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A perspective on bismuth based materials for the photodegradation of organic pollutants

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ABSTRACT

The photoactive bismuth materials represent an interesting tool for facing the complexity represented by the organic contained wastewater streams and the engineering of their chemical and surface properties is the key to a solve the water pollution. In this review, we are discussing the use of bismuth based materials for photooxidative treatment of polluted water critically evaluating and highlighting the strengths and the weaknesses of the approach with a focus on the properties of the materials but reporting as well the currently available technologies providing an agile reference point in the field.

1. Introduction

The water resources depletion was recognized as the most dangerous for plenty of countries afflicted by drinkable water scarcity (Mukheibir, 2010) and it is recognised as one of the foremost global threat for human and environmental health (Goel, 2006). Together with climate change effects, the anthropic impact have induced a significant reduction in water quality (Singh et al., 2019). The contamination of superficial and groundwater is far more scary for those countries plagued with scarce economical resources and poor environmental regulations (Dagdeviren and Robertson, 2009) in which both organic pollutants and heavy metals and persistent organic are disposed of in rivers, soil, lakes and sea without any preliminary treatment (Pichel et al., 2019). The accumulation of these species in freshwater represents a great concern for human health (Schäfer et al., 2015). Accordingly, the development of cheap, solid and affordable technologies for water treatment has become part of the Sustainable Goals of United Nations (Alcamo, 2019). The scientific community is yet to single out the best approach for pollutants removal (Bhojwani et al., 2019). Actually, there are two main ways to face the issues represented by adsorption and degradation of contaminants (Igunnu and Chen, 2014). Adsorption of pollutants is the most used route to remove the contaminants from drinking water (Ranjan et al., 2020) and it can be performed by using several materials without specific chemical characteristics except for superficial ones (Yousef et al., 2020) while degradation is generally performed by photo-(PO) or electro-oxidation (EO), two processes requiring a fine chemical tuning of the active material (Kaur et al., 2020; Monfort and Plesch, 2018; Kazemi and Sobhani, 2023; Sobhani, 2023; Zinatloo-Ajabshir et al., 2019; Zinatloo-Ajabshir et al., 2024; Zinatloo-Ajabshir and Salavati-Niasari, 2019; El Messaoudi et al., 2022; Muñoz et al., 2007; Muñoz et al., 2006; Wu et al., 2014). However, despite the development of suitable adsorptive materials being far easier compared to the design of PO and EO catalysts such materials have critical issues concerning both regeneration and end-life management (Fouad et al., 2021; Franceschini et al., 2022). PO and EO designed materials could reduce sensibly the energy required for their end-life treatments and will lead to the production of less harmfully wastestreams (Ajiboye et al., 2021) even if their high cost compared to simple adsorption has slowed down their use. Nonetheless, the PO and EO routes represent the most advanced solution for the removal of recalcitrant organic pollutants (Švancara et al., 2010; Gupta et al., 2022) although the choice between the two categories is still matter of debate. Bismuth based materials (BBMs) represent an interesting test bench for the comparison between PO and EO because of their good performances in both cases (Nosaka and Nosaka, 2017) as proved by the great deal of attention attracted during the last decades for the production of both electro- and photo-active species (Lang et al., 2022; Zhao et al., 2017; Li and Meng, 2020). In this review, we critically discuss the use of BBMs evaluating their performances in PO degradation of pollutants providing also some insight on more advanced technologies. We provide also a critical guideline for the choice of correct

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approach to be use for the treatment of polluted water based on scientific and economic analysis that can also be used as guidelines for evaluating could be used also for all similar applications.

2. BBMs as PO catalysts: theoretical background

The PO activated catalysis basic mechanism mediate by ROS for the degradation of organic species is sketched in Fig. 1.

The absorption of a photon allows photoactive materials to excite an electron from the valence band (VB) to the conduction band (CB). This electron activates a cascade reactions pathway in which reactive oxygen species (ROS) are formed and able to degrade organic species. The key step determining the efficiency of the PO process in a water medium is generally the generation of active ROS (i.e. $^{\bullet}O_2^{-}$, H_2O_2, $^1O_2$, $^{\bullet}OH$). As shown in Fig. 1, $^{\bullet}OH$ and $^{\bullet}O_2^{-}$ formed during H_2O_2 dissociation are the active species during leading to the PO of organic material in several photoactive materials (Ferhat and Zaoui, 2006) included bismuth halides (König et al., 2021) but this is not true for all BBMs. Following Li et al. (Leontie et al., 2002), BBMs production of both $^{\bullet}OH$ and $^{\bullet}O_2^{-}$ was negligible and the PO activity of BBMs was mainly due to the reaction of adsorbed species. By comparing BBMs with titania, authors suggested that the differences in reactivity were most probably due to the shorter lifetime of photogenerated charge carriers on BBMs surface. Nevertheless, Sun et al. (Karen et al., 2021) reported that oxygen vacancies further improve the light response to a wide range of wavelengths acting as effective trap carriers.

Generally, BBMs photocatalytic prowess lies in their electronic structure that allows the simultaneous presence of multiple valence states species such as Bi(III) and Bi(V) (Feng et al., 2015). This characteristic contributes to a range of energy levels that can be harnessed during photocatalytic processes that allows the use of BBMs as PO catalysts under a wide range of wavelengths including visible light (Xu et al., 2005).

Furthermore, the defectiveness and complexity of BBMs surface is the key for tuning the band gap values as shown in Table 1 using single or hetero- structures with different phases and stoichiometry as summarized in Fig. 2.

As reported in Fig. 2, the common precursor of BBMs is bismuth nitrate that can be converted into subnitrates ($Bi_lO_mN_n$) by simple thermochemical routes originating nevertheless very complex species (Kodama, 1994; Yu et al., 2011; Levin and Roth, 1964; Lei et al., 2020; Greenwood and Earnshaw, 2012; He et al., 2018). On the contrary, bismuth oxides, despite their simple stoichiometry, can arrange themselves in four different crystal structures each one with its own characteristics (Balint et al., 2021). α-Bi_2O_3, a distorted monoclinic lattice, is the stable equilibrium structure at room temperature but at higher temperature it is converted into β, δ or γ phases. These phases are characterized by more defective surfaces with randomly distributed oxygen vacancies filled with O^{-2} together with Bi(III) and Bi (V) sites (Liu et al., 2021). Bismuth halides are also used for PO, showing different crystals structures due to the halogen presence. Bismuth oxohalides are also used even if they are considerably unstable compared with other species as they decompose into species of variable stoichiometry (Ranjan and Singh, 2020). Despite the wide range of properties that single bismuth based oxide have a single material could be not sufficient to match the requirement of band gap and stability of PO processes so that the production of heterojunctions between different oxides species could be necessary. As mentioned above, the active mechanism of BBMs is based on surface interactions that allowed also the ROS formation but this could lead to a BBMs poisoning during the PO process. Tailoring the surface with species able to generate ROS by modifying the BBMs reactivity is a sound way to tackle this issue and enhance lifetimes as shown in Fig. 3 in which the coupling between Bi_2O_3 and FeOOH is reported.

As reported by He et al. (Ranjan et al., 2021), FeOOH/Bi_2O_3 heterostructures promoted the shifting of BBMs reactivity towards a Fenton-like reaction with the massive formation of $^{\bullet}OH$ and $^{\bullet}O_2^{-}$ under visible light stimuli. These materials could lead to the total disruption of organics converting them into water and carbon dioxide preserving at the same time the BBMs surface from poisoning. However a deeper look to the effect of pollutants adsorption on the BBMs surface is compulsory and will be discussed more in detailed in the next section.

3. An assessment on the role of adsorption on BBMs performances

As mentioned, the phenomena occurring in the interfacial region between BBMs and polluted water are of capital relevance to properly evaluate the PO performances. Neat BBMs have found few applications as adsorptive materials due to their disposal issue but they showed

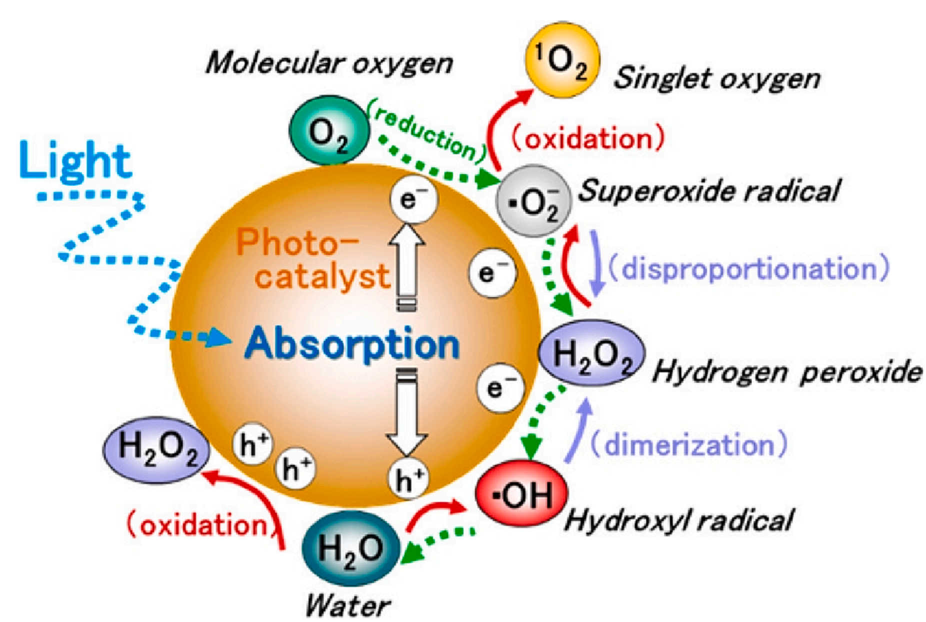

Fig. 1. Mechanism of action through ROS generation on the surface of PO catalysts as reported by Nosaka et al. (Sun et al., 2019)(Copyright © 2017, American Chemical Society).

Table 1
Overview of band gap ranges of BBMs without the presence of any other metal species.

Materials	Band gap (eV)	Advantages	Disadvantages	Ref.
Bi_2O_3	2.3–3.1	▪ Easy to be synthesized ▪ Absence of leaching due to poor solubility in water medium.	▪ Defective surface area hard to be controlled. ▪ Reduction of activation with surface modification during the use.	(Lai et al., 2019)
$Bi_lO_mN_n$	2.3–2.7	▪ Tuneable chemical surface.	▪ Synthesis sensible to temperature uniform.	(Alzamly et al., 2019)
BiX_3 (X = F, Cl, Br)	1.3–3.9	▪ High reactivity. ▪ Easy to be synthesized.	▪ Narrow band gap. ▪ Poor stability. ▪ Leaching.	(Gadhi et al., 2019; Lu and Zhu, 2014; Yang et al., 2013)
BiOX (X = F, Cl, Br)	1.9–4.0	▪ High reactivity. ▪ Easy to be synthesized.	▪ Narrow band gap. ▪ Poor stability. ▪ Leaching.	(Zahariev et al., 2012)

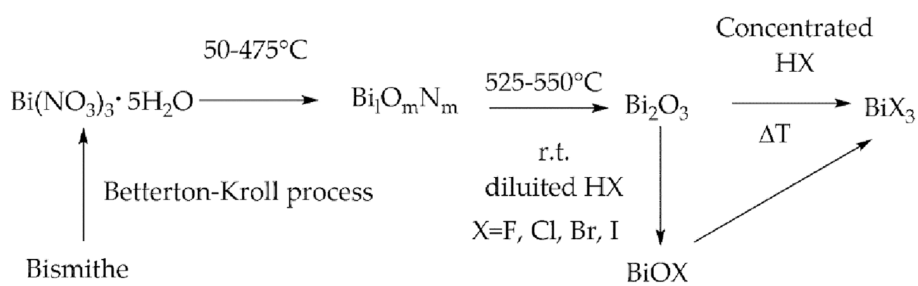

Fig. 2. Simplified scheme of BBMs production by thermal treatment of bismite and bismuth nitrate.

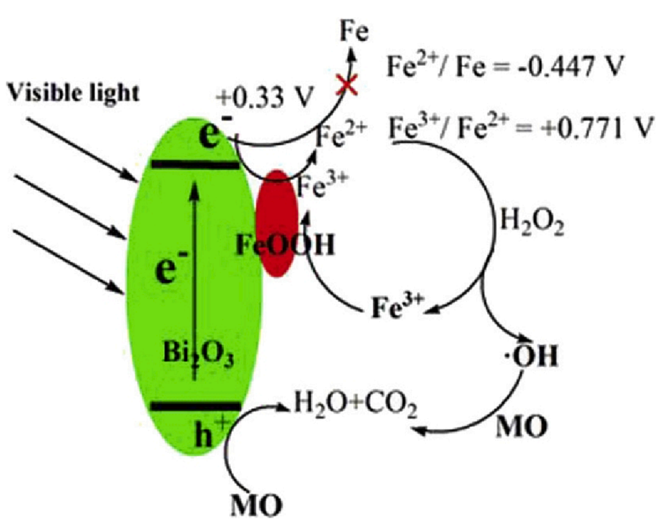

Fig. 3. Z-scheme reactivity of $FeOOH/Bi_2O_3$ heterostructures as reported by He et al. (Ranjan et al., 2021). Reprinted with all permissions from Elsevier.

remarkable performances for arsenic removal, achieving a removal efficiency up to 31.6 and 33.1 μmol/m^2 for As(V) and As(III) respectively (Jatav et al., 2021). As proved by the authors, BBMs surface defectiveness represents the key feature for tuning the interfacial properties by inserting Bi^{3-x} and Bi^{5+} sites (Najdanović et al., 2020), hydroxyl residues (Kazemi and Yaqoubi, 2019) or altering the Bi-O arrangement by inserting cations (Hernández-Gordillo et al., 2019). These modifications affected the degradative performances of BBMS by modifying the electron mobility but also by altering the interaction between the organic pollutants and the BBMS surface.

Organic pollutants can interact with BBMs surface through several different routes promoting an adsorption-degradation effect able to boost the real degradative activity of suspended or immobilized PO catalysts (Wang et al., 2017; Zhang et al., 2019; Suresh et al., 2022).

Furthermore, the corrected evaluation of adsorption contribution to PO activity is of capital relevance to the understanding of the mechanism and the evaluation of the application perspectives of the materials but it is generally overlooked by most studies. Hernández-Gordillo et al. (Sharma et al., 2019) deeply investigated the relevance of adsorption on three dyes in a wide range of pH as reported in Fig. 4.

The evaluation of real dyes concentration was evaluated by considering the amount of adsorbed dye (θ_{dye}) at pH 3, 6.8 (point of zero charge, PZC, of Bi_2O_3) and 9.7. Authors conclude that the current literature lacks a rigorous approach and has not sufficiently considered the adsorption and its relation with properties of both organic molecules and BBMs surface overestimated the PO. Nevertheless, BBMs are widely used for the removal of inorganic due to their good adsorption properties and the easiness to regenerate them (Ranjan et al., 2020).

4. A critical view on the state of the art of BBMs based PO catalysts for pollutants degradation

The first and simple approach for tuning the BBMs material properties is based on the selection of the chemical species among bismuth halides, oxohalides, oxide and heterostructures (i.e. doped materials, heterojunction, species, complex salts). The choice should be driven by two factors equally valuable and relevant: the band gap and the stability in the operative conditions. The band gap range define the possible use of BBMs under solar light stimuli. This is a relevant issue as at ground level 40 % of the solar irradiation is in the photon energy range from 1.8 up to 3.1 eV and only 5 % of the irradiation at ground level has energy higher than 3.1 eV (Arumugam et al., 2021).

BBMs stability is a matter of discussion particularly for halides, oxohalides and heterostructures. Bismuth halides are generally unstable in presence of both air and water (Miao et al., 2020) preventing their direct use in PO. Nevertheless, their attractive band gap range attracted a relevant interest and several authors used halide derivatives such as complex perovskite structures in which BiX_3 is present together with organic or inorganic species (Kása et al., 2022) that are expected to counter their instability.

As mentioned above, oxohalides have band gaps ranging from 2.1 eV for BiOI up to 2.7 eV for BiOF (Gadhi et al., 2019; Zahariev et al., 2012)

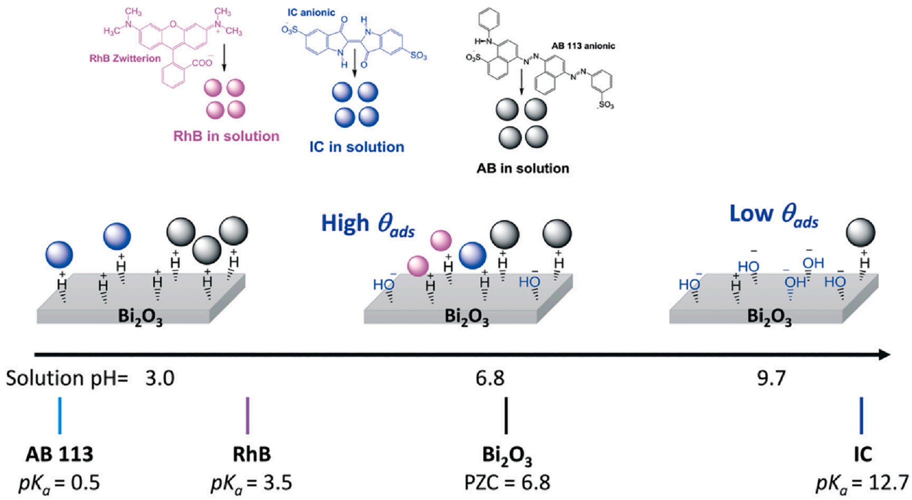

Fig. 4. Three dye adsorption on Bi_2O_3 surface as function of pH. Reprinted with al permissions from (Sharma et al., 2019).

matching the energy range of sunlight active materials. PO activity of BiOX is due to many structural factors such as a layered structure and a stoichiometry that promotes the formation of a high dipole moment up to 2 Debye (Li et al., 2019) even if pure oxohalides showed a fast recombination of photogenerated charge carriers limiting their use (Song et al., 2016). The halogen np states reduced the hole mobility but not the electron one improving the separation of the charge carrier. These features combined with a highly hydrophobic surface promoted the massive formation of photo-generated carriers together with O_2^- leading to efficient organic pollutants degradation (Gao et al., 2021). Furthermore, oxohalides are considerably more stable in air and water environment compared to the simple halides as reported by Arumugam et al. (Song et al., 2016). Nevertheless, bismuth oxohalides could undergo a degradative process during PO of oxalic acid, formic acid, salicylic acid, malonic acid, and ascorbic acid as reported by Kása et al. (Zhang et al., 2019). Authors reported the modification of BiOX surface and even its bulk in presence of oxalic acid while $BiVO_4$ and Bi_2WO_6 remained partially intact. The formation of superficial complex enlightens the necessity to deeply consider the full composition of the waste stream treated. Oxohalide complex of organic acids are still active in both degradation of tetracycline and photo reduction of Cr(VI) (Rashid et al., 2020). A close related approach is based on the doping of oxohalides with small amount of metals such as Sn(II) improving both the light absorption and the photoinduced charge carriers separation (Arumugam et al., 2022). Several ternary oxohalides has also been used to improve their stability under PO conditions such as the addition of BiOI to a pure BiOCl (Naing et al., 2022) (Onwumere et al., 2020). This modification increments the stability of the material but also narrows the bandgap from the BiOCl value exceeding 3.1 eV to a value better suitable to exploit the visible part of the solar spectrum. Similarly, bismuth oxohalides could be incorporated into carbonaceous (Ali et al., 2020; Arghavan et al., 2021), inorganic (Li et al., 2020) or polymeric (Zahid and Han, 2021; Huang et al., 2021; Gadhi et al., 2017) matrixes to improve their durability. Another promising approach to boost the PO performances of oxohalides is the production of heterostructures combining them with active materials such as bismuth selenide as reported by Li et al. (Xiao et al., 2013). With this approach the authors were able to degrade recalcitrant organic pollutants by using a simple visible LED system.

Simple bismuth oxide represents an alternative solution to the use of complex structured materials even if it is highly sensible to the production condition used and hence it requires a high degree of control of the production process. A lot of efforts have been devoted to the optimization of selective phase synthesis of bismuth oxide polymorphs to avoid the formation of the thermodynamically stable α phase over the room temperature metastable β and γ that show superior PO performances (Yan et al., 2014). The other strategy adopted to tailor the bismuth oxide PO activity is the modifications of the surface as reported by Huang et al. (Gadhi et al., 2016). Authors evaluated the degradation of chlorophenol by introducing oxygen vacancies on a bismuth oxide evaluating several Bi(3+x)+/Bi^{3+} ratio. The controlled vacancies promoted both the efficient interactions between chlorophenol and Bi_2O_{3+x} and the formation of $^1O_2$ together with photogenerated holes. As stated before, the PO mechanism for bismuth oxide arises from lattice structure and involve the rapid conversion of $^1O_2$ into $O_2^{\cdot}$. This specie was the main responsible for the dechlorination and PO of organics but its production could be inhibited by the presence of other species such as carbonates.

The bismuth oxide species could be further engineered through the realization of heterojunction materials in order to tune both bandgap and shape. As reported by Gadhi et al. (Gadhi et al., 2019), the morphology of bismuth oxide can be tuned by changing the support used moving from a polyhedral (glass support) to a lamellar structure (silica support). Authors proved that the lamellar material was the more performing due to the better adsorption phenomena occurring. The other common morphology evaluated is the spherical one with or without empty structures (Kargar et al., 2021; Fei et al., 2011) with a band gap close to 3 eV. The other route used to modify the PO activity by combining several phase as reported by Gadhi et al. (Gadhi et al., 2018). Authors produced a α-Bi_2O_3/β-Bi_2O_3 heterojunction by thermal degradation of bismuth nitrate at 550 °C in air with a final band gap of 2.3 eV. It is possible to create a similar materials in which the heterojunction is made by β-Bi_2O_3 over $Bi_5O_7NO_3$ (Gu et al., 2021) or titania (Zhang et al., 2022) reaching a band gap of 2.4 eV.

Moving to BBMs containing other metal elements, $BiFeO_3$ is quite interesting due to the appropriated band gap and its tunable morphology (Chellammal Gayathri et al., 2022). Gadhi et al. (Raza et al., 2018) exploited the properties of $BiFeO_3$ by producing hybrid materials with neat, dimeric and iron doped species for the mineralization of several dyes. Interestingly, these materials possess a high magnetization value suggesting their easy recovery by magnetic drainage from a water medium. Zinc oxide or zinc spinels doped with bismuth showed similar properties without the presence of magnetic features (Trinh et al., 2019; Lai et al., 2014) and similar findings are reported for aluminum or heavy metal doped BBMs (Trinh et al., 2016; Xu et al., 2019).

Among the other BBMs, $BiVO_4$ has been widely used due to the wide range of phases and morphologies available by simple modifications in the productive routes (Wang et al., 2012). As reported by Lai et al. (Channa et al., 2021), $BiVO_4$ could can be used for to degrade real recalcitrant pesticide pollutants reaching a full mineralization in 5 h with the fast consumption of harmful intermediates formed during the PO (Bisht et al., 2022). This a very attractive feature that is not so common as for example in the case of Bi_2MoO_6 that leads to the formation of hardly degradable intermediates during the PO of hard to be removed molecules such as ciprofloxacin (Liu et al., 2024). Furthermore, $BiVO_4$ inhibits the bacterial growth on its surface (Zhang et al., 2024) as observed also for Bi_2O_3 (Li et al., 2024; Li et al., 2024). This a key finding to produce filters for on field applications.

A peculiar advantage of BBMs is that can be integrated into composites species promoting a synergistic activity boost. Liu et al. (Xiong et al., 2024) reported the coupling of BiOBr with titanium based metal organic frameworks (MOFs) in order to overcome the limitation of bismuth oxohalide related to active site accessibility. Authors reported an improvement of methyl orange degradation from 38 % up to 91 % due to the formation of a Z-heterojunction. Zhang et al. (Jia et al., 2023) used a very similar approach combining BiOCl with an iron based MOF named MIL-101 (Fe) increasing also in this case the removal of a recalcitrant pollutant such as tetracycline reaching 49 %. Alternatively, Li et al. (Wang et al., 2020) doped Bi_2MoO_6 hierarchical microspheres with Bi (0) atoms, enhancing the photocatalytic activity due their high activity. Several authors (Kowalska and Rau, 2010; Alnaizy and Akgerman, 2000) tuned the activity of BBs by incorporating them into quasi zero-dimensional materials boosting their activity due to the onset of quantum effects (Zhang et al., 1998).

5. A techno-scientific trade-off: From lab scale to on-field applications

PO of organic pollutants is a green and sound approach but it presents several critical and unsolved technical issues. The first of all is directly connected to the reactors set-up that should be able to process great water volumes without producing harmful compounds during PO treatments (Villaverde et al., 2007). While the chemical reactivity could be tuned by tuning the materials, geometrical and physical constrains are unavoidable (Molinari et al., 2000). The first problem to be faced concerns the illumination source that can be placed either inside (Dijkstra et al., 2001) or outside (Imoberdorf et al., 2007) the reactor. In the first case the illumination is more homogenous, but the reactor realization is far more complex while with the external illumination reactors are simpler but affected by parasitic absorption of the light leading to a less efficient exploitation of the irradiated power. A compromise between these two set-up could be reached by using complex geometries like spiral reactors in which the light source is place in the middle of the spiral (Imoberdorf et al., 2007). Nevertheless, the optimum reactor should work in flow under sunset irradiation minimizing the energy request for its operational work (Puma and Yue, 2003). The distribution of the catalysts is also of capital importance and must be designed to have the maximum contact area with the water but also to absorb the maximum possible irradiation from the light source. This a very challenging task and several routes have been tested such as the production of membrane (Romero et al., 2009), packed (Gering, 2004) or fixed bed (Funken et al., 2003), slurry (Hupka and Zaleska, 2009) reactors or by simply suspend the catalyst into the water flow. As a matter of fact few PO reactors have reached the industrial application stage as reported by Romero et al. (Gonzalez-Martin et al., 2000). They reported a real case study in which a PO reactor was assembled with an internal light source and titanium oxide suspended into the flow. The reactor had a volume of 12.5 l and was able to operate in semi-batch conditions suggesting the use for treatment of special water waste streams instead of urban water ones.

Other patented technologies has focused on the solar driven PO as reported by many patents (Dong et al., 2022; Cai et al., 2022; Latif et al., 2022) but also membrane reactors have found space in applications (Shen et al., 2023).

The present approach to PO reactors is quite various as far as conformation and light source are concerned but it is highly limited for what concerns the PO catalyst selection. BBMs could represent an interesting innovation able to drive the PO technology from lab to real field applications because of the fast and efficient degradative routes that they are able to promote. There are plenty of solutions based on BBMs that are in perspective able to face the challenge of real world application with a relative low effort needed for their realization. Dong et al. (Grao et al., 2022) successfully produced a glass like material coated with a layer of needle shaped BiOBr by a simple scalable process. This approach is quite suitable for a scale-up of the production to an industrial level but it still affected by the instability issue typical of bismuth oxohalides materials. However, BiOBr could be combined with carbon fibres cloth for the production of resilient PO active filters able to reduce the chemical oxygen demand by 94 % (National-Minerals-Information-Center, Mineral Commodity Summaries, 2023). This material could be used even for a domestic scale solution due to its ability of working under sunlight exposure and its compatibility with previously installed filtration systems. This is of capital relevance because it could be a simple and low-tech approach that could be established in low income and rural areas without requiring skilled operators. Similarly, Bi_2O_3 could be immobilized into clay filter for the realization of a solar light PO system as the one shown in Fig. 5.

Latif and co-workers reported a degradative efficiency on a colorant based water polluted model up to 70 % suggesting that the low cost of this BBMs based reactor represents a solid solution for both domestic and industrial water treatment.

BBMs have been used also in reactors purposely designed for large scale use inserting Bi_2WO_6 into a fixed bed reactor operating in flow with a capacity of 50 mL/min (Xu et al., 2023) or by simply coating the inner part of a reactor with a bismuth titanate film (Argus, 2023).

Despite the many economical and performance advantages, water purification using BBMs has still to successfully face the challenge, shared with the other PO routes, of providing a cost-effective economical balance. This despite the fact that, materials such as bismuth oxide can be easily produced by using scalable methods of conversion starting from simple precursors. Furthermore, bismuth is produced from bismite, a byproduct of the mining and refining of lead and copper so there is no need to mine it specifically, reducing both prize and possibility to increment the yearly production. Bismuth is currently included in the critical raw material list of the European Union due to the fact that about 80 % of its annual production is localized in China (Van der Bruggen, 2021) and it is mainly used in high value sectors such as cosmetic, food and technological industry (Boczkaj and Fernandes, 2017; Sarkar et al., 2006). Accordingly, the bismuth yearly production is totally consumed by these applications stabilizing the price to around 27 $/kg (Henze and

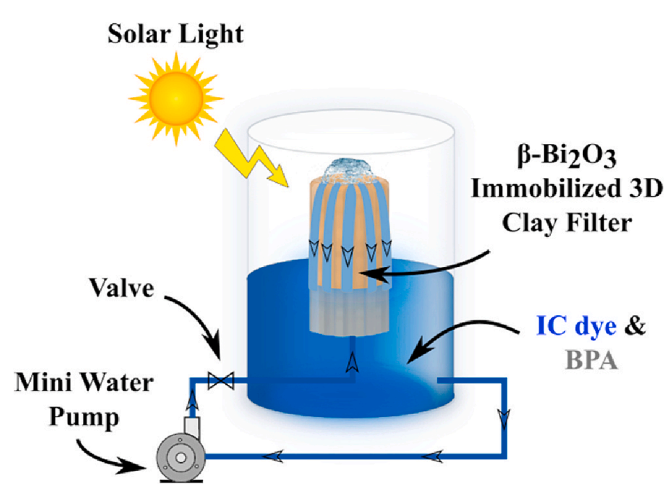

Fig. 5. Solar light PO system based on recirculating water in presence of β-Bi_2O_3 immobilized into clay filters as reported by Latif et al. (Salvador et al., 2012). Reprinted with all permission from Elsevier.

Comeau, 2008). This reduced the competitiveness of BBMs based PO compared with adsorption routes based on simple activated carbons or PO based on titania (Qiu et al., 2020). Furthermore, there is a generic issue relate to the physical and chemical properties of waste water. As first, it is noticeable that the wastewater streams generally show a wide range of pH from the very basic (Zhou et al., 2023) to the very acidic ones (Sun et al., 1997). This is represented a technical obstacle due to narrow pH range in which BBMs are exploiting the best operative conditions. Additionally, the inorganic species are varying greatly from one to another wastream (Norman, 1997) raising a relevant issue due to their adsorption and modification of BBMs surface. Accordingly, the complexity of waste water requires the development of integrate platforms in which the waste water is standardized prior to be treated with PO. This approach is technological feasible but it is poorly from the economical point of view drastically increased the resources consumption. Actually, there is still not unanimous consensus on the scheme of a BBMs platforms should have to be both technologically and economically solid even if curious approaches such as floating PO catalysts has been proposed (Cheng and Zhang, 2018). This materials are composed by a BBMs linked together with floating agents and can be easily disperse and recovery in water in common water treatments plants (Atwal and Cousin, 2016). The limited number of studies present in literature are still promising but far from the real on-application lacking in solid studies on leaching and biota interactions. In summary, BBMs water treatment systems production and deploy is a complex field that require an appropriated balance between scientific, technical, political and economic considerations.

Furthermore, it is of great relevance to focus on the consequences of BBMs leaching during the utilization of PO process. The first estimation of Hillemand safety levels of BBMs has been established to 50–100 μg/l (Dou et al., 2021) and there are several bismuth organometallic salts quite soluble in organic fluids (i.e. bismuth gallate, bismuth tartrate, bismuth salicylate) (Boczkaj and Fernandes, 2017; Wen et al., 2023). Several authors [139, 140] reported different maximum BBMs safety doses based on both administration route and chemical form. As reported by Dou et al. [141], Bi_2O_3 can undergo a photoinduced dissolution reaching concentration up to 0.80 mg/l, that represent a serious treat for human health. Authors decreased the dissolution of the BBMs by immobilizing it into a polyaniline structure. Wen et al. [142] observed a similar behavior for $BiVO_4$ at pH exceeding 8. These data suggest the mandatory need to establish a good practice of immobilization in order to avoid the replacement of organic with metal pollution.

6. Future outlooks

BBMs key advancement should represented by the solution of two main unresolved issue shared with all photocatalytic systems: i) production of harmful side products and regeneration/durability.

PO of polluted waters is composed by very complex and interconnected mechanisms that can significantly removed original pollutants but able to generate new harmful species. This challenging issue can be solved stressing out the performances of BBMs by conjugation or doping with other oxide with the promotion of Fenton reactivity. Particularly, the modification based on cheap but active species such as iron particles can represent a significant improvement in the field. Nevertheless, the durability still remain the major challenge for the future of BBMs due to harsh conditions of pH, organic matters and inorganics contained in polluted waters. The surface deactivation is an unavoidable phenomenon and required a well-balanced tuning of the chemistry and morphology of the BBMs without significant altering the band gap. The great efforts for increased BBMs life have not yet reached significant advancement compared with the state of the art of PO catalysts and it represents the last frontier of any photocatalytic system.

7. Conclusions

BBMs are promising solutions for the PO of organic pollutants contained in water wastestreams and in polluted water sources providing a cost-effective and sustainable PO solution. Nevertheless, adsorption processes are still far cheaper that PO based ones even if the end-life regeneration and disposal of the exhausted adsorptive materials contribute to resource depletion and environmental pollution.

The efforts in the engineering the BBMs chemistry and surface represent a positive and necessary action to further improve both durability and PO activity. These advancements can be fully exploited in the technological solutions discussed above. These are among the more virtuous route to face one of the great treats of this century, the limited access to water. Considering their simple production path, bismuth oxide and sub-nitrates are actually the top choice for the development of simple PO process with filter-based reactor on several scale, from domestic to industrial one. Even if more research is needed to reduce the BBMs systems costs, we firmly and honestly believe that BBMs are one of the best choices for the safety, preservation and quality improvement of water source.

CRediT authorship contribution statement

Mattia Bartoli: Writing – review & editing, Writing – original draft, Visualization, Conceptualization. **Alberto Tagliaferro:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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