



Comparison of an inexpensive photodegradation system with high performance oxidation process

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1- Introduction

The continuous investments in scientific research and technological development, have brought many benefits to modern society, such as the defeat of many diseases, the improvement of prosperity and literacy in most countries of the world and the solution to many problems related to lack of food and hygiene. On the other hand, the economic growth of society has caused pollution of air, water and soil. In particular, water pollution is a serious problem as it becomes increasingly difficult to find uncontaminated sources to exploit.

An effective method that can provide remedy to the problem of this kind of pollution is to purify wastewaters so that they can be reused for other applications (e.g. in agriculture, for industrial production, etc.). Decontamination would be necessary to clean these waters from the presence of synthetic substances (e.g. pesticides, herbicides, surfactants, etc..) that can be harmful for the environment and human health. The above mentioned pollutants often survive the normal purifying process in the traditional methods of water treatment, therefore it has been necessary to introduce more effective systems of degradation.

Among the more advantageous systems in the treatment of these pollutants (especially in urban wastewater) there are AOPs (Advance Oxidation Processes) and in particular the photodegradation, a technique based on the employment of various electromagnetic radiations of appropriate wavelength (often in the UV area) and semiconductor catalysts (mainly TiO₂) that can degrade polluting molecules. Due to its high intrinsic efficiency, heterogeneous photocatalysis is widely utilised in wastewater treatment. We must distinguish the degradation, i.e. the breakage of molecules in smaller fragments, from mineralisation, which is the complete destruction of the molecule with the formation, through complete oxidation, of the corresponding oxides at the highest oxidation state [1].

Literature describes numerous systems and methods for catalytic photodegradation of aqueous matrices. These systems seem to become ever more complex with method able to improve the efficiency of some steps, but also making them harder to handle and more expensive in terms of industrial installation and maintenance [2].

The aim of our work was to compare two systems of photodegradation. The first one (elaborate and expensive), consists of a 4W UV-C lamp, a photocatalyst like TiO₂ P25 from Degussa a microwave generator that radiates the sample and a complex recirculation and air flow method, while the second system, simpler and cheaper, consists of a 150W lamp with solar spectrum and the same type of TiO₂ used in the previous technique. From such comparison we tried to calculate the efficiency of photocatalysis for each system, according to operating time necessary to obtain the same degree of degradation. Ultimately we tried to evaluate whether a system so simple and cheap, although not very efficient, is suitable for the treatment of pollutants within an acceptable timeframe.

2- Materials and methods

The simple system of degradation, shown in **figure 1**, is constituted by:

- 1) a Osram Ultra-Vitalux lamp with emission spectrum (**figure 2**), intensity and focusing near the summer sun in the Mediterranean places and a wattage of 300W;
- 2) a beaker containing the degrading solution (an aqueous solution of our molecules and TiO₂ P25 Degussa in concentration of 50 mg/L). The beaker is placed 600mm below the lamp;
- 3) a mechanic stirrer from IKA Labortechnik that stirs and mixes the air and the solution for better degradation;
- 4) an aluminum sheet was placed below the reactor in order to convey, by reflection, more light to the beaker;
- 5) the stirrer and the lamp were connected to normal 230V AC.

The more complex system of degradation (**figure 3**)[3] is constituted by:

- 1) a cell in PMMA, containing an Heraeus NK4/4, low pressure Hg vapors lamp mainly emitting at 185 and 254 nm and with a electric power of 4W. The emission spectra is shown in **figure 4**;
- 2) a cell built in fused silica with transmittance from 180 to 1200 nm, volume of 50 mL and with holes for circulation tubing and air flows;
- 3) a laboratory microwave digesting system modified by CEM Italy, both in the firmware -to obtain a pulsated operation with a duty cycle of 5%- and in the hardware -to obtain the window as needed by the internal lamp. Inside the device was put a dichroic overvoltage lamp (Osram Decostar 35) without UV filter. The lamp's emission spectra is shown in **figure 5**;
- 4) one dual circuit peristaltic circulation pump, consisting of two teflon tubes which allows the solution (100 mL) to circulate in about 6 minutes and maintains the catalyst suspension;
- 5) a power supply to feed the Heraeus NK4/4 lamp and quartz dichroic overvoltage internal lamp in A.C.;
- 6) membrane air pump with splitter to insufflate the filtered (0.47 µm) room air, in the outside cell and the inside quartz cell. The air pump has a triple purpose: (i) to remove produced CO₂, (ii) to guarantee an oxygen excess in solution, (iii) to keep the catalyst in suspension. The 184.9 wavelength produce ozone that helps the degradation;
- 7) the digital thermometer allows to avoid the thermal microwave effect, monitoring by eyes the temperature variation (always under 40 °C);
- 8) the magnetic stirrer, from VELP Scientific, under the external cell, maintain the TiO₂ suspension.

The 4 molecules that we selected for our analysis are Acid Green 25 (C.I. 61570, CAS Number 4403-90-1), Phenol Red (CAS Number 143-74-8), Tartrazine (C.I. 19140, CAS Number 1934-21-0) and Naphthalene (CAS Number 91-20-3). These molecules are easy to find, solubilize and analyze because a simple UV-Vis spectrophotometer (Perkin-Elmer Lambda 16) followed the progress of the photodegradation [4]. We used the TiO₂ P25 Degussa because in a previous work it has shown great reactivity [5].

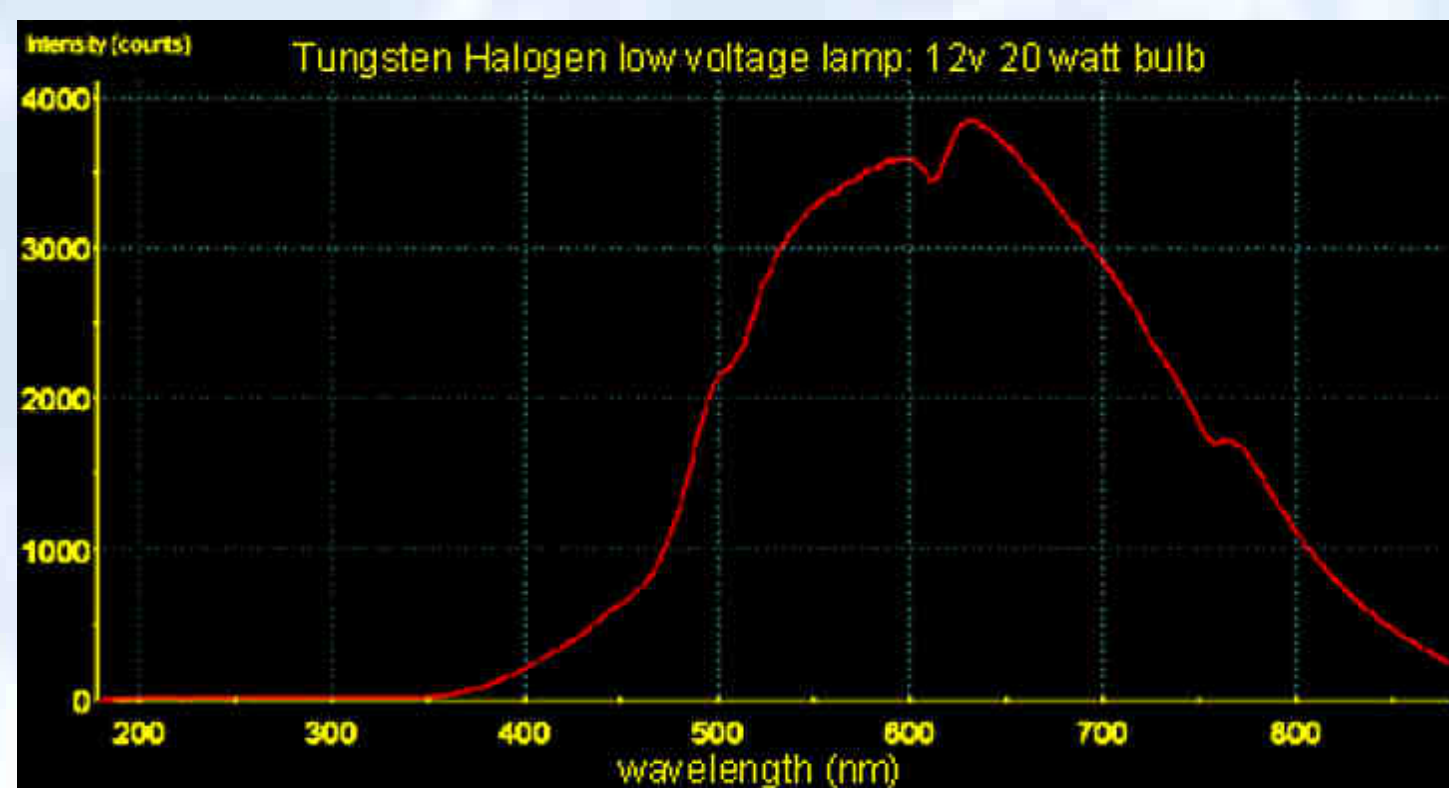


Figure 5

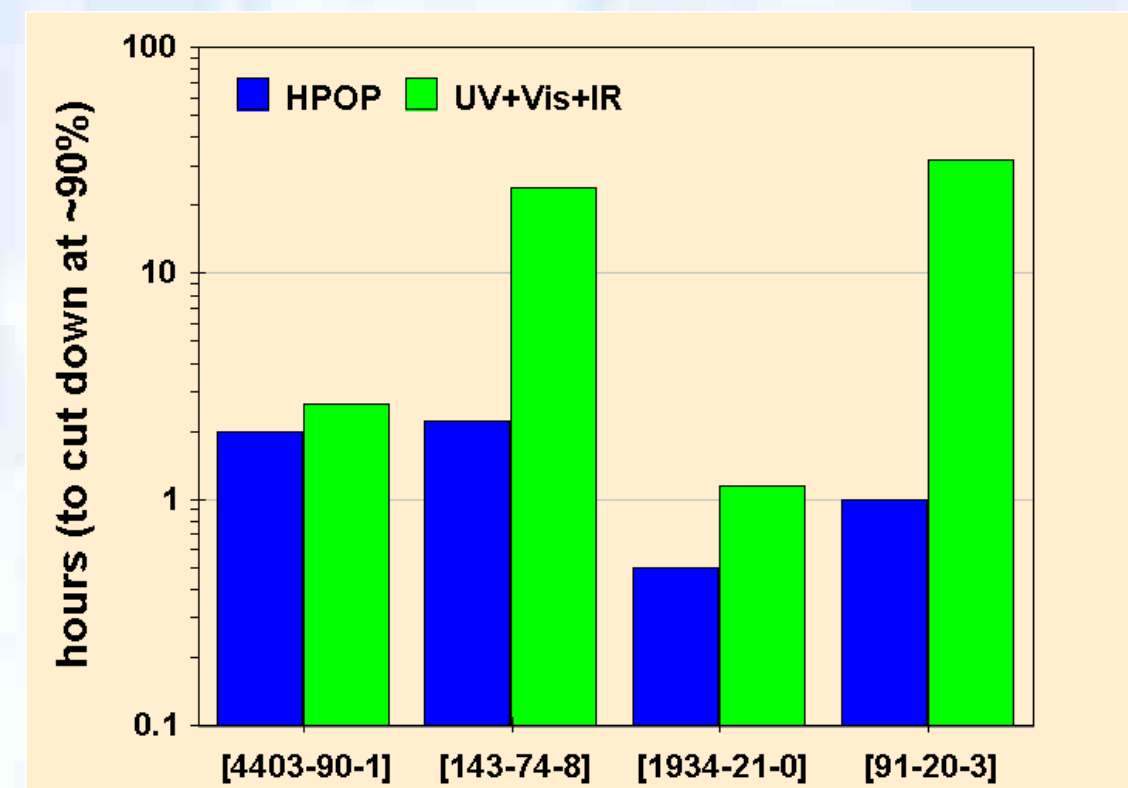


Figure 6

Table1: hours	HPOP (UV+TiO2+MW)	Simple System (UV+Vis+IR+TiO2)
Acid Green 25	2.0	2.65
Phenol Red	2.25	24.0
Tartrazine	0.5	1.15
Naphthalene	1.0	32.0
Dimethoate	1.12	8.1
Naproxen	0.9	1.2

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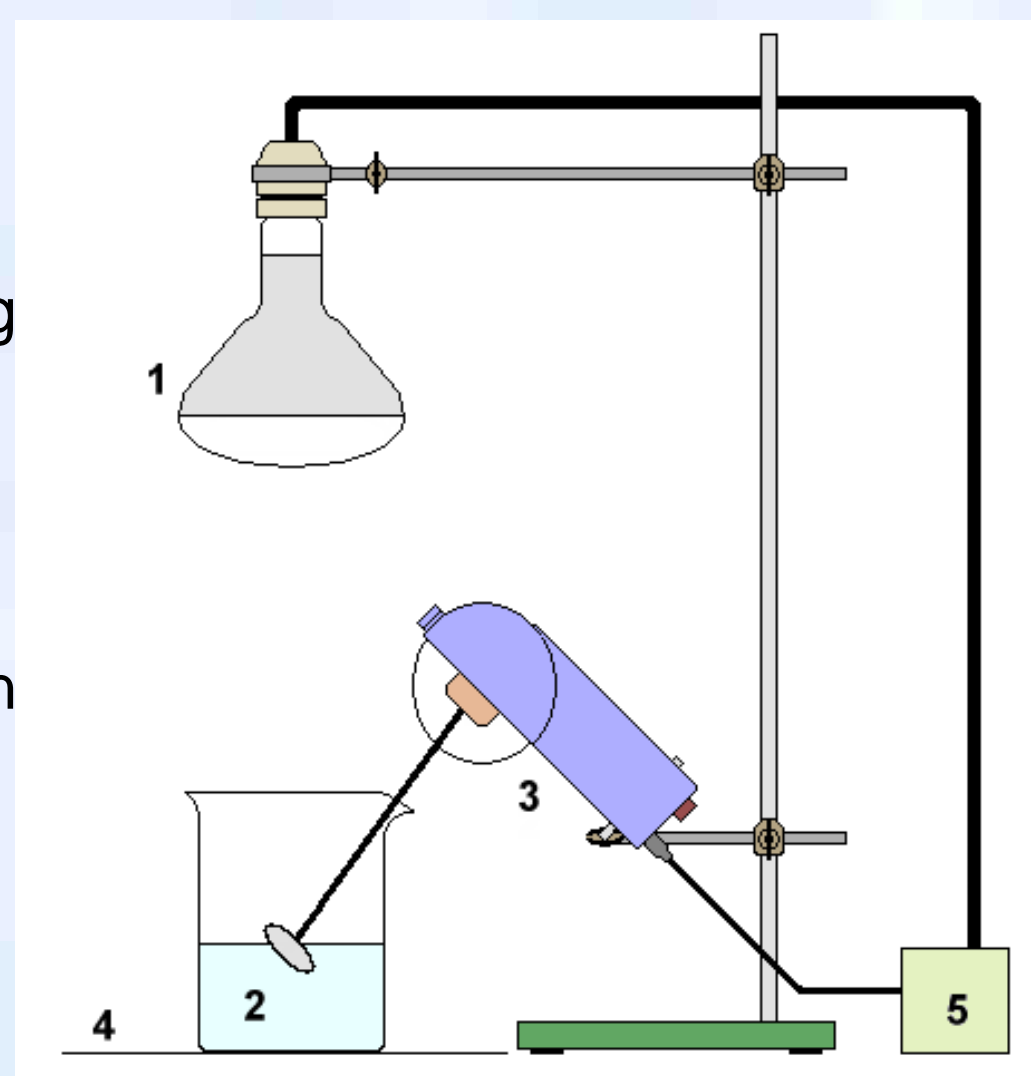


Figure 1

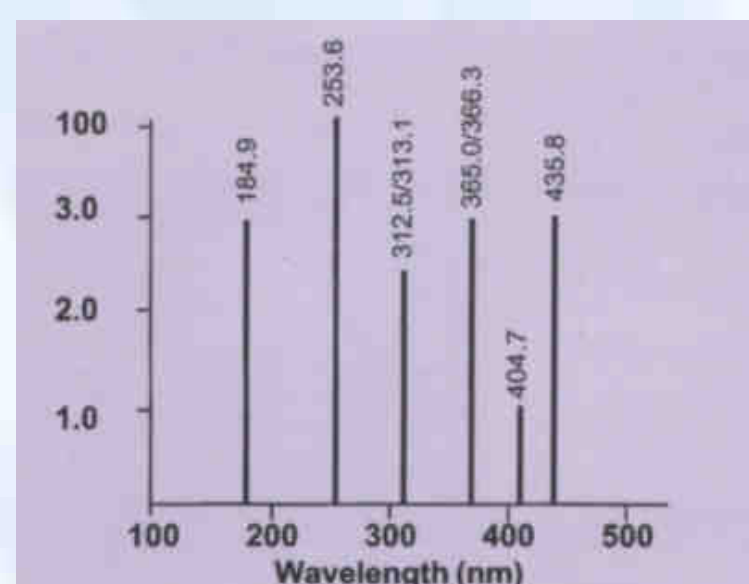


Figure 4

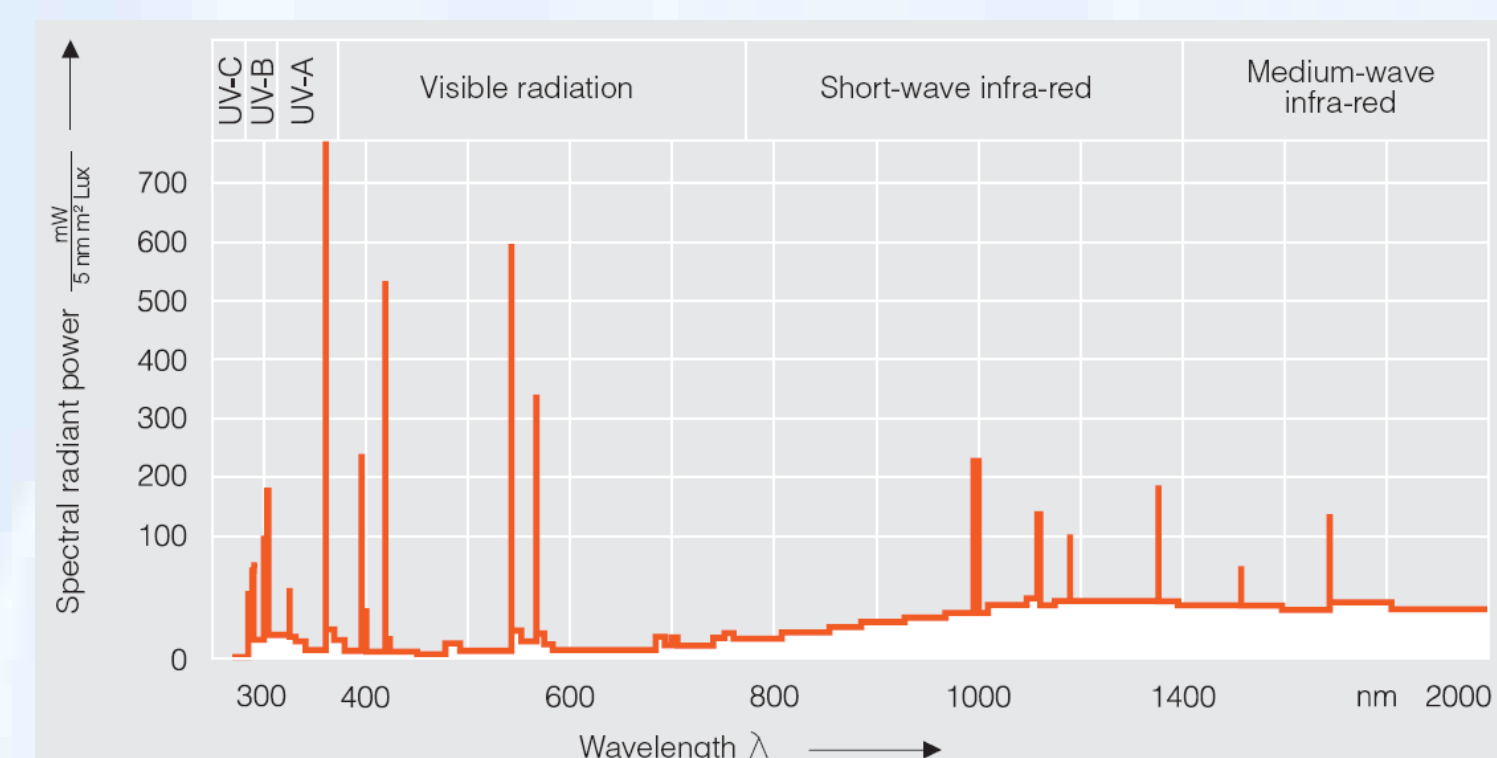


Figure 2

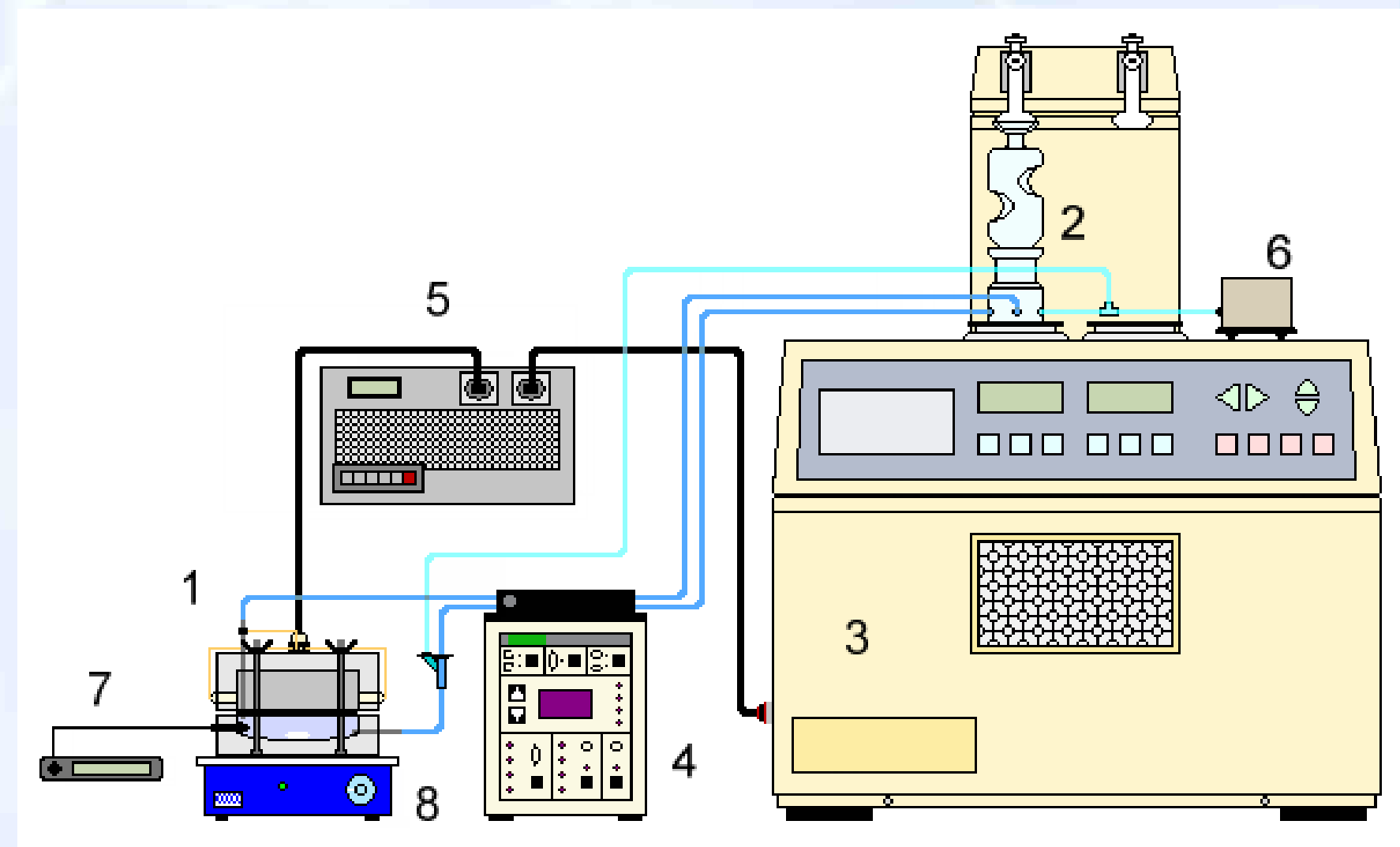


Figure 3

3- Results and discussion

In this work we have tried to compare two different systems of photodegradation, and to set parameters by studying the time required to achieve the same rate of degradation rather than the degradation rates obtained after the same time.

The graph in **figure 6** shows in the abscissa the 4 molecules (respectively Acid Green 25, Phenol Red, Tartrazine and Naphthalene) expressed by CAS Number, and in the ordinate (logarithmic scale) the time required to obtain approximately 90% degradation. The blue bars indicate the photodegradation performed with our system HPOP (High Performance Oxidation Process), while the green bars indicate the photodegradation carried out with the simple system that mimics a solar degradation.

It may be noted that some molecules such as Acid Green 25 and partly also Tartrazine, require a short time to be degraded with both systems. This indicates that there are molecules that can be degraded easily and quickly with inexpensive and easy to handle systems. The two other molecules (Phenol Red and Naphthalene) behave differently as they required a much longer time for effective abatement with the simple system compared than with our standard HPOP. Surely our new Four Phases HPOP, under development, reduce the time required for abatement.

The **Table 1** gives us the numerical values of the tests we carried out; we can also see other molecules tested previously, like Dimethoate (an organophosphate insecticide, CAS Number 60-51-5) and Naproxen (a non-steroidal anti-inflammatory drug commonly used and reported as frequently present in the environment, especially in rivers, CAS Number 22204-53-1). Also with these molecules the photodegradation carried out with a simple system requires more time for the abatement of the pollutants. Moreover, the incomplete degradation of dangerous molecules can lead to the formation of intermediates, which may be more toxic than the initial compounds.

4- Conclusions

From the starting point of experimental data obtained, we can conclude that to get a good degradation of organic pollutants in a short time, we must resort to complex systems. These simplex imply the use of expensive materials, discrete energy consumption and require maintenance and qualified personnel, especially if we want to create plants in industrial large-scale plants. A simple system of degradation such as the solar type, is cheaper and can be used by non-specialist but requires long time for the treatment of water. This system is less limiting in case of large installations. However, further and detailed study of this problem is necessary in order to assess the behavior of organic molecules present in most waste water, and therefore to determine the best typology of degradation system.