



## Review

## Recent advancements in supporting materials for immobilised photocatalytic applications in waste water treatment



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## ABSTRACT:

The aim of this paper is to provide a review on the usage of different anchoring media (supports) for immobilising commonly employed photocatalysts for degradation of organic pollutants. The immobilisation of nano-sized photocatalysts can eliminate costly and impractical post-treatment recovery of spent photocatalysts in largescale operations. Some commonly employed immobilisation aids such as glass, carbonaceous substances, zeolites, clay and ceramics, polymers, cellulosic materials and metallic agents that have been previously discussed by various research groups have been reviewed. The study revealed that factors such as high durability, ease of availability, low density, chemical inertness and mechanical stability are primary factors responsible for the selection of suitable supports for catalysts. Common techniques for immobilisation namely, dip coating, cold plasma discharge, polymer assisted hydrothermal decomposition, RF magnetron sputtering, photoetching, solvent casting, electrophoretic deposition and spray pyrolysis have been discussed in detail. Finally, some common techniques adopted for the characterisation of the catalyst particles and their uses are also discussed.

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## 1. Introduction

Recently, the use of photocatalysis for the treatment of a variety of pollutants such as dyes (Babu et al., 2016; Mahmoud and Fouad, 2015; Paschoal et al., 2015; Wang et al., 2015b; Zhu et al., 2016), pesticides (Cruz et al., 2015; Gar Alalm et al., 2015; Quiñones et al., 2015; Radwan et al., 2016), pharmaceuticals and various endocrine disrupting compounds (Ahern et al., 2015; Fathinia et al., 2015; He et al., 2016; Hernandez-Gordillo et al., 2015; Maeng et al., 2015; Naraginti et al., 2016) is rapidly increasing. In this regard, researchers are focusing their attention on producing economically viable, non-toxic, stable and photo-corrosion resistant catalysts (El-Roz et al., 2013). While there is great concern over such pollutants, treatment using conventional techniques have not been successful. Advanced Oxidation Processes (AOPs) prove to be particularly useful in achieving the degradation of such harmful pollutants. AOPs are light induced processes, which involve the treatment of polluting compounds, by making use of hydroxyl radicals ( $\cdot\text{OH}$ ). Among various Advanced Oxidation Processes as mentioned in Fig. 1, Photocatalysis is of great interest due to the relative ease of the process. The advantage of the process is that it can completely mineralise recalcitrant pollutants into simpler compounds that are benign or can be processed by natural mechanisms to harmless constituents. Moreover, this method does not transfer the pollutant from one phase to another, as in case of certain conventional treatment techniques such as adsorption but rather eliminates the target compound. Photocatalysis, apart from pollutant degradation has many other applications, some of those applications are as mentioned in Fig. 2. Generally, transition-metal oxides, with semi conducting properties like  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{NiO}$ ,  $\text{WO}_3$  (Asahi et al., 2001; Doerffler and Hauffe, 1964; Justicia et al., 2002; Khan et al., 2002; Muller and Steinbach, 1970) sulphides such as  $\text{MoS}_2$ ,  $\text{ZnS}$ ,  $\text{In}_2\text{S}_3$ ,  $\text{CdS}$  (Matsumura et al., 1985; Zhang and Li, 2004; Zhao et al., 2007) and halides like  $\text{AgCl}$ ,  $\text{BiOI}$  (P. Wang et al., 2009a, 2009b) etc. are

used as photocatalysts for environmental pollution remediation.

The recovery and the reuse of such nano-particles from the bulk of effluent streams on an industrial scale, is quite difficult. In this regard, it is quintessential to observe that, the use of the above mentioned nano-particles for the photochemical degradation of the pollutants is very challenging on an industrial scale. If  $\text{TiO}_2$  and  $\text{ZnO}$  nano-particles, present in treated water stream after the photocatalytic degradation, are not removed, they can exhibit serious genotoxicity and cytotoxicity to aquatic and human lives (Kim et al., n.d.; Premanathan et al., 2011; Song et al., 2010; Vevers and Jha, 2008) Thus, in this context, the usage of techniques that facilitates the reuse of spent catalyst will come a long way in making the photocatalysis process eco-friendlier. Many authors have reported the feasibility of using immobilised catalyst for the photo degradation of organic pollutant molecules (Akerdi et al., 2016; Barrocas et al., 2016; Dong et al., 2014b; Ghoreishian et al., 2016; Jansson et al., 2016; Lee et al., 2017; Li et al., 2015; Lin et al., 2016; Marothu et al., 2014; Miranda-García et al., 2014; Mohite et al., 2016; Nadarajan et al., 2016; Ramasundaram et al., 2016; Ray and Lalman, 2016; Razak et al., 2014; S.S et al., 2016; Sabri et al., 2015; Veréb et al., 2014; Wang et al., 2015a; Yadini et al., 2014; Zeng et al., 2010). Various techniques have been successfully used to immobilise the catalysts on different supporting materials such as Glass substrates, Zeolites, Metallic supports and Photo-electrodes etc. Immobilisation has also been carried out on natural matrices like *Luffa cylindrica* fibres (El-Roz et al., 2013), Chitosan (Nadarajan et al., 2016), Cellulose (Zeng et al., 2010) etc. A non-exhaustive list of such immobilised catalysts reported are as mentioned in table-2, given in section-4.

Natural fibres are found to be increasingly employed for immobilising catalysts and enzymes. The prime reason for this can be attributed to their easy availability, cost, environmentally benign nature, biodegradability and renewability. Such fibres generally

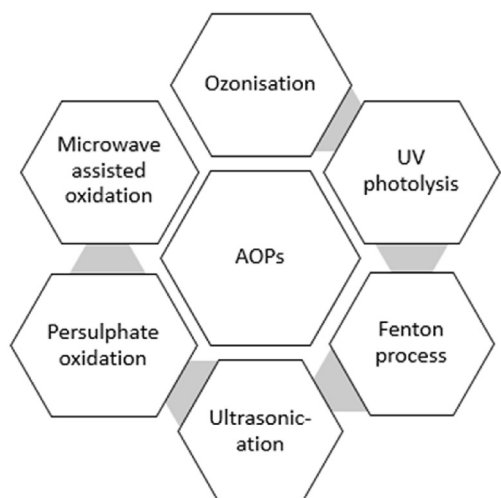


Fig. 1. A broad representation of the types of Advanced Oxidation Processes.

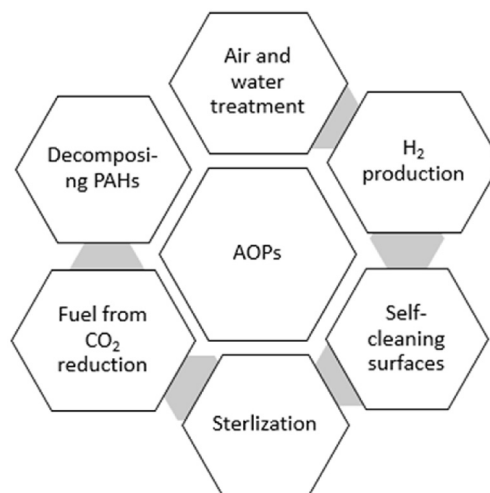


Fig. 2. A non-exhaustive list of the potential applications of Advanced Oxidation Processes.

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