

## A brief review on the importance use of solar energy in the treatment of recalcitrant effluents applying advanced oxidation processes

Marluce Teixeira Andrade Queiroz<sup>1</sup>, Millor Godoy Sabara<sup>1</sup>, Lucas Barbosa Alvim<sup>1</sup>, Carolina Andrade Queiroz<sup>1</sup>, Monica Maria Diniz Leão<sup>1</sup>, Camila Costa Amorim<sup>2</sup>

Centro Universitário do Leste de Minas Gerais, MG, Brasil  
Universidade Federal de Minas Gerais, UFMG, MG, Brasil

### Abstract

*Several studies have reported the adverse effects of persistent compounds in the wastewater, showing the fragility of the biologic treatment. Harmful effects for both aquatic biota and human being are caused by those compounds. In order to minimize the adverse environmental impacts, Advanced Oxidation Processes (AOPs) are used in the degradation of those pollutants to achieve high removal rates. In the present the comparisons between the efficiency of AOPs using natural and artificial Ultra Violet light (UV) were made based on the literature review, addressing constructive and operational characteristics of the reactors. The findings indicated that the high levels of solar energy, which are registered in different regions of Brazil, show the viability of the AOP using natural radiation to the decontamination of industrial effluents. Thus the inclusion of advanced oxidation in the treatment of wastewater could be considered as a significant contribution to the supported development in Brazil.*

**Keywords:** *Recalcitrant Compounds, Advanced Oxidation Processes, Decontamination, Tropical natural UV irradiance.*

### Resumo

*Inúmeras pesquisas têm abordado os efeitos adversos dos compostos persistentes nas águas residuais, comprometendo o desempenho dos tratamentos biológicos. Destacam-se os efeitos nocivos para a biota aquática e para o ser humano através da biomagnificação na cadeia alimentar podendo redundar em distúrbios neuropáticos quando em concentrações superiores aos Limites de Tolerância Biológica (LTB). No esforço para minimizar os impactos ambientais adversos se encontra o uso dos Processos Oxidativos Avançados (POA) utilizados na degradação daqueles poluentes e alcançando elevadas taxas de remoção. Nesse estudo, com base na revisão da literatura foram estabelecidas comparações entre a eficiência com o uso da luz Ultra Violeta (UV) natural e artificial, abordando características construtivas e operacionais dos reatores. Os achados indicaram que os altos níveis de carga solar, encontrado nas diversas regiões do Brasil mostram a viabilidade dos POA com irradiação natural visando à descontaminação dos efluentes industriais. Entende-se que a inclusão da oxidação avançada na linha de tratamento contribui para o desenvolvimento suportado do País.*

## 1 Introduction

Anthropogenic pollution is the main cause of disorders that affect ecosystems (FERREIRA *et al.*, 2015). Corporate responsibility imposed by specific legislation requires the search of methodologies capable to ensure the eco-efficiency in many economic sectors (AIZEMBERG *et al.*, 2014).

According to the World Business Council for Sustainable Development (WBCSD), eco-efficiency is reached by providing goods and services at competitive prices that satisfy human needs and bring quality of life, gradually reducing the environmental impact and consumption of natural resources over the cycle of life, respecting the estimated sustaining capacity of the Earth (WBCSD, 2015).

The United Nations Industrial Development Organization (UNIDO) points out that one of the strategies to achieve eco-efficiency is the application of Cleaner Production (CP), which integrated to the productive process operates, for instance, by not generating toxic waste, having significant benefits in biodiversity protection (UNIDO, 2015).

In this context, it is worthy to highlight the treatment of industrial effluents, since their wastewater often has a high concentration of recalcitrant compounds (TWARDOKUS *et al.*, 2005). Typically, this wastewater contained of cumulative effect on lipid layer and can reach concentrations above the Biological Tolerance Limit (BTL) and could resulting in death for some organisms such as invertebrates and fish. In addition, those compounds can reach humans through the biomagnification in the food chain and could cause disabling injuries, such as cancer, neurological disorders, among others (LEDAKOWICZ *et al.*, 2001).

Peixoto *et al.* (2011) point out that the deposition of recalcitrant substances on river sediments also constitutes an adverse environmental condition. Those substances can percolate through the soil and reach the water table affecting the health standard of groundwater. This situation poses a serious risk to public health, mainly affecting the rural community.

The boost in quality about the protection of ecosystems increases as balancing relations are established between the decontamination and treatment costs, aiming the removal of recalcitrant and/or persistent pollutants.

In this context, the development of techniques linking biodiversity protection and economic viability has grown in recent years. In attendance of these questions, the Advanced Oxidation Processes (AOPs) are an interesting alternative.

AOP are considered as clean technology since AOP produce no sludge formation neither pollutants phase transfer. Furthermore, the final products are carbon dioxide, water, inorganic ions and less toxic by-products (MOLINARI *et al.*, 2002).

In this work, the use of AOP using both artificial and natural sources irradiation were emphasized and established. The relevance of this study is based on the production of results about measures that contribute to the treatment to be inserted in the concept of Cleaner Production (CP), aiming the environmental sustainability.

## 2 Materials and Methods

This study was conducted based on a review of the specialized literature, books and periodicals available in the libraries of the Federal University of Minas Gerais, Brazil. Scientific articles were selected through a search in Scielo database from the use of relevant terminologies to the descriptors in engineering and technology. The following keywords were used: photo reactors, advanced oxidation process, and recalcitrant compounds. The studies of AOP using ultraviolet irradiation as well as comparative studies between this and other types of wastewater treatment were selected to the writing of this paper.

## 3 Advanced Oxidation Processes

The chemical oxidation is the chemical phenomenon whereby the removal of electrons from a substance happens, which increases its oxidation state. The reactions involving oxidants such as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) or ozone (O<sub>3</sub>) are generally thermodynamically spontaneous. However, they are kinetically slow.

AOPs are based on the generation of hydroxyl radical ( $\bullet$ OH), a strong oxidizing agent, capable of degrading organic molecules resistant to biodegradation. The oxidation potential of the radical  $\bullet$ OH is equal to 2.80V, higher than the chlorine gas (Cl<sub>2</sub>), ozone (O<sub>3</sub>), and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) that correspond to 1.36V, 2.07V, and 1.77V, respectively (Table 1).

**Table 1** – Oxidation potential of some chemical species.

| Oxidizing Agent  | Oxidation Potential (V) |
|--|-------------------------|
| Radical hidroxila ( $\cdot$ OH)<br>Hydroxyl Radical                          | 2.80                    |
| Ozônio (O <sub>3</sub> )<br>Ozone  | 2,07                    |
| Cloro molecular (Cl <sub>2</sub> )<br>Chlorine Gas                           | 1,36                    |
| Peróxido de Hidrogênio (H <sub>2</sub> O <sub>2</sub> )<br>Hydrogen Peroxide | 1,77                    |

Source (Adapted): PERA-TITUS *et al.*, 2004 ; MAZUR *et al.*, 2014.

AOPs are classified in homogeneous systems, which use hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) along with iron ions II (Fenton Reagent), ozone (O<sub>3</sub>), ultraviolet light (UV) or ultrasound (US); and in heterogeneous systems, which use

photoactive oxides or metals, such as titanium dioxide (TiO<sub>2</sub>), the most catalysts used in this treatment (MAZUR *et al.*, 2014). Table 2 shows the main systems by which the hydroxyl radical can be generated.

**Table 2** – Typical systems of advanced oxidation processes.

|  |  |
|--|--|
| <b>Homogeneous Systems</b>                           | <b>Use of irradiation</b>                                |
|  | O <sub>3</sub> /UV                                       |
|  | H <sub>2</sub> O <sub>2</sub> /UV                        |
|  | Beam of electrons  |
|  | US   |
|  | H <sub>2</sub> O <sub>2</sub> /US                        |
|  | US/UV  |
| <b>Heterogeneous Systems</b>                         | <b>Without irradiation</b>                               |
|  | O <sub>3</sub> / H <sub>2</sub> O <sub>2</sub>           |
|  | O <sub>3</sub> /HO <sup>•</sup>                          |
|  | H <sub>2</sub> O <sub>2</sub> /Fe <sup>+2</sup> (Fenton) |
|  | <b>Use of irradiation</b>                                |
| TiO <sub>2</sub> /O <sub>2</sub> /UV                 |  |
| TiO <sub>2</sub> / H <sub>2</sub> O <sub>2</sub> /UV |  |
| <b>Heterogeneous Systems</b>                         | <b>Without irradiation</b>                               |
|  | Eletron-Fenton   |

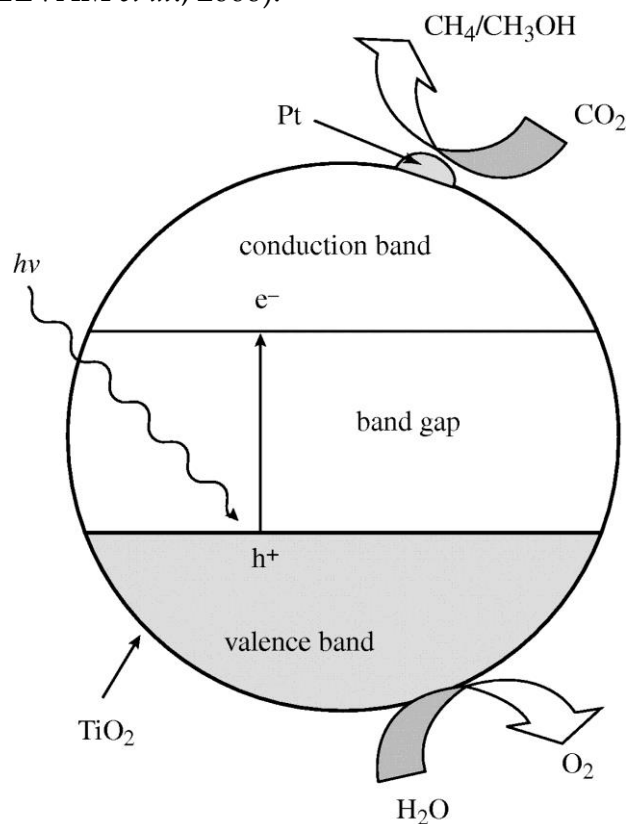
Source (Adapted): MAZUR *et al.*, 2014.

In general, the use of UV radiation along with strong oxidizers, such as ozone and hydrogen peroxide promotes greater removal of recalcitrant compounds and/or persistent compounds in homogeneous systems. (BAHNEMANN, 2004; PEREIRA *et al.*, 2014).

Many studies which approach heterogeneous systems also indicate that the use of UV light improves the process yield in order to decontaminate the effluents. The higher the energy, the greater the quantity of •OH radicals generated in the reaction medium, thus increasing pollutant degradation rates (GALINDO *et al.*, 2001).

UV radiation is used to promote the photo activation of the catalyst (TiO<sub>2</sub>) in homogeneous systems, which occurs once the semiconductor is illuminated by a highly energetic photon. Such energy should be greater or equal than the energy difference between the valence band (VB) and the conduction band (BC), called "band-gap" energy. The electron previously located in the conduction band is promoted to the valence band (electronic transition), creating the pair electron/gap (SELVAM *et al.*, 2006). Then, the irradiated photocatalyst promotes the electronic transition of an electron creating oxidizing and reducing sites (Figure 1) capable of catalyzing oxidation

reactions of several organic compounds, which can result in high levels of mineralization (SELVAM *et al.*, 2006).



**Figure 1** - Representation of the semiconductor particle and its activation.

BV: Valence band; BC: Conduction band.

Source: ZHU *et al.*, 2011.

In general, the degradation rate of organic matter rises as the light intensity increases in homogeneous and heterogeneous systems. This is relevant to optimize the process, maintaining a continuous flow. The operating time must be determined experimentally, taking into consideration that there are other confounding variables, such as the initial concentration of the contaminant, the temperature, and pH (GUMY *et al.*, 2009). The long contact time required for oxidation as well as the difficulty of recovery of the system reagent are obstacles in the use of the process. Furthermore, homogeneous catalysts are being replaced by heterogeneous systems consisting of supported metals due to the toxic contamination and the need of removal of homogeneous catalysts from the solution through a second stage of treatment as outlined by Rangel *et al* (2008). In this context, the proper selection of UV radiation sources is a priority condition for achieving eco-efficiency.

The relationship between the Cleaner Production (CP) and eco-efficiency has a direct link, and it is the primordial basis for sustainable development. The eco-efficient industry ensures that the production takes place

at adequate levels with thrifty use of natural resources by avoiding any waste. From this perspective, the industry fits itself in the CP requirements, which aimed at reducing pollution at its source and thus requires internal cleaning program to the institution (good house-keeping); qualitative and quantitative evaluation of the generated waste in order to decontaminate it; and the responsible reuse intending to reduce the environmental liabilities.

The CP and eco-efficiency are essential management tools that help to achieve operational efficiency. The adoption of these techniques may enable the taking of decisions that brings high economic and environmental return. This assumption points to the use of ultraviolet radiation in the decontamination of effluents.

#### **4. Artificial sources of ultraviolet radiation**

Ultraviolet light can be generated artificially through the lamps. A discharge of electrical current in an atmosphere containing a gas takes place inside these lamps. The gas molecules are excited, and when they return to their initial state, they emit energy in the form of electromagnetic radiation. The emission characteristics depend on both the nature and pressure of the gas. The mercury (Hg) and xenon (Xe) vapour lamps have great applicability in the market (NEYENS and BAEYENS, 2003; BRITO *et al.*, 2012).

Mercury vapour lamps could operate under low, medium and high pressure. A quartz housing in which is introduced a gaseous material, and is also permeable to radiation of a smaller wavelength as well as resistant to the pressure reached by the gas is found internally. The drawback is the low irradiance among the peaks of emissions in the lamps that operate under low pressure, between 1 and 300atm (WINDMÖLLER *et al.*, 2015) as shown in Table 2.

The gas is located in a quartz envelope at a pressure between 20 and 40atm in xenon lamps. These lamps emit a spectrum very close to the solar one, but presenting a much broader UV segment. They can constitute great simulators of solar radiation with some correction devices; however, they have the disadvantage of only radiating small areas and requiring frequent adjustments (Table 3) (NEYENS and BAEYENS, 2003).

**Table 3** - Comparisons between mercury and xenon vapour lamps.

| Lamp           | Pressure (atm)                    | Disadvantages  |
|----------------|-----------------------------------|--|
| Mercury Vapour | $1 \leq \text{pressure} \leq 300$ | Lamps operating at low pressure.<br>Low irradiance between the emission peaks. |
| Xenon          | From 20 to 40                     | Lamps radiate small areas.<br>Adjustments are frequent.                        |

Source (Adapted): NEYENS and BAEYENS, 2003.

The UV irradiation is an essential requirement for the process efficiency. However, the lamps used have a lifetime which depends on the compound treated (some compounds may destroy the lamp by chemical reaction), and how the reactor is fed (batch or continuous), as examples. Such interferences can result in the increasing or reducing of the number of times in which the lamp is switched on or off (Table 3). Furthermore, it should be ensured that the light intensity complies with the requirements of the treatment through rigorous and effective control. The most modern lamps have automatic and continuous measurement system overload their value on the market (PERINI *et al.*, 2014).

Another important aspect related to the use of an artificial source of UV radiation is the energy cost, which can be calculated by Equation 1 (TIDRE *et al.*, 2013):

$$\text{Energy cost} = \text{UV dose} \times \text{Electricity Cost (0,08KWh}^{-1}) \quad (\text{Equation 1})$$

The UV dose required will depend on the contaminant concentration and the reactor operation mode (batch or continuous). However, the high energy cost (Table 4) for the implementation of the AOP using artificial irradiation is considered one of its disadvantages.

**Table 4 - Main disadvantages of using reactors with artificial lamps.**

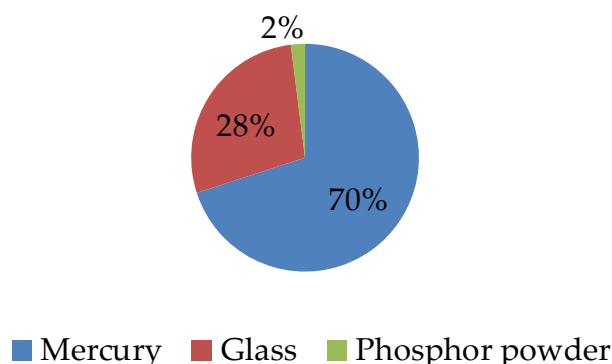
| <b>Disadvantage</b>                        | <b>Related factors</b>   |
|--|--|
|  | Reactor batch operation  |
|  | Chemical attack to the lamp by the contaminant treated   |
| Energetic Cost                             | Increase of the contaminant concentration<br>Contaminant resistant to chemical degradation   |
| Operational Conditions                     | Demand of transport from the effluent to the station of treatment<br>Demand of effluent aeration<br>Unfeasible for high density of contaminant   |
| Environmental risk of mercury vapour lamps | The lamp glass is made by 70% of mercury.<br>The lead concentration in glass exceeds 0,1mg.kg <sup>-1</sup><br>The phosphor powder is 2% of the total mass, and has Al, Cd, Pb, Cu, Cr, Mn, Ni e Hg. |

Source (Adapted): PERINI *et al.*, 2014.

The most used lamps are mercury vapour which presented higher luminous efficiency and longer lifetime. The lifetime of a mercury lamp is 3 to 5 years, or an operating time of approximately 20,000 hours under normal usage conditions (ALMEIDA *et al.*, 2014). However, these lamps belong to the class of hazardous waste since its presenting levels of toxic metals exceeding 0,1mg.kg<sup>-1</sup> as established by the Brazilian Association of Technical Standards (NBR 10.004/04).

The mercury vapour lamp is made by a sealed glass tube with 70% by weight of mercury. The white layer, usually called phosphor powder, which covers the tube of the fluorescent lamp is generally a mixture of compounds containing aluminum (Al), cadmium (Cd), lead (Pb), copper (Cu), chromium (Cr), manganese (Mn), nickel (Ni), and mercury (Hg), which corresponds to 2% of the total mass (RODRIGUES *et al.*, 2013). Furthermore, the mercury vapour lamp also contains 28% of glass (Figure 2), which is a mixture of silica (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>), calcium oxide (CaO), magnesium oxide (MgO), and potassium oxide (K<sub>2</sub>O). The inner tube is filled with argon gas and mercury vapour while the lamp terminals are made of aluminum or plastic, and the electrodes are composed of tungsten, nickel, copper or iron (RODRIGUES *et al.*, 2013).





**Figure 2** - Composition of the case of the mercury vapor lamp.

Source (Adapted): QUEIROZ *et al.*, 2014.

According to Figure 2, 72% of the solid mass of the mercury vapour lamp are made of toxic metals that can cause harm to human health (Table 4) (Mendes, 2005). Although all toxic metals presented in the mercury vapour lamps pose risk to the environment and human health (Table 5), the manufacturers OSRAM and European Lighting Companies Federation (ELC) declare that only mercury is potentially more dangerous, this metal has more volatile state and composition at ambient conditions (RODRIGUES *et al.*, 2013). A diagnosis of EPA (2005) pointed out this kind of lamp as the second largest source of mercury in urban solid waste (GUSMÃO *et al.*, 2014).

**Table 5** - Major adverse effects caused by metals found in mercury vapor lamps.

| Heavy metal | Damage to human health  |
|-------------|---|
| Aluminum    | Osteoporosis, Alzheimer, Parkinson, and hyperactivity in children         |
| Cadmium     | Changes in the skeletal system, irritation of the stomach and lung cancer |
| Lead        | Osteoporosis, anemia, damage to the liver and kidneys                     |
| Copper      | Heart disease and Alzheimer   |
| Chrome      | Carcinogenic when found in hexavalent form                                |
| Manganese   | Brain injuries, damage to the testicles and impotence                     |
| Nickel      | Disturbs in lung function, lung cancer and nasal injuries                 |
| Mercury     | Neuropathies, Parkinson, damage to the liver and kidneys                  |

Source (Adapted): GIL and GURGEL, 2009

Costs related to recycling and decontamination of waste generator depends on the volume, distance and specific services selected by the managers of the enterprise. In Brazil, the average cost of decontamination is considered

high, besides the further increases due to transport, packaging and accident insurance (RODRIGUES *et al.*, 2013).

Another negative aspect is the exposure of employees to mercury vapours, which can lead to severe neuropathies, and in a long-term, vegetative life and/or death (ESPINOZA-QUIIÑONES *et al.*, 2015).

To ensure safety, all procedures performed in recycling should be enclosed in order to prevent fugitive emissions of mercury. Efficient local exhaust ventilation system equipped with air capture/collection/treatment device is highly recommended to the recycling activity (SAMBINELLI and SOSA ARIAS., 2015), (OSHA 2007).

However, the recycling activity alone is not enough to ensure that the requirements of the Cleaner Production (CP) are met since serious environmental dysfunctions can occur. The demanding for new technologies aiming the sustainable development is highly important in this process.

### 5. The use of solar radiation

The possibility of using the solar radiation in the photo catalytic process is one of the attractive features in industry. Unfortunately, no more than 3-4% of the solar flux reaching the Earth's surface is useful to activate the  $\text{TiO}_2$  (for activating it, the radiation should be between 380/390nm). On the other hand, studies with different configurations of photo catalytic reactors, using this source of UV, have been conducted for better utilization of solar flux (CASSANO and ALFANO, 2000). Several works performed in Almeria (PSA) Solar Platform in Spain (Figure 3) have demonstrated the high efficiency of the concentrator parabolic reactor to mineralize many organic substances (MALATO *et al.*, 2007).

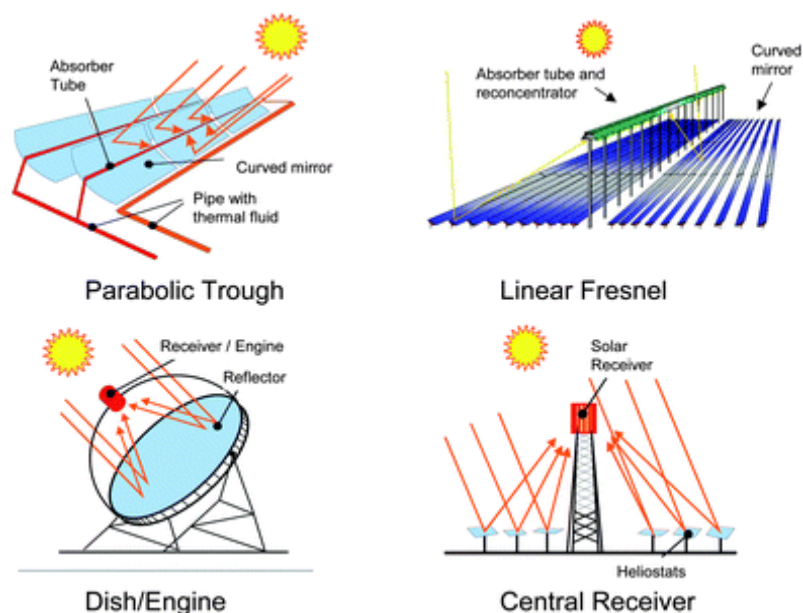


**Figure 3** - Solar platform in Almeria (PSA), Spain.

Source: MALATO *et al.*, 2007.

The reactors from PSA are also known as Parabolic Trough Collectors (PTC), and they are made by reflecting parables which converge the incident radiation to transparent polyethylene pipes set parallel to it (Figure 4). The tilt angle of the set of parables can be adjusted automatically in order to get the maximum use of solar radiation. This system has an engine that allows the

collectors to track radiation, so that the collector surface is always perpendicular to the sunlight (NOGUEIRA *et al.*, 2005). Early applications of this type of reactor were to photodegradation of organic pollutants in water using heterogeneous photo catalysis with  $\text{TiO}_2$  (NOGUEIRA *et al.*, 2007).

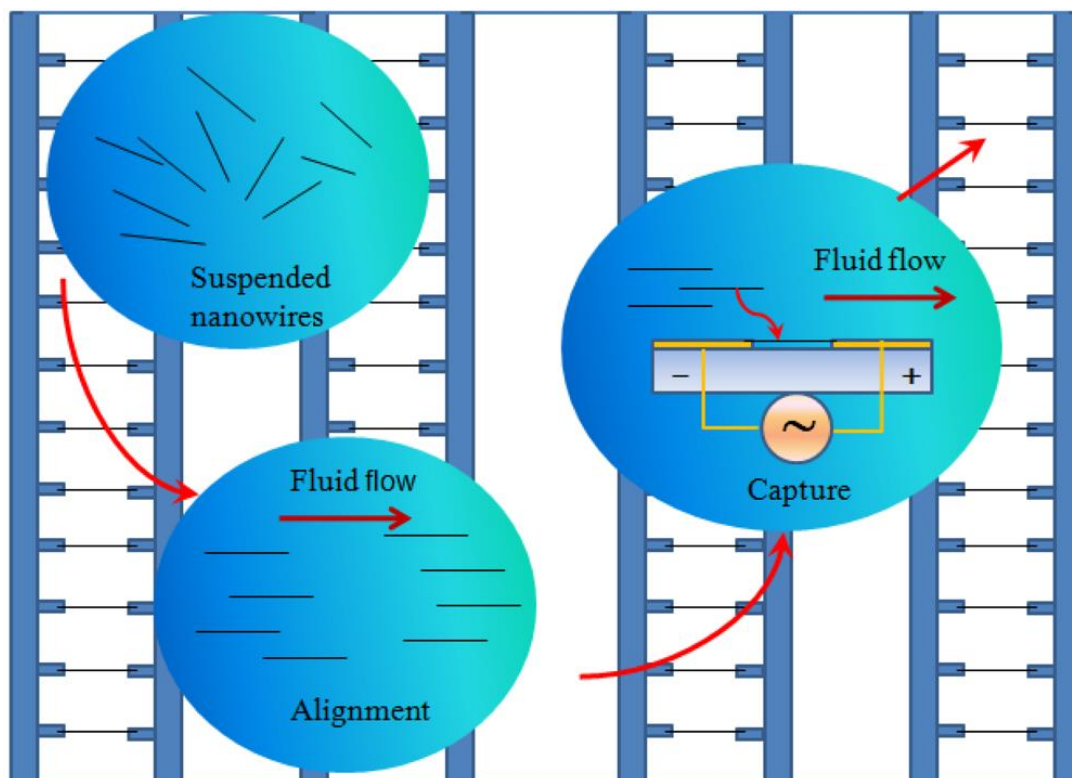


**Figure 4** - Parabolic cylindrical solar reactor.

Source: CHENG and MELO FILHO, 2010.

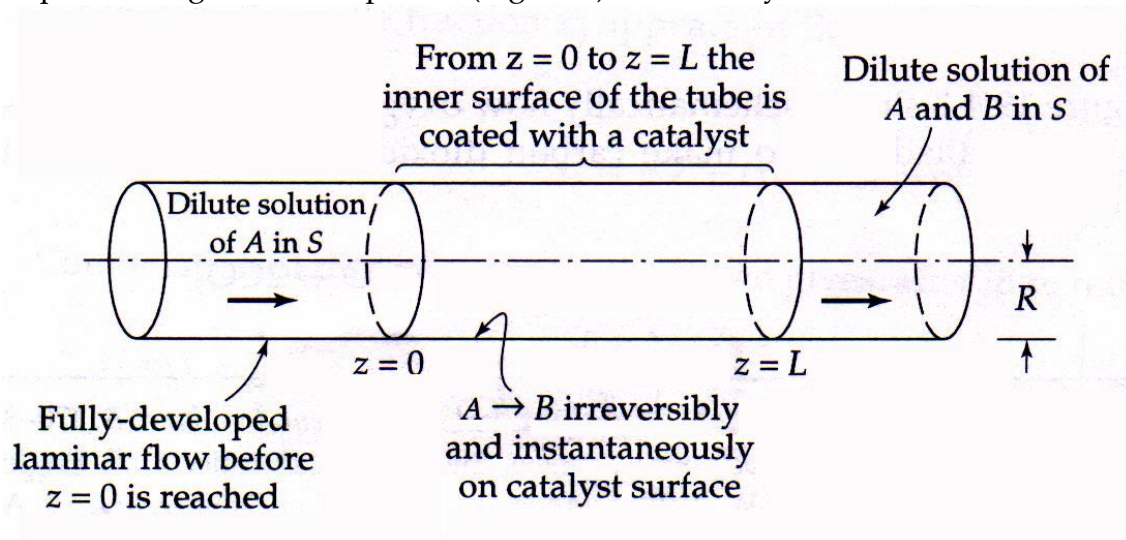
The use of only direct radiation is one of the disadvantages of the PTC due to loss of diffuse radiation that cannot be concentrated in a point (focal axis of the parabolic trough collectors). Other disadvantages are the high cost and sample overheating problems (GÁLVEZ and RODRIGUES, 2003 *apud* WALNUT *et al.*, 2007).

Another type of reactor is the laminar flow, which does not focus sunlight, and it is based on the irradiation of a solution blade containing the target compound. This compound passes in a laminar flow over a glass plate (containing immobilized  $\text{TiO}_2$ ) with a tilt angle generally set (Figure 5), which depends on the local latitude (NOGUEIRA *et al.*, 2007).



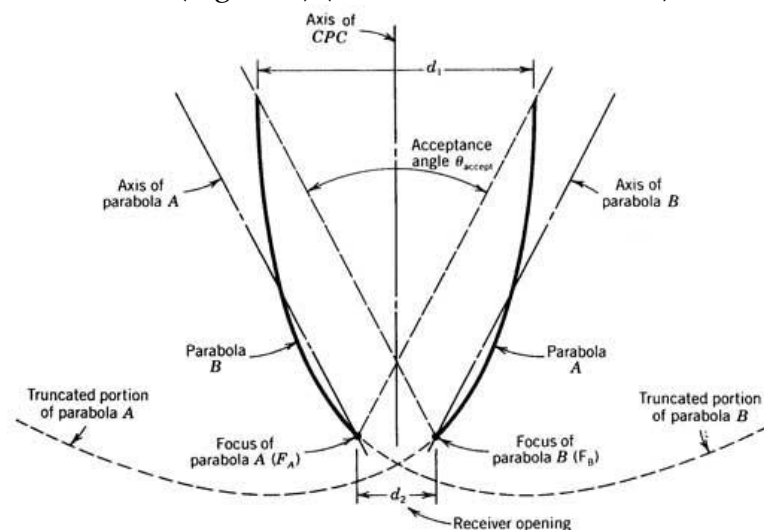
**Figure 5** - Solar reactor of laminar flow.  
Source: MOREIRA and CHENG, 2010.

The laminar flow reactor has advantages compared to the PTC, such as the simplicity and low cost of implementation and maintenance. However, it requires a large area of exposure (Figure 6), which may restrict its use.



**Figure 6** - View of the exhibition area of the laminar flow reactor.  
Source: MALATO *et al.*, 2007.

The combination of PTC to laminar flow reactor resulted in the Compound Parabolic Collector reactor (CPC). CPCs are probably the most used solar reactors, because they have the best optical relation to solar energy. These reactors are static presenting a complex reflecting surface around the reactor cylinder. In this design, virtually all radiation is harnessed (direct and diffuse). The reflected radiation is distributed in the lower part of the tube, illuminating the entire circumference (Figure 7) (NOGUEIRA *et al.*, 2007).



**Figure 7** - Reflection profile of the compound parabolic collector.

Source: SOUZA *et al.*, 2009.

The application of CPC has been increasingly widespread for removing pesticides and surfactants through the AOP. The main advantage of CPC is the simplicity similar to laminar flow reactor, ensuring lower maintenance costs compared to others (MALATO *et al.*, 2007).

The choice of the collector requires study about the advantages, disadvantages and the financial availability. Table 6 provides comparisons among the laminar flow collectors, the parabolic collectors, and the compound parabolic collectors; highlighting the CPC efficiency due to the low cost of maintenance and operation.

**Table 6** - Comparison among the laminar flow collectors, parabolic collectors, and compound parabolic collectors.

| Photo reactor | Use of TiO <sub>2</sub> | Harness of UV radiation | Advantages                            | Disadvantages   |
|---------------|-------------------------|-------------------------|---------------------------------------|---|
| Laminar Flow  | Immobilized             | Direct flow             | Low cost of maintenance and operation | Big area demand. Fixed equipment.                                       |
| PTC           | Suspended               | Diffuse flow            | Perpendicular to the sunlight         | High cost of implementation and operation. Overheating of the effluent. |
| CPC           | Immobilized             | Direct and diffuse flow | Low cost of maintenance and operation | High cost of implementation.  |

Source (Adapted): NOGUEIRA *et al.*, 2007.

Several studies have explicated that the type of collector is critical in relation to UV harness (Table 7), resulting in a higher or lower amount of energy available. Therefore, it is important to define the photoreactor model as the contaminant chosen to be degraded.

Moraes *et al.* (2004) have successfully reduced approximately 90% and 66% of the total organic carbon concentration (TOC) from both an aqueous gasoline solution and an effluent of a petroleum refinery, respectively. The authors used the laminar flow reactor. Other compounds, such as vanillin, gallic acid, coumaric acid and L-tyrosine have also been mineralized efficiently using such equipment (NOGUEIRA *et al.*, 2007).

Machado *et al.* (2003) evaluated the use of CPC in the degradation of effluents from a potato processing industry. The authors estimated that a reactor having a collector surface of 370 m<sup>2</sup> is able to reduce by 50% the Chemical Oxygen Demand (COD) of 10m<sup>3</sup> of effluent/day. The use of CPC for the mineralization of imidacloprid, methomyl, diuron, and formetanate also showed its versatility for pesticide degradation reaching 95% removal of TOC (NOGUEIRA *et al.*, 2007).

Rodrigues *et al.* (2002) and Teixeira *et al.* (2003) identified the applicability of the parabolic collector in the degradation of nitrobenzene, aminosilicone, and phenol (Nogueira *et al.*, 2007). Oliveira *et al.* (2007) were able to remove 90% of the TOC in contaminated water with gasoline. Table 7 shows some examples of

contaminants which could be eliminated by specifying the type of collector used.

**Table 7** - Contaminants subject to degradation and their corresponding photoreactor.

| Contaminant   | <i>Photo reactor</i> | <i>Removal(%)</i> | <i>Reference</i>              |
|---------------|----------------------|-------------------|-------------------------------|
| Gasoline      | Laminar flow         | 90% of TOC        | MORAES <i>et al.</i> , 2004   |
| Petroleum     | Laminar flow         | 66% of TOC        | MORAES <i>et al.</i> , 2004   |
| Food effluent | CPC                  | 50% of COD        | MACHADO <i>et al.</i> , 2003  |
| Pesticides    | CPC                  | 95% of TOC        | NOGUEIRA <i>et al.</i> , 2007 |
| Gasoline      | PTC                  | 90% of TOC        | OLIVEIRA <i>et al.</i> , 2007 |

## 6. Comparison between treatments using natural and artificial ultraviolet radiation

Several researchers have reported similar results in relation to decontamination of wastewater by natural irradiation processes. It is highlighted that such treatment implies a cleaner production since it decreases the disposal of mercury lamps, presenting economic and environmental benefits.

Some of those studies are presented in Table 8. The results point out the broad options to reduce operating costs of the AOP applying natural irradiation.

**Table 8** - Comparison with regard to degradation of recalcitrant compounds using sunlight and artificial irradiation.

| Contaminant            | Treatment                    | TOC removal (%)   |                | Reference                    |
|------------------------|------------------------------|-------------------|----------------|------------------------------|
|                        |                              | $UV_{artificial}$ | $UV_{natural}$ |                              |
| Phenols                | Photon-Fenton                | 95%               | 95%            | NOGUEIRA E MODÉ, 2002        |
| Herbicides             | Photon-Fenton                | 100%              | 100%           | TROVÓ <i>et al.</i> , 2005   |
| Chlorophyll a          | Photocatalysis               | 76%               | 76%            | CABRAL, 2010                 |
| M. aeruginosa          | Heterogeneous Photocatalysis | 89%               | 89%            | CABRAL, 2010                 |
| Recalcitrant Compounds | Heterogeneous Photocatalysis | 53%               | 61%            | PASCOAL <i>et al.</i> , 2007 |
| Cr (VI)                | Heterogeneous Photocatalysis | 52%               | 62%            | PASCOAL <i>et al.</i> , 2007 |

The removal of TOC using  $UV_{artificial}$  and  $UV_{natural}$  were exactly the same in the experiments with phenols, herbicides, *Microcystis aeruginosa*, and chlorophyll a (Table 7). Furthermore, Pascoal *et al.* (2007) achieved better results using  $UV_{natural}$  in the mineralization of recalcitrant compounds and chromium VI. The results show that the effluent treatment using AOP with  $UV_{natural}$  reaches the eco-efficiency associating properly the economic and environmental factors. The rational use of energy, the decrease in the risk of accidents, and the preservations of natural resources justify such affirmative.

Nogueira and Mode (Table 8) systematized studies with natural photoreactor using the Photon-Fenton process in the city of Araraquara, São Paulo, Brazil, from 7 to 17h, from January to December, under clear sky conditions. The study showed a 40% difference in the removal of TOC in aqueous solution of dichloroacetic acid between June and January. The researchers concluded that the intense summer and the high radiation peaks at 12pm were the main factors for this significant difference.

Therefore, it is important that the residence time of the contaminant in the reactor is established on the basis of the intensity variations of solar radiation during the day and the time of the year. In this way, it is possible to create opportunities to maximize the efficiency of the treatment (NOGUEIRA *et al.*, 2007).

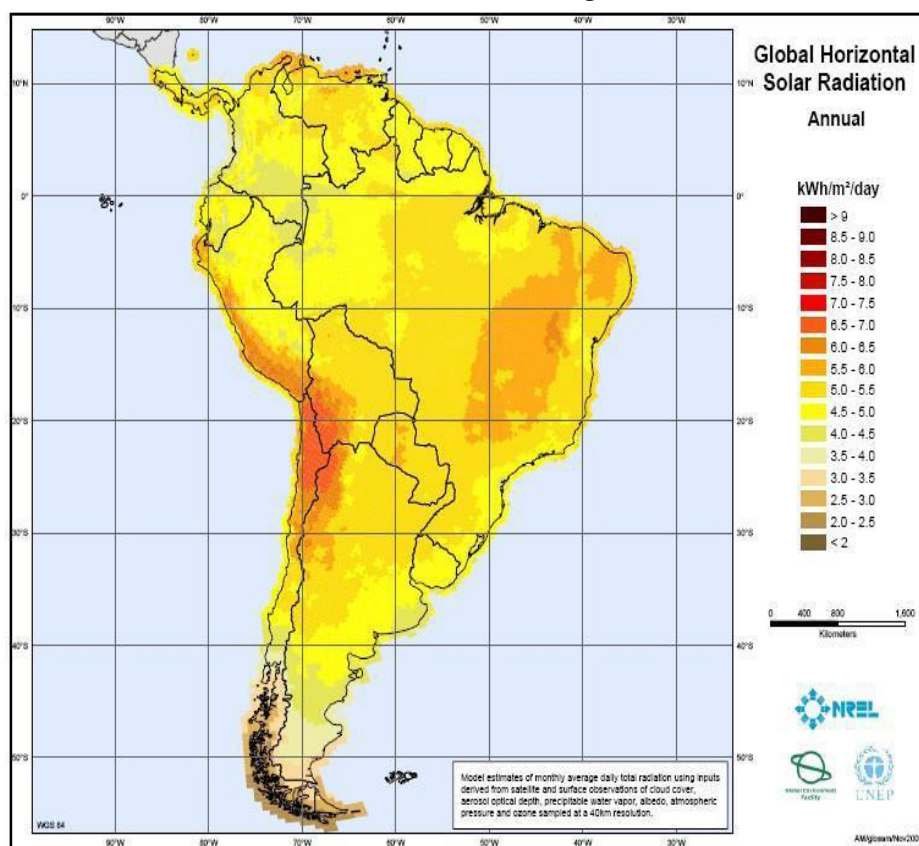
The research results presented in Table 8 show that the treatment process of effluents with the use of solar energy achieve results similar to those using the artificial irradiation catalysts. However, companies must be prepared for environmental weather, such as rainy days or with hazy conditions that affect the incidence of solar radiation on Earth's surface (MOREJON *et al.*, 2012).



## 7. Solar radiation in Brazil

The availability of solar radiation, also called the total incident energy, on the Earth's surface depends on the weather such as cloudiness or relative humidity, the local latitude, and the position of the Earth in function of its translational motion around the Sun (BRAZIL, MINISTRY OF MINES AND ENERGY, 2015).

Most of the Brazilian territory is located relatively close to the Equator, so large variations in daily solar term are not observed. The daily insolation reaches up to a period of eight (8) hours in some regions of Brazil (BRAZIL, MINISTRY OF MINES AND ENERGY, 2015) (Figure 8).



**Figure 8** - Extension of the average daily insolation in Brazil  
Source: BRAZIL, MINISTRY OF MINES AND ENERGY, 2015.

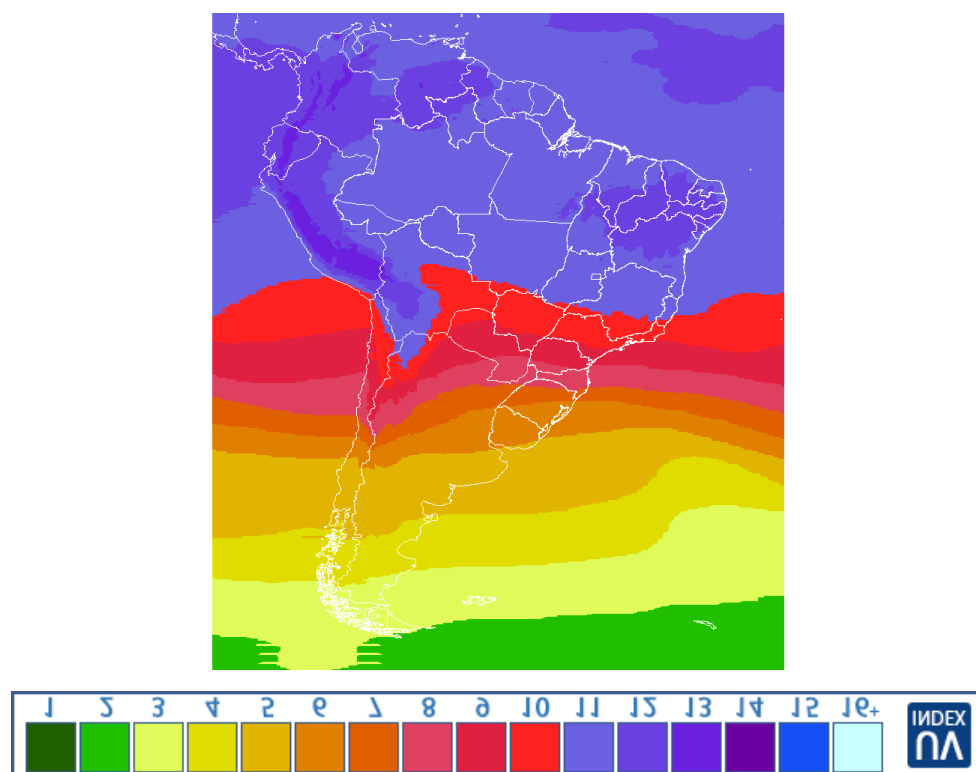
However, the largest companies and, as consequence, the largest producers of waste are concentrated in more distant regions of Equator. Therefore, in order to maximize the utilization of solar radiation, it is necessary to adjust the position of the collector according to the local latitude. For example, a fixed solar collection system should be oriented to the North having a tilt angle similar to the slope of the local latitude in the Southern Hemisphere (BRAZIL, MINISTRY OF MINES AND ENERGY, 2015).

It is important to highlight that estimates indicate that the solar energy incident on the Earth's surface is 10,000 times the world's energy consumption (BRAZIL, MINISTRY OF MINES AND ENERGY, 2015).

The solar radiation can be absorbed by the solar collectors, at relatively low temperatures (below 100°C). The use of this technology in Brazil occurs predominantly in the residential sector, but there is a significant demand for applications in other sectors, including the Advanced Oxidation Process (AOP).

However, the Ministry of Mines and Energy, Brazil (2015) reports the main technical restriction for the solar energy application was the low efficiency of energy conversion systems. Thus resulting in large areas energy harvesting its necessary in order to meet the business project and make it feasible.

For example, studies by the National Institute for Space Research (INPE) show that Brazil has high Ultra-Violet Index values (UVI) in several regions. There is the northeast region located in an area where rainfall occurs a few times a year. This is the area that receives little influence of humid air masses from the south and cold. Soon, it remains exposed to high UVI (Figure 9) for long periods of the year. Such conditions favor the use of solar energy production processes.



**Figure 9** - UVI maximum daily.

Source: INPE, 2015.

In this context, there is a highly demanding to design the systems that could operate integrally, complementing the existing light levels. Not to mention, the use of natural light implies a significant contribution to the reduction of both energy consumption and waste generation (disposal of mercury vapour lamps) (PEREIRA *et al.*, 2014).

In a waste treatment system that uses natural light properly designed, incorporating energy conservation as a criterion for achieving eco-efficiency, the artificial light would be switched off or reduced when a sufficient quantity of solar radiation was detected to provide the energy required ensuring the degradation of pollutants (FREIRE *et al.*, 2014).

The cost of technologies that minimize the consumption of electricity has proven a period of return that justifies their applicability in most cases. In addition, hydroelectric, in general, causes the flooding of large areas of food production and forests, affects terrestrial and aquatic ecosystems, and contributes to the generation of waste due to the maintenance of its equipment, resulting in deterioration of environmental quality (SURERUS *et al.*, 2014).

## **8. Final Considerations**

The expansion of industries reflected in the increase of the generated wastewater volumes, requiring the application of advanced technologies for the treatment and remediation of surface water. Thus, the implementation of the AOP could give a significant contribute to the supported development.

The application of AOPs using UV radiation for both homogeneous and heterogeneous systems, present a great efficiency in mineralization of recalcitrant compounds. However, the high cost of this type of decontamination process due to the need of specific catalysts as well as the consumption of oxidizing agents could be considered as a challenges for industrial scale implementation.

Many companies that operate in Brazil are related to the global market. Such situation leads to the revision of concepts for sustainable development. This study showed that government incentives are necessary to disseminate the use of solar radiation in order to promote advances in the socio-environmental context.

The use of solar radiation implies a cleaner production. In consequence, there are the rational uses of natural resources including improvements in both health and safety aspects and permanent reduction of the total costs; thus considering the efficient use of the energy. The statement is based on the information of the Ministry of Mines and Energy regarding the insolation level in Brazil, which reinforces the premise that it is possible to improve the relation cost versus benefit. Such improvement may result in advances with respect to the use of technologies that contribute to the sustainability of the planet.

It is important to highlight that the adoption of the cleaner production

increases the competitiveness of the companies, reducing the likelihood of fines and penalties due to environmental damage. Such situation facilitates access to credit lines for the enterprises and provides improvements to the company, the community and the environment, representing advances in terms of social and environmental responsibility of public and private institutions.

#### References

- ABNT (2004). Associação Brasileira de Normas Técnicas, NBR 10.004a: Classificação de Resíduos. Rio de Janeiro: p. 71. 2004.
- AIZEMBERG, L.; ROBOREDO, M.C.; RAMOS, T.G.; SOARES DE MELLO, J.C.C.B.; ANGULO MEZA, L.; ALVES, A.M. (2014). Measuring the NBA Teams- Cross-Efficiency by DEA Game. *American Journal of Operations Research*, v. 04, p. 101-112.
- ALMEIDA, P. S. ; BENDER, V. C. ; BRAGA, H. A. C. ; MARCHESAN, T. B. ; COSTA, MARCO A. DALLA ; ALONSO, J. M. (2014). Static and Dynamic Photoelectrothermal Modeling of LED Lamps including Low-Frequency Current Ripple Effects. *IEEE Transactions on Power Electronics*, v. PP, p. 1-1.
- BAHNEMANN, D. (2004). Photocatalytic Water Treatment: Solar Energy Applications. *Solar Energy* v.77, n.5, pp.445-459.
- BRITO, W.R. ; QUIRINO, W.G. ; LEGNANI, C. ; PONCIANO, C.R. ; CREMONA, M. ; ROCCO, M.L.M. (2012). Ultraviolet Photodegradation of Tris (8-hydroxy-quinolinat) Aluminum (Alq3) thin Films Studied by Electron and Laser Stimulated Desorption. *Optical Materials (Amsterdam. Print)*, v. 35, p. 29-32.
- BRASIL. Ministério de Minas e Energia (2015). Matriz Energética Nacional. Colaboração: Empresa de Pesquisa Energética Nacional. MME: EPE.
- CABRAL, S.M. (2010). Avaliação da remoção de microcystis aeruginosa e microcistina – LR de águas eutrofizadas utilizando fotocatalise heterogênea. Dissertação de mestrado. Centro de Ciências e Tecnologias, Universidade Estadual da Paraíba.
- CASSANO, A. E, ALFANO, O. M., BRANDI, R. J. (2001). Diseño de Reactores para Fotocatálisis: Conceptos Fundamentales. In: BLESÁ, M. A., Eliminación de Contaminantes por Fotocatálisis Heterogênea, capítulo 10, La Plata, Argentina, Red CYTED VIII-G.
- CHENG, L. C. ; MELO FILHO, L. R. . Platform Conceptual Model in QFD for Generic Drug. *Product (IGDP)*, v. 8, p. 3-16, 2010.
- COLNAGO, G R.; CORREIA, PAULO B.; GOMES, A. G.; FERNANDES, P T. (2010). Otimização do Potencial de Geração de Usinas Hidrelétricas. In: Congresso Brasileiro de Automática - CBA, 2010, Bonito - MS. Anais do XVII, Congresso Brasileiro de Automática.
- CREA/MG (2011) – Conselho Regional de Arquitetura e Engenharia de Minas Gerais. Sustentabilidade e Eficiência Energética no Ambiente Construído.
- EPA (2005) - Environmental Protection Agency. Evaluation of Mercury Emissions from Fluorescent Lamp Crushing.
- ESPINOZA-QUIÑONES, F. R. ; MODENES, A. N. ; PAULI, A. R. ; PALÁCIO, S. M. . Analysis of Trace Elements in Groundwater Using ICP-OES and TXRF Techniques and Its Compliance with Brazilian Protection Standards. *Water, Air and Soil Pollution (Print)*, v. 226, p. 32, 2015.
- FREIRE, L. F. A.; DA FONSECA, F. V.; YOKOYAMA, L.; TEIXEIRA, L. A. C. (2014). Study of solar photo-Fenton system applied to removal of phenol from water. *Water Science and Technology*, v. 70, p. 780.
- FERREIRA, R. C.; NASCIMENTO JÚNIOR, A. B.; SANTOS, P.J.P.; BOTTER-CARVALHO, M.L.; PINTO, T. K. O. (2015). Responses of Estuarine Nematodes to an Increase in Nutrient Supply: An in Situ Continuous Addition Experiment. *Marine Pollution Bulletin*, v. 90, p. 115-120.
- GALINDO, C., JACQUES, P., KALT, A. (2001) Photooxidation of the phenylazonaphthol on TiO<sub>2</sub>: Kinetic and mechanistic investigations. *Chemosphere* v 45, pp.997-1005.
- GIL, L. F.; GURGEL, L. V. A. (2009). Adsorption of Cu(II), Cd(II), and Pb(II) from Aqueous Single Metal Solutions by Succinylated Mercerized Cellulose Modified with Triethylenetetramine. *Carbohydrate Polymers*, v. 77, p. 142-149.
- GUIMARÃES, J. R., LITTER, M. I., PIZARRO, R. (2004). Eliminación de Contaminantes por Fotocatálise Heterogênea. 1. ed. Madrid: Editorial Ciemat, v. 1. , 388 p.

- GUMY, D., GIRALDO, S.A., RENGIFO, J., PULGARIN, C. (2008). *Applied Catalysis B: Environmental*.v. 78, p. 19.
- GUSMAO, K. A. G.; GURGEL, L. V. A.; MELO, T. M. Do S.; CARVALHO, C. De F.; GIL, L. F. (2014). Adsorption Studies of Etherdiamine onto Modified Sugarcane Bagasses in Aqueous Solution. *Journal of Environmental Management*, v. 133, p. 332-342.
- LEDAKOWICZ, S., SOLECKA, M., ZYLLA, R. (2001). Biodegradation, Decolourisation and Detoxification of Textile Wastewater enhanced by Advanced Oxidation Processes, *J. Biotechnol.* v. 89 pp.175-184.
- MACHADO, A.E., MIRANDA, J.A., FREITAS, R. F., DUARTE E. T.F.M., FERREIRA, L. F., ALBURQUERQUE, Y.T.D., RUGGIERO, R., SATTLER, C., OLIVEIRA, L. (2003). Destruction of the Organic Matter Present in the Effluent from a Cellulose and Paper Industry Using Photocatalysis. *J. Photochemistry and Photobiology A: Chemistry*, v. 155, p. 231 – 241.
- MALATO, S.; BLANCO, J.; VIDAL, A.; RICHTER, C. (2007). Photocatalysis With Solar Energy at a Pilot-plant Scale: An Overview. *Applied Catalysis B: Environmental*. V.37, p. 1-15.
- MAZUR, L.; PERALTA-ZAMORA, P. G.; DEMCZUK, B.; HOFFMANN RIBANI, R (2014). Application of Multivariate Calibration and NIR Spectroscopy for the Quantification of Methylxanthines in Yerba Mate (*Ilex Paraguariensis*). *Journal of Food Composition and Analysis (Print)*, v. 35, p. 55-60.
- MOREIRA, R.I. A. ; CHENG, L. C. . Proposal of managerial standards for new product portfolio management in Brazilian pharmaceutical companies. *Brazilian Journal of Pharmaceutical Sciences (Impresso)*, v. 46, p. 53-66, 2010.
- MOREJON, C. F. M.; LIMA, J. F. DE;; POSSA, R. D.. New model of municipal solid waste management. *International Journal of Environment and Sustainable Development*, v. 11, p. 238-249, 2012.
- INPE – Instituto Nacional de Pesquisas Espaciais, Ministério de Minas e Energia do Brasil, 2015. Disponível: <<http://satelite.cptec.inpe.br/uv/>>, Acesso: 15/09/2015.
- MOLINARI, R., PALMISANO, L., DRIOLLI, E. (2002). Studies on Various Reactor Configurations for Coupling Photocatalysis and Membrane Processes in Water Purification. *Journal of Membrane Science* v. 206 n. 1-2 pp. 399-415.
- NEYENS, E.; BAEYENS, J. (2003). A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials*, 98: 33-50.
- NOGUEIRA, R.F.P; OLIVEIRA, M.C.; PATERLINI, W.C. (2005), Simple and Fast Spectrophotometric Determination of H<sub>2</sub>O<sub>2</sub> in Photo-Fenton Reactions Using Metavanadate, *Talanta*, 66, pp. 86-91.
- NOGUEIRA, R. F. P.; MODÉ, D. (2002). *Química Nova*, v. 27, p. 169.
- NOGUEIRA, R. F. P.; TROVÓ, A. G.; MODÉ, D. F. (2002). *Chemosphere*, v. 48, p. 385.
- NOGUEIRA, R. F. P., TROVÓ, A.G., SILVA, M. R.A., VILLA, R. D., OLIVEIRA, M. C. (2007). Fundamentos e aplicações ambientais dos processos fenton e foto-fenton. *Quím. Nova*, São Paulo, v. 30, n. 2.
- OLIVEIRA, D.F., PEREIRA, A.C., FIGUEIREDO, H.C.P., CARVALHO DA SILVA, G, NUNES, A.S., ALVES, D.S., CARVALHO, H.W.P.(2007). Antibacterial activity of plant extracts from Brazilian southeast region. *Fitoterapia* 78: 142-145.
- OSHA (2007). Occupational Safety e Health Administration. Available: <<http://www.osha.gov/>>. Acess: 17/01/2015.
- PEREIRA, A. R.; DA COSTA, R. S. ; YOKOYAMA, L. ; ALHADEFF, E. M. ; TEIXEIRA, L. A. C. (2014) . Evaluation of Textile Dye Degradation Due to the Combined Action of Enzyme Horseradish Peroxidase and Hydrogen Peroxide. *Applied Biochemistry and Biotechnology*, v. 174, p. 10.
- PASCOAL, S.A., LIMA, C.A.P. SOUSA, J. T., LIMA, G. G.C., VIEIRA, F. F. (2007). Aplicação de Radiação UV solar e artificial sem Tratamento fotocatalítico de efluentes de Curtume. *Química Nova*, São Paulo, v. 30, n. 5, p.15
- PEIXOTO, R. S. ; CARMO, F. L. ; SANTOS, H. F. ; ANDRAD, L. L. ; PAES, J. E. ; CURY, J. C. ; ROSADO, A. S. (2011) . Biomonitoramento: Bioindicadores microbianos da presença de óleo em manguezais. *Microbiologia in Foco*, v. 14, p. 8-13.
- PERA-TITUS, M.; GARCIA-MOLINA, V.; BAÑOS, M. A.; GIMÉNEZ, J.; ESPLUGAS, S. (2004). Degradation of Chlorophenols by Means of Advanced Oxidation Processes: a General Review, *Applied Catalysis B. Environmental*, v. 47, p. 219 – 256.
- PERINI, A. P.; NEVES, L. P.; CALDAS, L. V. E. (2014). Development and Characterization of a Graphite-walled Ionization Chamber as a Reference Dosimeter for <sup>60</sup>Co beams. *Radiation Physics and Chemistry* (1993), v. 104, p. 248-251.

- PUMA, G. L., YUE, P. (2001). La Novel Fountain Photocatalytic Reactor: Model Development and Experimental Validation, *Chemical Engineering Science*, v. 56, pp. 2733-2744.
- QUEIROZ, M. T. A.; QUEIROZ, C. A.; SABARÁ, M. G. S.; LEAO, M. M. D.; AMORIM, C. C. (2014). Valor Agregado: Inserção da Produção Mais Limpa na Indústria Têxtil. *Revista de Química Industrial*, v. 744, p. 54-61.
- RANGEL, M. C.; BRITTO, J. M.; OLIVEIRA, S.B.; RABELO, D. (2008). Catalytic Wet Peroxide Oxidation of Phenol from Industrial Wastewater on Activated Carbon. *Catalysis Today*, v. 133-35, p. 582-587.
- RODRIGUES, C. R. B. S.; ALMEIDA, P. S.; SOARES, G. M.; BRAGA, M. F.; BRAGA, H. A. C. A. (2013). Novel Linear Circuit For Current Equalization In Led Strings. *Eletrônica de Potência (Impresso)*, v. 18, p. 1109-1117.
- ROBINSON, T., MCMULLAN, G., MARCHANT, R. (2001). Remediation of Dyes in Textile Effluent: a Critical Review on Current Treatment Technologies with a Proposed Alternative, *Bioresour. Technol.* v.77 pp. 247-255.
- SAMBINELLI, F. ; SOSA ARIAS, C. (2015). Augmented Reality Browsers: A Proposal for Architectural Standardization. *International Journal of Software Engineering & Applications (IJSEA)*, v. 6, p. 1-9.
- SELVAM, K., MURUGANANDHAM, M., MUTHUVEL, I. (2006). The influence of Inorganic Oxidants and Metals Ions on Semiconductor Sensitized Photodegradation of 4-fluorophenol. *Chemical Engineering Journal*.
- SMAHA, N.; GOBBI, M.F., 2003. Implementação de um modelo para simular a eutrofização do Reservatório do Passaúna - Curitiba - PR. *Revista Brasileira de Recursos Hídricos* 8 (3): 59-69.
- SURERUS, V.; GIORDANO, G.; TEIXEIRA, L. A. C. (2014) . Activated Sludge Inhibition Capacity Index. *Brazilian Journal of Chemical Engineering (Impresso)*, v. 31, p. 385-392.
- SOUZA, L. G. M.; FÉLIX, L.F.; CUADROS-ORELANA, S.; SILVA LIMA, Á.; ARAUJO, P. M. M. (2009). Solar Water Disinfection in Northeast Brazil: Kinetics of the Process and the Study for the Development of a Pilot Plant. *Journal of Engineering Science & Technology*, v. 4, p. 328-343.
- TIDRE, P. V.; BIASE, N. G.; SILVA, M. I. S (2013).. Utilização dos modelos de séries temporais na previsão do consumo mensal de energia elétrica da região Norte do Brasil. *Revista Eletrônica Matemática e Estatística em Foco*, v. 1, p. 57-66..
- UNIDO (2015). *Cleaner Production Toolkit. Introduction into Cleaner Production. Volume 1*, p. 1- 34. Available: <<http://www.unido.org/>>, Access: 25/01/2015.
- WBCSD. *Water for Business: Initiatives guiding sustainable water management in the private sector* (2009). Available: <<http://www.wbcd.org/>>, Access: 25/01/2015.
- WINDMÖLLER, C.C.; DURÃO Jr., W. A.; OLIVEIRA, A.; VALLE, C. M.. (2015). The redox processes in Hg-contaminated soils from Descoberto (Minas Gerais, Brazil): implications for the mercury cycle. *Ecotoxicology and Environmental Safety*, v. 112, p. 201-211.
- ZHU, J.; YU, X.; LOULA, A. F D. (2011) . Mixed Discontinuous Galerkin Analysis of Thermally Nonlinear Coupled Problem. *Computer Methods in Applied Mechanics and Engineering*, v. 200, p. 1479-1489.