

## Photocatalytic reactors and their scale up: literature review

### Reatores fotocatalíticos e sua ampliação de escala: revisão bibliográfica

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#### RESUMO

As reações de fotocatalise tem sido muito estudadas para a degradação de substâncias recalcitrantes. Sabe-se que a ativação do fotocatalisador ocorre com a absorção de fótons de energia maior ou igual ao band gap, fazendo com que elétrons da banda de valência sejam transferidos para a banda de condução, surgindo então uma lacuna na banda de valência. Em escala laboratorial muitos trabalhos já foram desenvolvidos. A configuração mais utilizada é o reator cilíndrico, onde a fonte de iluminação é colocada ao centro, mergulhado no meio reacional, protegida por uma célula de quartzo. As lâmpadas de Xenônio, LED e mercúrio são as mais utilizadas devido ao comprimento de onda no qual emitem radiação eletromagnética. Também são utilizados catalisadores heterogêneos para melhorar a eficiência do processo, porém quando utilizados dispersos no meio, há uma dificuldade em separá-los após a operação, e quando utilizados imobilizados, existem barreiras relacionadas à sua fixação no sistema. Para o aumento de escala, observou-se alteração na fonte de iluminação para a luz solar, substituição do quartzo pelo vidro, e diferentes formas de reutilizar os catalisadores para uma maior economia.

**Palavras-chave:** Fotocatálise heterogênea; Reator fotocatalítico; Aumento de escala.

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#### ABSTRACT

Photocatalysis reactions have been extensively studied for the degradation of recalcitrant substances. It is known that the activation of the photocatalyst occurs with the absorption of photons of energy greater than or equal to the band gap, causing electrons from the valence band to be transferred to the conduction band, resulting in a gap in the valence band. On a laboratory scale, many works have already been developed. The most used configuration is the cylindrical reactor, where the light source is placed in the center, immersed in the reaction medium, protected by a quartz cell. Xenon, LED and mercury lamps are the most used due to the wavelength at which they emit electromagnetic radiation. Heterogeneous catalysts are also used to improve the efficiency of the process, but when used dispersed in the medium, there is a difficulty in separating them after the operation, and when used immobilized, there are barriers related to their fixation in the system. For the scale up, a change in the lighting source to sunlight, replacement of quartz by glass, and different ways of reusing the catalysts for greater economy were observed.

**Keywords:** Heterogeneous photocatalysis; Photocatalytic reactor; Scale up.

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## INTRODUCTION

It is known that water is an abundant natural resource on planet Earth, however only a limited amount is viable for use, since much of it is salt water. A major concern that has been discussed is the progressive decrease of this resource, since urbanization, industrialization, agriculture, inadequate pollutant disposal techniques and changes in climatic conditions have drastically affected the physical-chemical and microbiological conditions of the water (Kaur, Umar e Kansal 2016; Hoang, et al., 2021). Therefore, the conscious use of this resource, as well as the appropriate application of treatments are essential for its good quality and removal of organic, inorganic and mineral substances in water courses.

The term “emerging contaminants” refers to products with toxic potential that are not removed or eliminated by traditional processes for treating water for human consumption, and the effects of these substances are still poorly understood in the long term. Among them, endogenous hormones, synthetic hormones, contraceptives, drugs of various compositions, caffeine, sucralose, nanomaterials, bactericides, insecticides, algacides, herbicides, cleaning and personal hygiene products, sunscreens, chlorination and water ozonation products stand out, among others.

With the rapid pace of industrial and urban growth, the number of contaminants has increased significantly, and it demands for new treatment methods. With the aim of eliminating these pollutants from water, techniques such as advanced oxidation processes (AOP) have been developed, which include photocatalysis (Kaur, Umar and Kansal, 2016). Photocatalysis, in turn, is based on the process of generating reactive oxygen species that are not selective and have the ability to oxidize recalcitrant compounds by dehydrogenation or hydroxylation, and which are finally mineralized into final products (Ahmad et al. 2016).

Due to its efficiency and great potential for removing contaminants, this technique has attracted a lot of interest from researchers, with a focus on overcoming challenges such as light intensity distribution, catalyst doping to increase the reach of the process to visible light and recovery of catalysts for large-scale photocatalysis systems. Other alternatives related to the materials used, the lighting source and reactor design have also been evaluated.

Photocatalytic reactors can be separated into two classifications, for production and for degradation. The first ones have been applied mainly for the generation of H<sub>2</sub> for

energy production. Degradation reactors aim to degrade recalcitrant substances, which often do not receive adequate treatment.

Different reactor geometries have been studied, both in the case of production and degradation. However, these studies are advanced on a laboratory scale. Many variables that change the results have been used, such as the reactor material, the lighting source, the heterogeneous catalyst and the way it will be used, directly affect the efficiency of the process.

The expansion of scale must receive great attention since for its applicability it is necessary that all obstacles are corrected for a good functioning, so that companies and the population in general can enjoy this technology. Technical feasibility and economic feasibility are the two main factors that must be considered when talking about scaling up (Piriyah and Knmani, 2020). As well as on a laboratory scale, all operational variables must be considered and adapted so that there is feasibility in the application of the project.

This work aims to present a review of the literature on used photocatalytic reactors. It is also proposed to review approaches to scale up the laboratory scale to a pilot scale of photocatalytic reactors for the degradation of emerging pollutants.

## **METHODOLOGY**

This study is theoretical and based on a bibliographic review about the photocatalysis process, laboratory projects of photocatalytic reactors and projects to scale up these reactors. The presentation of photocatalytic reactors was divided into laboratory scale and pilot scale, highlighting the most frequently used projects.

The data collection consists of a range of approximately 50 articles covering the mentioned subjects. The articles were selected prioritizing the most recent (years 2020, 2021 and 2022), but there are also some older works due to their relevance. The keywords used were photocatalysis, photodegradation, photoreactor and photocatalytic reactor. The work has several images adapted from the reviewed articles and the Canva website was used as a tool to create these illustrations.

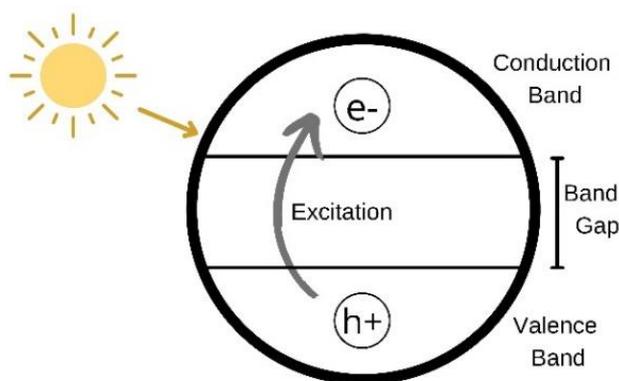
## **RESULTS AND DISCUSSION**

### **Photocatalytic Reactors**

Photocatalysis

According to Bora and Mewada (2017), the basic mechanism of heterogeneous catalyst activation begins with the absorption of photons of energy greater than or equal to the band gap of a photocatalyst, causing electrons ( $e^-$ ) in its valence band (VB) to be transferred to the conduction band (CB), then a gap ( $h^+$ ) appears in the VC, as illustrated in Figure 1. One of the accepted mechanisms suggests that the photogenerated electrons and holes react with the available oxidants and reductants, forming radicals that later react with the pollutant, forming a series of intermediate species and resulting in the complete mineralization of the pollutants.

**Figure 1** - Mechanism of action of photocatalysts



Source: Adapted from Bora and Mewada (2017).

Ahmad et al. (2016) state that a wide variety of materials have been identified as photocatalysts, each of which has a different band gap energy. The author also cites another accepted mechanism for the process, in which the charged components ( $e^-$ ) formed by the absorption of light photons can migrate to the surface of the catalyst and initiate redox reactions with the adsorbed pollutants or can recombine dissipating energy.

The process still has some problems to be solved, such as the more efficient use of visible light, the rapid recombination of the charged species and the separation of the catalyst from the aqueous medium after the process. When talking about recombination, Bora and Mewada (2017) explain that after the electron migrates to the conduction band and leaves the hole in the valence band, if this is not eliminated quickly, it will result in reduced efficiency. This recombination can be avoided through techniques applied to catalyst synthesis, such as the addition of dopants, co-catalysts or by heterogeneous coupling. In some cases, the use of sacrificial reagents in the reaction medium is still indicated to reduce the rate of recombination of the charged species through reactions with the gap, reducing their availability.

Ohtani (2010) states that any photocatalyst can be active under visible light irradiation if it is modified through metallic or non-metallic elements. As an example, the  $\text{TiO}_2$  is cited, which is widely used as a catalyst, but which would need a wavelength in the ultraviolet region (greater than 400 nm) for its activation with maximum efficiency. To solve this problem, nitrogen doping has been studied, among other strategies, since this element is very stable, has an atomic size compatible with oxygen and needs a low ionization energy to be introduced. Methylene blue, methyl orange and rhodamine have been proven to be effectively degraded by nitrogen-doped  $\text{TiO}_2$  (Ahmad et al. 2016).

Another way to improve the efficiency of the process is to increase the contact surface of the heterogeneous catalyst with the medium, for which slurry reactors have been used, in which the catalyst is dispersed in the liquid reaction medium. However, in this configuration it is necessary to consider a system to separate the catalyst particles at the end of the process (Ahmad et al., 2016). As a possible solution, the immobilization of the catalyst is pointed out. In this context, membrane technology consists of the immobilization of solid particles, being an efficient process. It has a simultaneous separation process of the photocatalyst and the product of the reaction system, separates the photocatalyst from the treated water and keeps the solid particles confined in the reaction system.

When referring to laboratory photocatalytic reactors, the light used can be artificial, using one of the types of lamps, and the wavelength can be chosen according to the catalyst used for a better reactor performance. However, with the increase in scale, seeking energy savings, the objective becomes the use of sunlight.

Regarding the classification, they can be separated into production and degradation reactors. Production reactors are characterized by the production of gases, like as hydrogen, for conversion into clean energy. Degradation processes aim to remove recalcitrant substances that remain in the water. The production ones have the difference in the design that concentrate the gases inside, while the degradation ones do not have this concern. Next, both will be explored.

#### Laboratory reactors for gas production

The photocatalysis process has been applied for the production of gases of interest, especially for the generation of clean energy. In this context, the photocatalytic production of hydrogen from the photolysis of water stands out with great potential. The

reactors and operating conditions developed for these processes, despite having peculiarities inherent to the application, can also be successfully used in systems for the degradation of emerging pollutants.

Vincentini et al. (2020) studied the efficiency of two photocatalytic reactors. The first is an Annular reactor, using an 18 W UVC lamp as a source of radiation protected by a quartz tube and positioned on the axis of the reactor. The second is called a quartz reactor. This system can combine up to three 18W UVC lamps simultaneously, arranged in an Aluminum refractory arc. The author observed that the quartz reactor has a hydrogen generation rate approximately 7 times higher than that of the annular reactor, so this reactor has a better use of the emitted photons.

Jing et al. (2010) studied a photocatalytic reactor for hydrogen production based on a parabolic concentrator. One of the main objectives is to demonstrate the efficiency of using direct sunlight. The most important challenges to be solved are uniform lighting, more efficient catalysts under sunlight, as well as their low cost. The reactor consists of glass, reflective surface, flow meters and the Compound Parabolic Concentrator (CPC), which has an inclination of 35°, Xi'an latitude, China, and was operated between 12 and 13 h at maximum power, and until 15:00 there was a small decrease.

Enzweiler and colleagues (2020) analyzed the effect of catalyst concentration Pd-TiO<sub>2</sub>/ZSM-5, ethanol content and pH of the solution on the rate of hydrogen production under ultraviolet light irradiation. Using a stainless steel cylindrical reactor with a quartz tube immersed in solution, the light source was a UVC lamp ( $\lambda=254\text{nm}$  and 7W). The catalyst was kept dispersed in solution.

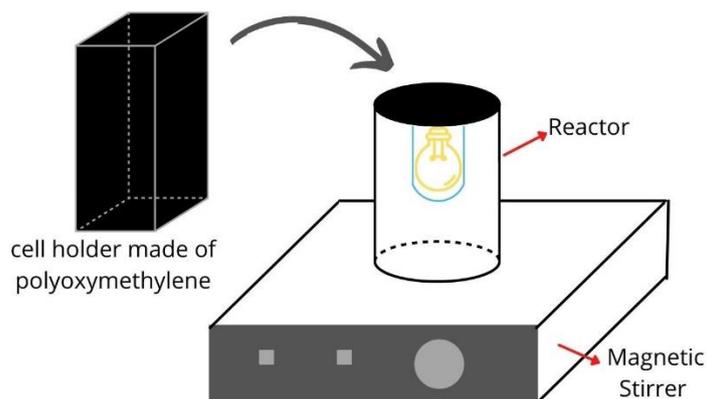
The generation of hydrogen, as well as other gases of interest, through the photocatalytic process compared to the application of the technique for the degradation of emerging effluents presents two fundamental differences. The first is the thermodynamic conditions for the reaction, since the generation of compounds is an *up-hill* process and photodegradations are classified as *down-hill*. Another difference is in the reactor design, as the production of gases requires closed reactors, to allow the accumulation and collection of products of interest, and photodegradation does not have this restriction, since the objective is the mineralization of the reagent usually in solution.

Laboratory reactors for photodegradation

Taking into account that the application of photocatalysis for the degradation of contaminants is a relatively new process, much has been studied so that the operational variables and the reactor design are improved and thus reach optimal efficiency. For this, several authors have developed different designs for reactors, with changes in geometry, material, light source and catalyst, in search of this improvement.

Jamali et al. (2013) studied the degradation of phenol with LED light using  $\text{TiO}_2$  as a catalyst. The photoreactor consisted of a cylindrical reaction cell with a diameter of 20 mm and a height of 50 mm, a polyoxymethylene (POM) cell holder to prevent the absorption of ambient light by the photocatalyst, as shown in Figure 2. The UV-LED was positioned vertically in the center of the support, it has a peak wavelength of 375 nm, temperature range between 30 and 80 °C. The highest percentage of degradation was 87% within 4 h of the experiment, the catalyst concentration varied between 0.17 to 1.8  $\text{gL}^{-1}$ . A disadvantage is still the non-uniform distribution of light.

**Figure 2** - Schematic representation of a photoreactor with LED light.



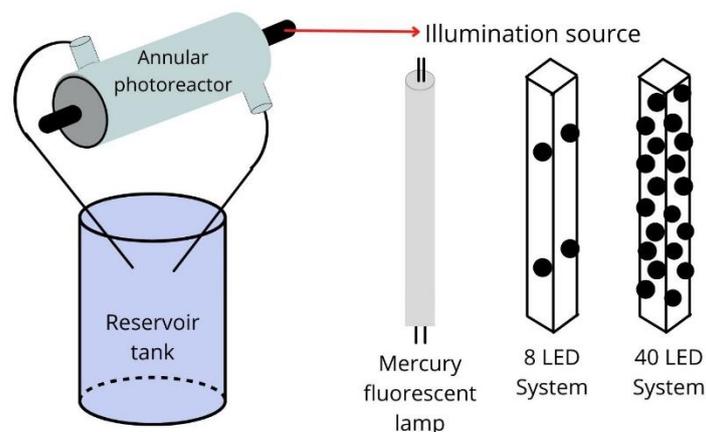
Source: Adapted from Jamali et al. (2013).

Fogaça et al. (2021) used a UV-LED mini-reactor for the degradation of methylene blue dye and tartrazine. The reactor had a volume of 3.0 mL and a radiation source with a power of 5 W and maximum emission at 365 nm. Graphene oxide was supported on  $\text{TiO}_2$  and used as a catalyst. The reactor layout had a heat sink and fan and a magnetic bar inside a quartz cuvette (reactor) to disperse the catalyst particles. The entire reaction system was mounted inside a spectrophotometer.

Martín-Sómer and collaborators (2017) studied the efficiency of different lighting sources for methanol oxidation. Comparing three different sources of UVA (a mercury fluorescent lamp, a system based on 8 LEDs and a system based on 40 LEDs) with different light distributions. The photoreactor used was an annular model, operating in a

closed recirculation circuit, with a reservoir tank as shown in Figure 3. The experiments were carried out using  $\text{TiO}_2$  free in the concentration of 0.1 g/L.

**Figure 3** - Schematic representation of annular photoreactor

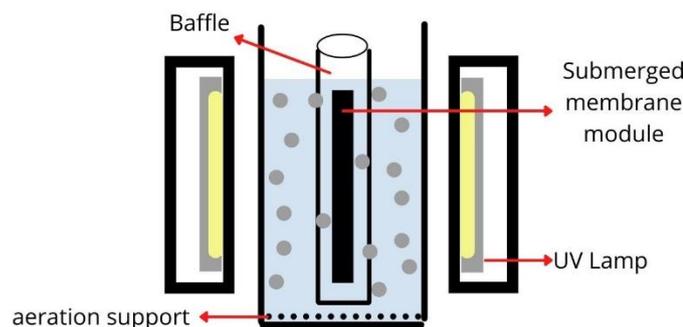


Source: adapted from Martín-Sómer et al. (2017).

The results of Martín-Sómer and collaborators (2017) point out that the mercury lamp promotes a more homogeneous distribution of light, however for the 8 LEDs, the place where the LED is is highly irradiated, while other areas do not receive radiation homogeneously. When the experiment was carried out with 40 LED points, an improvement in the distribution homogeneity was obtained, however the mercury lamp still promoted better results.

Fernandez et al. (2014) performed experiments with a set of 33 drug compounds simultaneously. The photoreactor system used had a cylindrical shape of borosilicate glass, with a total volume of 4 L. The membranes were hollow fiber polyvinylidene fluoride (PVDF). Ultrafiltration membranes have pores of 0.04  $\mu\text{m}$ . The membrane module was placed in the center of the reactor and has the role of separating the catalyst and a selective barrier for the molecules to be degraded. UV radiation was provided by 7 lamps (blue black light, 8W). The author also cite having used aeration through a system installed at the bottom of the reactor. This was used in order to increase the photo-oxidation of molecules (reducing the sacrificial recombination of electrons), fluidize the system to ensure a homogeneous mixture and provide turbulence along the submerged membrane. Figure 4 illustrates the reactor. With the results, the author stated that compounds with reaction rate constants greater than  $0.0544 \text{ min}^{-1}$  are effectively removed in the photoreactor under the operating conditions used.

**Figure 4** - Schematic representation of a submerged membrane photocatalytic reactor

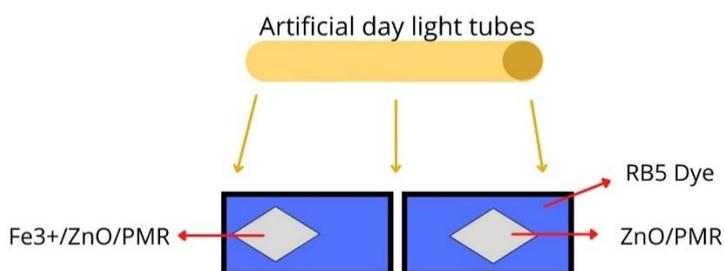


Source: adapted from Fernandez et al. (2014).

Wang and colleagues (2021) also studied a submerged membrane photocatalytic reactor for the removal of *residual p-nitrophenol* (PNP). The reactor had a volume of 9 L, being composed of a quartz tube, a light source and the membrane module. The light source used was a 500 W Xenon lamp, as it resembles natural sunlight. The hollow fiber microfiltration membrane module made of PVDF was attached to the inner wall of the reactor. The catalyst used was Fe(III)-ZnS /gC<sub>3</sub>N<sub>4</sub>. Under optimal operating conditions, a high percentage of PNP removal was obtained through photo-fenton reactions under simulated sunlight irradiation. Membrane filtration quickly and effectively separated the catalyst inside the reactor, preventing its loss.

Powder photocatalysts are being widely used for photocatalysis, however their recovery is difficult. Ashar et al. (2020) suggest that the catalyst can be adhered to a substrate, in their case they used polyester fabric added with nano-ZnO and doped with Fe<sup>3+</sup>. After the tissue was prepared, the reactor was structured with a glass container with a volume of 1.6 L. Illumination was provided by artificial daylight tubes, with 72 W, according to the schematic diagram in Figure 7. Finally, the author concluded that the doping of ZnO with Fe<sup>3+</sup> can make the acid capable of capturing high content of sunlight. The use of catalyst immobilization on polyester decreased the agglomeration of the particles and acted as a new reusable material for the photocatalytic treatment of the studied RB5 dye.

**Figure 5** - Schematic diagram of photocatalytic reactor with polyester supported photocatalyst



Fonte: adaptado de Ashar et al. (2020).

Table 1 presents information on laboratory scale photocatalytic reactors used in scientific works published in the literature. The compound to be degraded, the irradiation source and some observations made during the review are highlighted in order to facilitate the comparison of different laboratory scale photocatalytic reactors.

**Table 1** - Laboratory reactors for photodegradation

(to be continued)

| REACTOR   | DEGRADED COMPOUND                | IRRADIATION SOURCE  | CATALYST  | OBSERVATIONS  | REFERENCE                  |
|---|----------------------------------|---|---|---|----------------------------|
| Cylindrical reaction cell (glass) photoreactor with membrane module | Phenol                           | UV-LED lamp ( $\lambda_{max} = 375\text{nm}$ )  | ---   | Radiation source positioned vertically in the center of the reactor.  | Jamali et al. (2013)       |
| Photoreactor with membrane module                                   | Municipal sewage                 | UV-C germicidal lamp (16W, $\lambda_{max} = 254\text{ nm}$ )  | ---   | Membrane module separate from the reactor for ultrafiltration   | Moza et al. (2014)         |
| Annular photoreactor  | Methanol                         | UVA lamps (mercury lamp, 8 LED's and 40 LED's)  | ---   | Mercury lamp has a more homogeneous distribution of light.  | Martín-Sómer et al. (2017) |
| Submerged membrane photoreactor                                     | 33 drug compounds simultaneously | 7 UV lamps (8W)   | ---   | Use of aeration to increase reactor efficiency  | Fernandez et al. (2014)    |
| Submerged membrane photoreactor                                     | Residual p-nitrophenol (PNP)     | Xenon lamp (500W) simulating solar irradiation  | TiO <sub>2</sub> used in powder (free)                    | Membrane filtration quickly and effectively separated the catalyst inside the reactor, preventing its loss. | Wang et al. (2021)         |
| Cylindrical glass photoreactor                                      | Formaldehyde in indoor air       | UVC lamp (16 W, 365 nm)<br>UV lamp (UVA, 12 W)<br>30 or 40 UV-LEDs (20 mW per UVLED, $\lambda = 383\text{nm}$ ) | Ag/TiO <sub>2</sub> coated on plate holders or glass rods | Gaseous reaction medium   | Shie et al. (2008)         |
| Photocatalytic hydrogen production reactor                          | Hydrogen production              | direct sunlight   | TiO <sub>2</sub> (free)                                   | Use of a composite parabolic concentrator in the reactor and pilot scale reactor proposal.                  | Jing, et al. (2010)        |

**Table 1** - Laboratory reactors for photodegradation

(to be continued)

| REACTOR  | DEGRADED COMPOUND  | IRRADIATION SOURCE  | CATALYST  | OBSERVATIONS  | REFERENCE                              |
|--|--|---|---|---|--|
| Fe <sup>3+</sup> @ZnO/polyester based solar photocatalytic membrane reactor                              | RB5 dye reduction  | D65 artificial daylight tubes (72 W)                      | ZnO undoped and in ZnO doped with Fe <sup>3+</sup> polyester fabric support | Illumination tubes positioned above the reactor horizontally  | Ashar et al. (2020)                    |
| Quartz UV Reactor  | Diclofenac drug  | Xenon Lamp (1500W)  | TiO <sub>2</sub> (free)   | Degradation in 50 mL of solution contaminated with different concentrations of diclofenac and catalyst  | Calza et al. (2006)                    |
| Photocatalytic membrane reactor, with hybrid catalysis-ultrafiltration system with TiO <sub>2</sub> /UVA | Diclofenac drug  | Four 24W black light bulbs, encased in acrylic containers | TiO <sub>2</sub> . (Free)   | Reactor volume of 0.7 L, made of aluminum due to the higher reflectance of UV irradiation and the inner surface was anodized for corrosion protection | Sarasidis et al. (2014)                |
| Polymethylmethacrylate (PMMA) cylindrical photoreactor   | Methylene blue dye, Orange II dye and the antibiotic levofloxacin (Separately) | UV-A lamp   | Bismuth titanate coated glass rods  | ---   | Grao et al. 2022                       |
| Membrane photocatalytic reactor  | Industrial textile effluent  | Ultraviolet lamp (UVC) $\lambda = 253.70$ nm              | ZnO covered with Polyethylene Glycol particles                              | Presence of zinc oxide coated with polyethylene glycol nanoparticles and polypiperazine-amide (PPA) ultrafiltration membrane                          | Desa et al. (2019)                     |
| Photocatalytic reactor with ultrafiltration  | Sodium alginate polysaccharides  | Three 30W blue light bulbs $\lambda = 365$ nm             | TiO <sub>2</sub> (Free)   | Total system volume is 9 L, light intensity is 8.3 mW/cm <sup>2</sup>   | Sarasidis, Patisios e karabelas (2011) |
| Mini reactor   | Methylene blue and tartrazine  | UV-LED lamp (5 W, $\lambda = 365$ nm)                     | TiO <sub>2</sub> (Free)   | Photoreaction system coupled to a spectrophotometer   | Fogaça et al. (2021)                   |
| Channel reactor  | pyrimethanil drug  | Xenon lamp ( $\lambda = 300-800$ nm)                      | Fe(II) (free)   | Three levels of irradiance (18, 32 and 46 W/m <sup>2</sup> ) and three concentrations of iron (8, 20 and 32 mg/L)                                     | Reina et al. (2017)                    |
| Cylindrical reactor with LED light   | Dodecylbenzenesulfonate Surfactants  | 180 LEDs ( $\lambda = 375$ nm) in 10 strips with 18 units | TiO <sub>2</sub> (Free) in different concentrations                         | The reactor consisted of a PVC cylinder with LED strips adhered directly to this vessel. Inside it fits a glass reaction vessel.                      | Dominguez et al. (2014)                |

**Table 1** - Laboratory reactors for photodegradation

| REACTOR                                       | DEGRADED COMPOUND                                    | IRRADIATION SOURCE                            | CATALYST   | OBSERVATIONS  | REFERENCE                         |
|---|--|---|--|---|-----------------------------------|
| Photodegradation by Fe(III)-citrate complexes | Propranolol drug                                     | Xenon Lamp 150 W ( $\lambda > 300\text{nm}$ ) | Fe(III)-citrate complexes                                | The reactor consisted of a cylindrical glass vessel being irradiated laterally, the glass acted as a filter.  | Chen et al. (2011)                |
| TiO <sub>2</sub> coated rotary drum reactor   | Aniline  | sunlight and/or artificial UV light           | TiO <sub>2</sub> (Free)                                  | Consisting of a tank with rotating quartz cylinders, being open to receive sunlight and at the same time having UV lamps inside the drums along the axis. | Dúran et al. (2018)               |
| Reactor with side and top light source        | Methylene blue and methyl orange dye                 | Mercury lamp (30W)                            | TiO <sub>2</sub> -coated glass sheets and optical fibers | Reactor made of quartz with two configurations, one with side lighting and one above the sample   | Barton, Matejec e Matousek (2016) |
| Submerged photocatalytic membrane reactor     | Secondary wastewater from the municipality of London | UV-A lamp ( $\lambda=365\text{nm}$ , 13W)     | Suspension nanosized TiO <sub>2</sub>                    | Reactor composed of a quartz cylinder, with a lamp positioned laterally and a membrane module immersed in the solution. The system is aerated.            | Gupta, Gomma e Ray (2021)         |

Source: author, 2022.

Through the table it is possible to observe that different reactor configurations have been studied for better efficiency of laboratory scale photocatalytic processes, as well as changes in the lighting source and changes in the catalyst. It is observed that the most used sources of irradiation in bench scale are Xenon lamps, LED's and mercury. Many experiments use wavelengths ( $\lambda$ ) greater than 300 nm aiming at the development of systems for application under visible light.

The material used in the reactors mostly consists of quartz cells, which leads to high costs, especially for scaling-up. An alternative found would be the use of borosilicate glass, however this material only applies to visible light wavelengths. Another significant factor to be considered in a possible scale expansion is that the systems are all operated in batch, restricting the volume of the effluent to be treated.

Regarding the catalysts used, TiO<sub>2</sub> stands out, being used suspended and immobilized. However, other catalysts are also used in the published works. Reactors with dispersed catalysts have a simpler configuration and those with immobilized catalysts stand out for being easier to separate the solid later.

Table 1 also shows the application of the photocatalytic process for the degradation of different emerging pollutants. Among the main substances are dyes and pharmaceuticals. They cause great concern in removal, as dyes cause color change in the environment and drugs, in the long term, may be responsible for mutations to the affected fauna and flora.

## **Scale up of photocatalytic reactors**

### **Fundamentals**

For a photocatalytic reactor to be deployed for larger scale operation, two factors must be taken into account: technical feasibility and economic feasibility. There must be a balance between these characteristics and one must consider the limitations of mass and photon transfer, as well as efficient performance (Piriyah and Knman, 2020). These authors mention that the heterogeneity of photocatalysis makes the reactor design involve significant interdisciplinary knowledge.

The need to scale up comes from an economic bias and for that it is necessary that the entire process is initially developed and operated on a small scale. There are phenomena that directly interfere with the amplification, being the mass and heat transfers the main ones. The problems related to these phenomena arise from the fact that these mechanisms need time to occur satisfactorily, and this time increases with increasing scale.

It is worth nothing that for scale expansion, the materials used must be carefully considered. In the case of photocatalytic reactors, the piping must be made of material that allows good penetration of light, and has good mechanical and chemical resistance. The inlet flow and velocity must be in accordance with the residence time of the substance in the reactor, and valves, pumps and recycle must support the effluent demand. In addition to all the technical factors, economic viability is very important, both for the construction of the reactor and for the maintenance and operation of the system.

In photocatalytic reactors, another challenge in scaling up is how the catalyst will be used, suspended or immobilized. Being suspended, it is necessary to develop a way to separate it from the effluent, so that it can be reused. With immobilized catalysts, it is necessary to properly select the support material, analyze the best form of immobilization and develop a methodology for fixation in the reaction system.

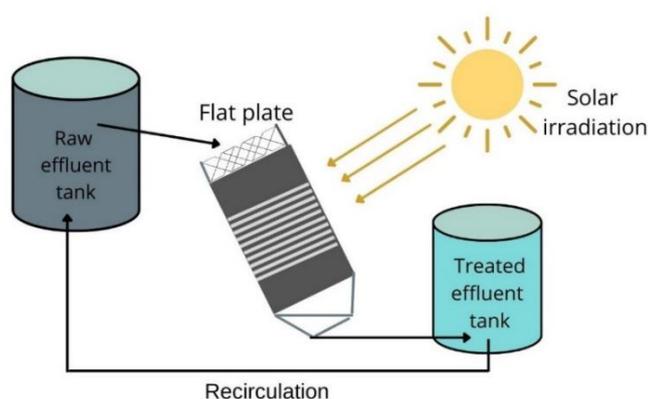
## Pilot scale photocatalytic reactors

The studies with laboratory scale photocatalytic reactors allowed some important conclusions, such as the most promising catalysts as well as their supports and the configurations that allow good light dispersion. In view of this, researchers have developed photocatalytic reactors on a pilot scale, testing their applicability and efficiency.

Plakas et al. (2016) developed a reactor in which the main components are the UV treatment system and the membrane vessel. The membrane vessel has a working volume of 10 L. The UV treatment system is made up of a chamber with a working volume of 15 L. The membrane module made with hollow fibers, for ultrafiltration, has a surface area of 4.19 m<sup>2</sup> and is submerged in the membrane vessel. UVC germicidal lamps were used, with a power of 52W and a wavelength of 253.7 nm, wrapped in quartz gloves and immersed in the UV camera. The total volume of the system is 25 L with an operating capacity of 1.2 m<sup>3</sup> of effluent per day.

Marculan et al. (2016) developed a pilot scale reactor for the degradation of dairy effluent using TiO<sub>2</sub> and solar radiation as shown in Figure 6. The system was composed of a metal plate with an area of 2160 m<sup>2</sup> coated with polyurethane resin and the catalyst. The effluent was stored in a tank, pumped evenly under the plate and exposed to sunlight. Afterwards, the effluent was collected in another container with a capacity of 5 L and redirected to the raw effluent tank. This cycle was repeated for 2 h.

**Figure 6** - Schematic diagram of photocatalytic reactor with flat plate.



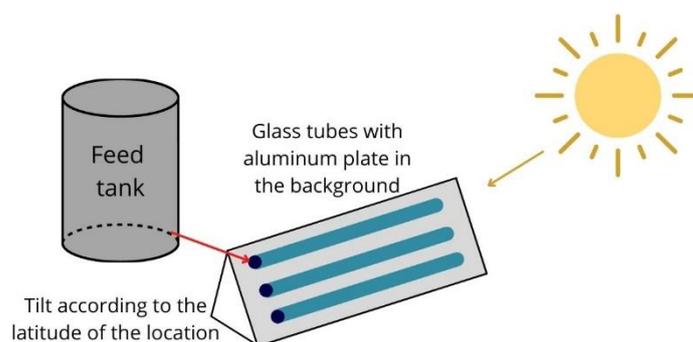
Source: Adapted from Marculan et al. (2016).

The author (Marculan et al., 2016) obtained good results since the treatment time is considered small when compared to a conventional effluent treatment plant. The parameters of the treated effluent complied with the legislation with a reduction in the

content of organic matter measured in chemical oxygen demand (66.5%) and biochemical oxygen demand (66.1%).

Durán et al (2018) comment that many researchers use reactors with parabolic concentrators. Generally, reactors are composed of borosilicate glass tubes with polished aluminum as a reflector, mounted on a fixed platform inclined at the local latitude, as in Figure 7. The plants also have storage tanks, pumps, filters and operating parameter controls. UV lamps can also be installed for use on cloudy days and even improve reactor efficiency.

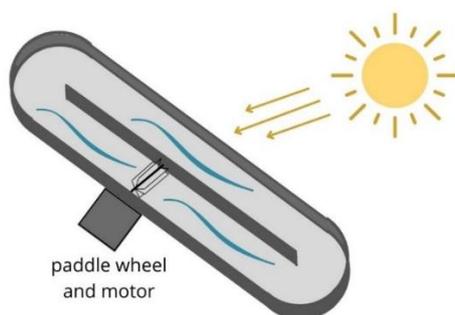
**Figure 7** - Schematic diagram of photocatalytic reactor with com parabolic concentrator



Source: Adapted from Durán et al. (2018).

Carra et al. (2014) cite a pilot scale flat-channel reactor made of glass fibers. In the proposed configuration, there is a tank with a length of 3.85 m, 0.64 m wide and approximately 0.15 m high, with a central wall, forming two channels. It also has a paddle wheel in one of the channels, to obtain a homogeneous system. The reactor has a total volume of 360 L. A schematic can be seen in Figure 8.

**Figure 8** – Schematic diagram of a channel photocatalytic reactor.



Source: Adapted from Carra et al. (2014).

Table 2 lists works in which pilot scale photocatalytic reactors were proposed. Information such as the compound to be degraded and some observations made during

the review are presented in order to facilitate the comparison of different photocatalytic reactors on a pilot scale.

**Table 2** – Pilot scale photocatalytic reactors.

| REACTOR  | DEGRADED COMPOUND   | CATALYST   | OBSERVATIONS   | REFERENCE                 |
|--|---|--|--|---------------------------|
| Non-concentrating solar fixed-bed reactor          | Pentoxifylline (PEN) drug                                   | Fe-TiO <sub>2</sub> composite in the form of free granules   | The total volume of the reactor is 5L, recirculating for 6h. The reactor was closed with plastic film to avoid evaporation losses. | Bansal e Verma (2018)     |
| Continuously stirred tank solar reactor            | Antipyrine in municipal effluent                            | Ferrioxalate.  | A Composite Parabolic Concentrator (CPC) was used  | Durán et al. (2014)       |
| Photoreactor with Composite Parabolic Concentrator | diclofenac  | TiO <sub>2</sub> was sensitized with methyl red dye.   | ---  | Diaz-Ângulo et al. (2020) |
| Photoreactor with CPC                              | Oil refinery wastewater                                     | H <sub>2</sub> O <sub>2</sub> and K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , used as oxidants; FeSO <sub>4</sub> heptahydrate, for supplying ferrous ions. | ---  | Pourehie e Saien, (2020)  |
| Cylindrical stirred reactor made of PVC            | Residual waters   | H <sub>2</sub> O <sub>2</sub> used as oxidants; FeSO <sub>4</sub> heptahydrate, for supplying ferrous ions.  | The maximum reactor volume was 18 L.   | Jiménez et al. (2019)     |
| CPC solar reactor                                  | Effluent from textile industries                            | TiO <sub>2</sub> , TiO <sub>2</sub> / H <sub>2</sub> O <sub>2</sub> , and photo-Fenton with ferrioxalate   | Total irradiated volume is 10 L, has by-pass and 2 independent tanks, allowing the use of 2 and 3 reaction tubes.                  | Castro et al. (2014)      |
| Continuous flow photocatalytic reactor             | Methyl orange dye   | TiO <sub>2</sub> -SiO <sub>2</sub> and glycerol film.  | The material of the tubes is glass, with a composite parabolic concentrator.   | Hoang et al. (2021)       |
| Photocatalytic reactor in channels                 | Micro pollutants (acetamiprid and thiabendazole pesticides) | H <sub>2</sub> O <sub>2</sub> used as oxidants; FeSO <sub>4</sub> for supplying ferrous ions.  | Glass fibers as reactor material.  | Carra et al. (2014)       |

Source: author, 2022.

In all the works presented in the table it was found that the lighting source used was sunlight. Aiming at energy savings and taking into account the observations of the consulted authors, it appears that this is the option that best suits these pilot-scale projects. Compound Parabolic Concentrators (CPC) are widely used in order to obtain a better use of this lighting. For a more uniform irradiation, an inclination according to the latitude of the city where the equipment is installed is also used.

It is known that tubular reactors have a hydraulic flow regime that, preferably, must be turbulent. This avoids the deposition of compounds in the equipment, enables homogenization and thus favors the reaction. In cylindrical reactors, a form of agitation is added to the system to achieve these benefits.

In order to reduce equipment costs, it appears that quartz is little used compared to bench scale reactors, being replaced by different types of glass. Some options indicated in the literature are borosilicate glass and glass with iron reduction in its composition.

All reactors studied showed good performance in the degradation of effluents, which confirms the feasibility of using this process as a treatment. It is mainly observed the degradation of dyes and medicines, and there is a variation in the percentage of removal of the compounds between 75% and 94%, which correspond to changes in the reaction medium, such as changes in the catalyst or effluent concentration, changes in pH and period of solar irradiation.

### Scale up Gaps

According to Ahmad et al. (2016), one of the main challenges for scale up and manufacturing photocatalytic reactors is in reactor configuration and lighting efficiency. The author states that there are two major restrictions, the first would be the distribution of light within the reactor through the absorption and scattering of liquid to the photocatalyst and the second is the large specific area for catalyst coating per unit volume of the reactor.

The same author comments that an efficient design must have uniform irradiation of the entire catalyst surface and almost complete elimination of mass transfer resistance. Therefore, when talking about increasing the scale, it is necessary to pay attention to the opacity of the effluent, consequently, with the penetration of radiation, dispersion of light in the medium.

The material in which the wall will be built is also considered, as it needs to allow the passage of the chosen radiation. Another concern is how the material behaves receiving sunlight for long periods of time. Generally, glass is used, bringing limitations such as size, problems with sealing and breakage, but on the other hand, it has good weather resistance, chemical resistance and does not wear out easily.

Plakas et al. (2016) cite many advantages with the use of photocatalytic reactors in pilot scale, such as ambient temperature and pressure, almost complete mineralization of the compounds, and low operating cost. However, they mention heterogeneous catalyst separation as a major challenge in this process.

One of the main obstacles found in this literature review is the way of using the catalyst (free or immobilized), since in the dispersed form there is difficulty in separating

at the end of the process and when using a material for immobilization there are difficulties in the application. Many researches are still carried out to improve the efficiency of catalysts, both modifications with supports (use of zeolite, polymers, metals) and their use in the process (use in paints, coatings and membranes) as mentioned by Marculan et al.(2016).

Considering the scale up, another difficulty is the material used in the reactor and the lighting source. On a laboratory scale, there is the possibility of using quartz tubes in which light passes through the material and also the use of lamps as a source of artificial lighting. Considering an increase in scale, quartz becomes unfeasible due to its cost, as well as lamps and their energy expenditure. In this sense, the use of natural sunlight becomes the focus of studies.

## **CONCLUSION**

Photocatalysis is a highlighted advanced oxidation process. Much research have been developed to improve this method. The development of reactors of different configurations has been much discussed, as well as the lighting source and the catalyst. Seeking improvements in process yield, researchers change many process variables, such as different lighting sources with variation in wavelength and power. Heterogeneous catalysts are used in dispersed and immobilized ways, varying the way they are immobilized and the material used, as well as the concentration in the medium.

When discussing projects on a laboratory scale, the published works are in greater numbers. In bench scale, the use of artificial light, batch operation, the materials used have higher acquisition costs and greater energy expenditure. Taking into account that these researches aim to verify the functionality of the process and that the equipment is small, little attention is paid to the somewhat high costs.

For scale up, technical feasibility and economic feasibility are highly evaluated. So, the exchange of equipment materials, use of sunlight as a source of lighting and reuse of catalysts are actions taken to improve the performance of the process with reduced costs. Considering that all these factors influence the efficiency of the process, all variables must be analyzed.

These advances in research related to photocatalysis are very important since this process is excellent both for the production of potential clean energy and for the removal of pollutants that are of great concern to the population. Therefore, with investments for

better yields, better treatment efficiency, energy efficiency and cost reduction, this process becomes much more viable and can greatly contribute to important environmental issues.

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