we have systematically sent to our water systems residues that are foreign to the natural recycling of components, making degradation of these materials improbable in the ecosystem's routes of operation. The presence of these alien compounds in a natural system disrupts the cycles and its adverse effects are included in our conception of "water pollution".

Water pollution by alien compounds or alien amounts of compounds in water systems can trace its sources to several anthropogenic activities. Agriculture is responsible, according to the United Nations Environmental Programme, "for 70% of all water use" and "shortage of [...] agriculturable [water] supplies now affect more than one-quarter of the world's population." [UNEP, 2000]

In agriculture, the use of pesticides and fertilizers have enabled a mass production of food, and have resulted in a mass production of persistent compounds that often end up dissolved in our waters. The use of pesticides for the last 60 years has released substantial amounts of organic and inorganic molecules that either do not exist in nature (man-engineered) or exist in minimal quantities. Pesticide-related concerns in Mexico include water pollution due to runoff of the cultivated land, poor handling of the pesticide by the peasants, little or no environmental monitoring, lack of safety measures and emergency plans, the disposal and non intended reuse of the containers.

Agrochemical empty containers, unlike other forms of packaging, are considered a different solid waste. The Mexican legislation in its *Norma Oficial Mexicana* (Mexican Official Norm) NOM-052-SEMARNAT-1993 annex 3, classifies "containers and drums used in the transport of hazardous materials and residues" as a hazardous residue [NOM-052-SEMARNAT-1993, 1993]. The same norm classifies in its annex 2, residues from the production of 2,4-D and atrazine as hazardous (Annex A). Published in 2003, the *Ley General para la Prevención y Gestión Integral de los Residuos* (LGPGIR) states in Article 33 Fraction IX that: "pesticides and the containers that have residues of pesticide will be subject to a management plan" [SEMARNAT, 2003].

Rinse water from a pesticide container still conserves important amounts of active chemicals that may harm the environment where it is released. To guarantee neutrality towards the living population in ecosystems there must be degradation of pesticides present in the rinsate from agrochemical containers. In urban environments, with the maintenance of gardens, parks, golf courses and other green areas, the rinsate is generally poured into the municipal sewage system, adding to the mix of compounds to be treated. In cities with municipal waste water treatment facilities, these compounds are toxic to the microbiological degradation stages, decreasing the plant's efficiency. In cities or towns without waste water treatment plants, sewage and its array of pollutants normally goes directly to superficial water systems (i.e. rivers, lakes, ocean).

Since traditional degradation techniques are ineffective in breaking down certain pesticides, alternative methods include those denominated advanced oxidation processes (AOPs). These include a series of methods that promote ·OH radicals to completely oxidize compounds to simpler inorganic acids, CO_2 and H_2O. Among the AOPs, solar photocatalysis presents itself as an energy efficient, sustainable technique.

Solar photocatalysis uses a combination of solar radiation plus a catalyst (i.e. Fenton reagent, TiO_2) to promote the liberation of ·OH radicals, non selectively attacking the stable organic or inorganic compounds and mineralizing them to easily degradable compounds.

Solar photocatalysis prepares water for conventional treatment or, at the very least, attenuates its toxicity in rural environments where it is released directly to the water systems.

Chapter 2 establishes the objectives, which in summary is to determine the best engineering parameters for a solar photocatalytic plant at a pilot level. The following three chapters (3, 4 and 5) give the theoretical bases in which the system is based (pesticides, hydraulics, and advanced oxidation processes respectively). Chapter 6 describes the work plan followed throughout the development of this work. It gives insight on the activities carried out and the materials used. Results and their discussion are given in chapter 7. It is here where the detailed assemblage for the plant is given with schemes. Costs and suppliers for selected parts are given. Also, the application of the selected figure-of-merit is explained and it is used to compare between the catalyst-pesticide systems. Two pesticides were used as degradation models, 2,4 dichlorophenoxyacetic acid (2,4-D) and atrazine using Fenton and a Fenton-like reagent (Co-PMS). Finally, chapter 8 points out the conclusions and suggests future investigation lines.