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Destruction of emerging organophosphate contaminants in wastewater using the heterogeneous iron-based photo-Fenton-like process

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ABSTRACT

Organophosphates have been identified as an emerging group of contaminants in wastewater with significant negative human health effects. Due to their persistence in the watershed, soil, and the food chain, their degradation during wastewater treatment and before the release has garnered significant interest. Advanced oxidation processes enable the degradation of organophosphates with high conversion and fast kinetics. Photo-Fenton and photo-Fenton-like processes utilize a light source to initiate the Fenton reaction and produce reactive oxygen species that are required for the reaction propagation. While homogeneous catalysts have been studied extensively, heterogeneous catalysts are emerging due to their ease of use, separation, and recycling. This review provides a summary of the current progress made in the field of organophosphate degradation using a heterogeneous photo-Fenton-like process when compared to the homogeneous process and highlights the need for the rational photocatalyst design as well as suggests future directions of research, including utilizing wastewater feeds that represent real-world compositional complexity as well as providing molecular-level catalytic process insights to better understand limitations of these catalysts.

Introduction

The population growth and increased urbanization have posed significant new challenges for both wastewater treatment and resource recovery (Kehrein et al., 2020). Wastewater from agricultural, industrial and urban sources presents a significant threat to human health, if not treated properly (Tufail et al., 2020; Ye et al., 2012). Due to the large variability in chemical properties stemming from the large diversity of the functional groups within the single-molecule, organophosphates have become widely used as herbicides, flame retardants, insect repellants, plasticizers and defoamers. For example, in 2013 up to 30 % of the flame retardants produced were organophosphates (Zhong et al., 2020). The contamination of soil and aquatic ecosystems with these organophosphates inevitably leads to these molecules entering human bodies (Bekele et al., 2019; Stasinska et al., 2014). Due to their resulting increased influx into the environment that has the potential to afflict great harm to human health (Bekele et al., 2019; Tran et al., 2018), organophosphates have received particular attention as emerging environmental contaminants. Designing methods to eliminate these trace organic substances from wastewater is a vital part of addressing the global challenges of water and food security (Environmental Engineering for the 21st Century, 2019). While biological degradation methods can successfully remove most organic molecules from wastewater, the recalcitrant organophosphates require chemical degradation methods, such as advanced oxidation processes (AOPs), to achieve near-complete conversion.

The Fenton process, reported by HJH Fenton first in 1894, utilizes aqueous Fe(II) in combination with H_2O_2 to partially oxidize organics, such as tartaric acid in the original report (Fenton, 1894). This process has proven to be highly effective towards degrading organics in wastewater and has been extensively studied. While homogeneous Fenton chemistry is highly effective at low pH values of the solution, the significant loss in efficiency at higher pH occurs while a large amount of sludge is accumulated after the coagulation stage to remove aqueous iron (Andreozzi et al., 1999). Thus, the use of a heterogeneous catalyst can lead to a more sustainable catalyst separation and reuse, while operating under less extreme pH conditions (Munoz et al., 2015). A Fenton-like process refers to the reaction initiated using the Fe(III) source, instead of the traditional Fenton reaction which is initiated using the Fe(II) source (Wang, 2008). Fe-based heterogeneous catalysts have been reported in the literature since iron can alternate between Fe(III) and Fe(II) oxidation states during the redox cycle, required for a Fenton-like process (Munoz et al., 2015; Pereira et al., 2012; Sun et al., 2019). Since iron is an abundant material, a low-cost catalyst can be fabricated. The H_2O_2 consumption is dependent on both the target pollutant concentrations and the concentration of dissolved organic matter (DOM) in the wastewater influent (effects of DOM on this process will be discussed in a later section). Finally, external energy sources such as light,

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electricity, or sonication, have been utilized to improve the efficiency of the heterogeneous catalysts (Dindarsafa et al., 2017; Wang et al., 2014; Zhu et al., 2019). Fig. 1 shows the homogeneous photo-Fenton and heterogeneous photo-Fenton-like process used for glyphosate degradation based on findings reported by Chen et al. (Chen et al., 2007).

While some work has been performed on organophosphate degradation using a heterogeneous catalyst based AOPs, there are gaps in knowledge of the design of the heterogeneous catalysts. Further, to our knowledge, no pilot-scale studies of organophosphate removal from wastewater feedstock with complex composition approaching that of real wastewater streams have been reported and no corresponding process design work has been reported using heterogeneous catalysts. This review aims to present a concise state of the art on Fe-based photo-Fenton and photo-Fenton-like catalysts for the removal of emerging organophosphates in wastewater and to provide future research directions to expand the understanding of this field.

Organophosphates as emerging wastewater contaminants

Organophosphates have emerged in the past two decades as widespread contaminants in soil and watershed posing a significant toxicological threat to aquatic ecosystems, soil and human health (Ji et al., 2019). Table 1 shows a compiled list of organophosphates from various sources that have been detected in water streams across the globe.

In particular, the widespread use of organophosphates in applications such as flame retardants, plasticizers, defoamers, and herbicides have caused significant leaching of this contaminant into aquatic environments through both municipal and industrial wastewater streams, as well as agricultural runoff (Cristale et al., 2013; Meyer and Bester, 2004; Yang et al., 2019). Wastewater discharged from factories and wastewater treatment plants (WWTP), as well as atmospheric deposition, are key pathways for organophosphates to enter aquatic ecosystems (Cristale et al., 2013; Meyer and Bester, 2004; Regnery and Püttmann, 2010). Many consumer products, such as furniture, electronics, textiles, carpets, as well as materials used in building insulation, can be significant sources of organophosphate leaching into the environment during the production, use, and recycling (Blum et al., 2019; Someya et al., 2016; Yang et al., 2019). Recent observations suggest that some organophosphates can cause serious health issues in humans, including impairments to metabolism, immunity, endocrine activity, cognitive functions, as well as other neurological issues due to the long-term exposure (Naughton and Terry, 2018). Notably, organophosphate flame retardants are added to materials to act as flame retardants, which indicates that the organophosphate is not chemically bonded to the materials (van der Veen and de Boer, 2012). This can lead to their higher leaching possibility compared to a chemically bonded (reactive) flame retardant (van der Veen and de Boer, 2012). Chlorinated organophosphates, such as TCEP and TDCPP, used as additive flame retardants, have been reported to be

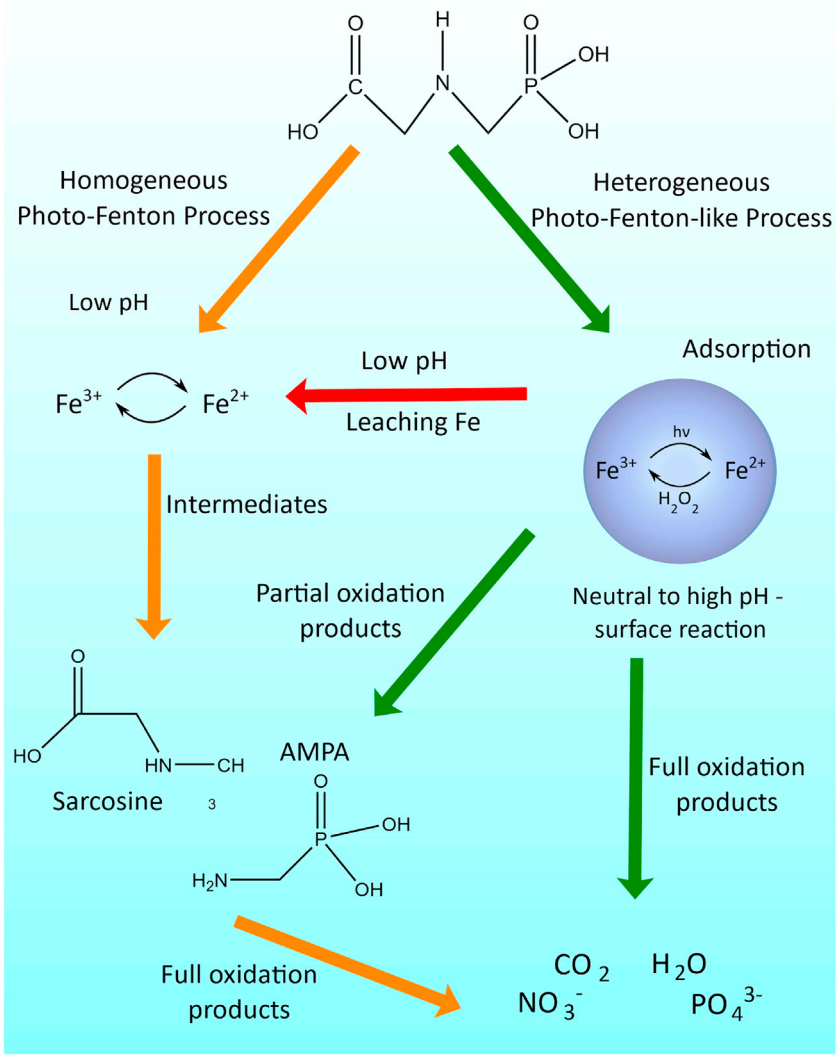

Fig. 1. Homogeneous photo-Fenton and heterogeneous photo-Fenton-like processes for the degradation of organophosphate glyphosate based on findings by Chen et al. (Chen et al., 2007).

Table 1
Emerging organophosphorus contaminants and their mean concentrations in the respective waste streams.

Contaminant	Use	Concentration (ng/l)	Source
Tris-(2-chloroethyl) phosphate (TCEP)	(FR), (P)	0.352−1400	Municipal WWTP (USA) (Kim et al., 2017), Municipal WWTP (Germany) (Fries and Püttmann, 2003), Household WW (USA) (Schreder and La Guardia, 2014), WWTP (Germany) (Meyer and Bester, 2004)
Tributyl phosphate (TBP)	(D), (FR), (P), (HC)	622−13000	Municipal WWTP (Germany) (Fries and Püttmann, 2003), STP (Sweden) (Marklund et al., 2005)
Tris(2-butoxyethyl)phosphate (TBEP)	(FR)	2955−30100	Municipal WWTP (USA) (Kim et al., 2017), WWTP (Germany) (Meyer and Bester, 2004), Municipal WWTP (Germany) (Fries and Püttmann, 2003)
Tris(1-chloro-2-propyl)phosphate (TCIPP)	(FR)	123–5120	Municipal WWTP (USA) (Kim et al., 2017), WWTP and river water (China)(Li et al., 2020c)
Tris-(1,3-dichloropropyl)phosphate (TDCPP)	(FR)	3480	Household WW (USA) (Schreder and La Guardia, 2014)
Tris-(methylphenyl) phosphate (TMPP)	(FR)	20.1	Municipal WWTP (USA) (Kim et al., 2017)
Triethyl phosphate (TEP)	(FR)	121−501	Municipal WWTP (USA) (Kim et al., 2017)Municipal WWTP (Austria) (Martínez-Carballo et al., 2007)
Tri-propyl phosphate (TPP)	(FR), (P)	21.2	Municipal WWTP (USA) (Kim et al., 2017)
Bis(1,3-dichloro-2-propyl) phosphate (BDCIPP)	(FR)	2900	Municipal WWTP (USA) (Kim et al., 2017)
Triphenylphosphine oxide (TPPO)	(S), (FR)	70.6 – 142	WWTP (China) (Li et al., 2020c)
Tri n-butyl phosphate (TnBP)	(E), (P)	<1	WWTP Influent (USA) (Kolpin et al., 2006)
Tris(2,3-dibromopropyl)phosphate (TDBPP)	(FR)	449	Municipal WWTP (USA) (Kim et al., 2017)
Tris(2- ethylhexyl)phosphate (TEHP)	(P), (FR), (S)	392	Municipal WWTP (USA) (Kim et al., 2017),
Malathion	(PC)	1.15×10^7	Agrochemical plant effluent (Zhang and Pagilla, 2010)
p,p′-1,3-phenylene *p,p,p′,p′*-tetraphenyl ester phosphate (PBDPP)	(FR)	462	Municipal WWTP (USA) (Kim et al., 2017)
Glyphosate	(HC)	<8300	WWTP influent (USA) (Kolpin et al., 2006), WWTP Influent (Switzerland) (Poiger et al., 2020)
Aminomethylphosphonic acid (AMPA)	Glyphosate metabolite	<3900	WWTP influent (USA) (Kolpin et al., 2006)

(D) – defoamer, (FR) – flame retardant, (HC) – herbicide, (P) – plasticizer, (S) – solvent, (E) – extractant, (PC) – pesticide, WWTP – waste water treatment plant, STP – sewage treatment plant.

toxic and carcinogenic (Kim et al., 2017). Other organophosphates, such as TBP, TPP, and TnBP, are predominantly used as plasticizers in floor wax and vinyl plastics, as well as defoaming agents (Regnery and Püttmann, 2010). These compounds have been detected in the concentration range of 10−870 ppb in river water in Germany (Andresen et al., 2004; Marklund et al., 2003). Ubiquitous in the environment, flame retardants in trace quantities have been shown to have negative effects on reproductive health, asthma and allergy-related diseases, and children's health (Doherty et al., 2019).

Herbicides and pesticides are other two important classes of organophosphate molecules provided the expansion in agriculture in the past several decades. These molecules are prevalent in agricultural runoff. Since agricultural runoff is a non-point source for organophosphates, treatment *via* a catalytic process is unfavorable. However, recent studies report the detection of some organophosphates typically used in agricultural applications in urban WWTPs and industrial wastewater, where catalytic treatment can be feasibly implemented (Ghanem et al., 2007; Kolpin et al., 2006). Malathion is a notable pesticide that has been detected in wastewater and has adverse effects on aquatic ecosystems (Relyea, 2009; Zhang and Pagilla, 2010). A widely used broad-spectrum herbicide glyphosate (included in RoundUp) has also been proven to have significant health effects, with a recent study showing that glyphosate and its harmful metabolites (*e.g.* aminomethylphosphonic acid, AMPA) can accumulate in soil and lead to antibiotic resistance in the soil microbiome (de Castilhos Ghisi et al., 2020; Riches, 2015; Van Bruggen et al., 2018). This antibiotic resistance can transfer from the soil to other ecosystems *via* run off of these microbiome species into wastewater, posing another severe issue caused by the application and accumulation of organophosphate-based herbicides into the environment. Finally, since fertilizer derived from the sludge resulting from wastewater treatment is utilized in agriculture, the presence of organophosphates in trace amounts raises the issue of them being taken up by the crops and resulting in the food chain (Eggen et al., 2013). Studies have shown that organophosphates have been detected in human blood, placenta, and milk which indicates that there is a possibility of organophosphates transferring over to newborns (Chen et al., 2012; Greaves and Letcher, 2014). The persistence of organophosphates and their abundance in daily use make this class of materials an emerging hazard that warrants significant research to better understand their successful environmental remediation.

Photo-Fenton-like catalyst design for organophosphate degradation

Both homogeneous and heterogeneous Fe-based catalytic systems have been used for the degradation of organophosphates in wastewater. Homogeneous Fenton reaction is the most efficient around pH ∼ 3, which can be challenging to implement at a large scale (Zhu et al., 2019). This limitation is due to the precipitation of iron from the aqueous phase at higher pH values. By adding chelating agents that prevent iron from precipitating, homogeneous Fenton studies have been conducted at near-neutral pH conditions in recent literature (O'Dowd and Pillai, 2020). A significant drawback of homogeneous Fenton processes is the accumulation of sludge after the iron removal step. To circumvent this issue, heterogeneous catalysts have recently been used since they offer better separation and reusability and do not generate sludge waste.

The Fenton process is comprised of three stages. Namely, (1) initiation, where reactive ROS (reactive oxygen species) species are generated, (2) propagation, where the radical species interact with contaminant molecules to break down bonds and (3) termination, where radical species combine and cease to be active (Vorontsov, 2019). The interfacial mechanism and rate constants have been discussed in depth in previous reviews (He et al., 2016; Zhu et al., 2019). Eqs. (1) and (2) show the reactions between each Fe-species and H_2O_2 to generate a reactive

oxygen species (ROS) and their respective reaction rate constants (Zhu et al., 2019).

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + HO^{\bullet} + OH^{-} \mathrm{k} = 40 - 80\,\mathrm{M^{-1}s^{-1}} \quad (1)$$

$$FeIII) + H_2O_2 \rightarrow Fe(II) + HO_2^{\bullet} + H^{+} \mathrm{k} = 0.001 - 0.01\,\mathrm{M^{-1}s^{-1}} \quad (2)$$

It is evident from the vast difference in the rate constants for these chain propagation steps in the Fenton process that Fe(II) is desired as the starting material in the catalyst. However, in the case of materials such as hematite (α-Fe_2O_3) or other Fe(III) based catalysts, a light source with the wavelength matching the ligand to metal charge transfer (LMCT) band position can photo-reduce the Fe(III) to Fe(II) (Giannakis, 2019; Herney-Ramirez et al., 2010; Pignatello et al., 2006; Ruales-Lonfat et al., 2015). This reduction allows for the step with the higher rate constant to initiate the reaction. Heterogeneous catalyst design should focus around iron active site property tuning to efficiently absorb light and produce the Fe (II) site required to initiate the reaction while offering stability, high recyclability and minimal loss inactivity. This suggests that key catalyst design parameters are (a) active iron surface site coverage (the concentration of the surface-active sites), (b) the reducibility of the Fe (III) site, as well as (c) the ability to tune the bandgap of the catalyst material. Bulk iron oxides, such as hematite, goethite, and magnetite have band gap values of 2.2, 2.5 and 0.1 eV respectively (Zhu et al., 2019), suggesting they have the potential to undergo charge transfer necessary while also serving as catalyst materials. Similarly, the bandgap of any catalyst supporting material can also play a key role in the activity given that typical supports, such as TiO_2, Ag_3PO_4, and $BiVO_4$, can generate electrons necessary for the Fe(III) to Fe(II) reduction (Xu et al., 2017, 2016a, 2016b; Zhu et al., 2019). Further promotion of the catalytic site activity has been reported in the heterogeneous Fenton literature by adding electron-rich materials to the catalyst, such as carboxylate ligands (Hou et al., 2016; Huang et al., 2017; Wang et al., 2011; Zhang et al., 2014), combining with carbon materials such as graphene oxide or C_3N_4 (Qian et al., 2018; Qin et al., 2018; Zubir et al., 2015), as well as nano zerovalent iron (nZVI) (Shi et al., 2014; Xi et al., 2014). The addition of such electron-rich species to the catalyst is intended for faster reduction from Fe(III) to Fe(II) by providing the electron for the reduction step which accelerates the overall reaction rate. However, Hou et al. have reported that the carboxylate ligand ascorbate when used with hematite causes reductive dissolution, leading to homogeneous Fenton reaction dominating at low pH (Hou et al., 2016). While Hou et al. have hypothesized the possibility of an adsorbed surface iron-ascorbate complex, this has not been confirmed with experimental evidence (Hou et al., 2016). Studying the surface of the catalyst under operating conditions can be challenging *via* spectroscopic methods and thus, elucidating the structure of the active site with such carboxylate promotors with experimental evidence has not yet been accomplished to the best of our knowledge. The reduction potential of carboxylic acids is much lower than that of Fe(III) to Fe(II) and, for example, ascorbate ion in particular promotes Fe(III) reductive dissolution (Hou et al., 2016; Huang et al., 2017) to generate peroxy radical, the process favored at low pH. However, solid-phase iron sites with bulky surface-bound ligands may potentially be less accessible to H_2O_2 reaction or contaminant adsorption. Hence the tradeoff between the modification of the surface with easily reducible organic molecules, such as those containing carboxylate moieties, to achieve enhanced catalytic activity *vs* any negative steric effects that prevent organophosphate molecule adsorption/reactions need to be investigated. Systematic studies that include outer- *vs* inner-sphere bonding, solution pH, carboxylic moiety number, molecule steric hindrance, bulk and surface concentration of both reducible organic molecules and organophosphates need to be considered. This suggests that theoretical calculations of adsorption of organophosphates on such iron centers with chelating agents in comparison to bulk iron oxides is an important avenue of future research. Related key consideration is tuning of the exposed crystal facet since the radical production efficiency using H_2O_2 is facet dependent on hematite and $CuFeO_2$ nanocatalysts (Dai et al., 2018; Huang et al., 2019, 2018).

From the catalytic material point of view, several heterogeneous catalysts have been reported for this reaction as both bulk catalysts and supported catalysts (Feng et al., 2004; Li et al., 2020a; Zhu et al., 2019). Bulk iron oxides are an abundant and cost-effective catalyst for this reaction but, the low surface area and lower number of exposed sites reduce efficiency. Supported iron oxides can be used to take advantage of higher dispersion over a high surface area support, which increases the number of exposed sites and uses less iron precursor. The higher support surface area and porosity lead to more favorable transport properties and utilizing highly insoluble support it is possible to synthesize a stable catalyst that can be recycled. Such an example is SBA-15, which has been reported as support for iron oxide in the heterogeneous Fenton literature (Lim et al., 2006; Shukla et al., 2010). These design parameters can be effectively characterized using techniques shown in Fig. 2. N_2 physisorption and Brunauer–Emmett–Teller (BET) theory are typically used for surface area characterization, while the Barrett-Joyner-Halenda (BJH) method is used for pore characterization. Physical properties such as particle morphology (characterized *via* SEM and TEM) as well as crystal facet characterization (characterized *via* TEM) are important aspects in studying the performance of the catalyst. The surface information gained by LEIS, XPS, or ToF-SIMS, as well as the electronic and molecular structure information from UV–vis DRS and XAS, are also critical for rational catalyst design (Fig. 2). The results of these key characterization techniques are not always present in current photo-Fenton work. In particular, presenting UV–vis spectra for catalysts is important since it provides insights on which light source to utilize and the range of wavelengths being absorbed. Providing the UV–vis DR spectra and specifying the LMCT band position as well as the region of light absorption is important in understanding the efficiency of a photocatalyst. In the organophosphate degradation literature several studies have not provided UV–vis DR spectra for their catalysts, thus providing incomplete characterization of the used photocatalytic systems (Yang et al., 2018; Zhang et al., 2019).

Table 2 lists previously designed catalytic systems of photo-Fenton and photo-Fenton-like processes reported in the literature for the degradation of organophosphates. In contrast to the number and diversity of organophosphates reported in Table 1, it is evident that not many organophosphates have been degraded using the photo-Fenton process. Homogeneous catalysts have been chiefly used for the herbicide glyphosate and pesticide fenitrothion, diazinon, profenofos, and malathion degradation (Badawy et al., 2006; Chen et al., 2007; Huston and Pignatello, 1999; Serra-Clusellas et al., 2019; Souza et al., 2013; Tran et al., 2019). All homogeneous reactions were conducted at pH values in the range of 2.8−6. By utilizing oxalate ions which form complexes with Fe(III), broader pH ranges have been explored (Chen et al., 2007). While these studies discuss the performance of the homogeneous systems, they do not discuss in detail the practical concerns, such as catalyst separation, which have important environmental and economic implications in sludge production and catalyst cost.

On the other hand, heterogeneous Fe-based catalysts that operate at low pH values are susceptible to dissolution and iron leaching. The leached iron will perform homogeneous Fenton chemistry but, the overall goal of a heterogeneous catalyst is for the reaction to occur *via* the heterogeneous pathway utilizing a surface reaction. At pH 3, goethite has been shown to leach iron which in turn performs homogeneous Fenton (Lu, 2000; Lu et al., 2002). To avoid this issue, neutral or higher pH values can be utilized for heterogeneous Fenton processes since it has been reported that above pH 7.5 no soluble iron is detected with ICP-MS (Ruales-Lonfat et al., 2015; Sulzberger and Laubscher, 1995). However, a small fraction of iron dissolution may be unavoidable due to the organic acids that are intrinsically present in wastewater. Therefore, a combination of dissolved and surface iron performing Fenton degradation *via* competing kinetics and mechanisms will take place but, is typically poorly described or accounted for in the current literature. Yang

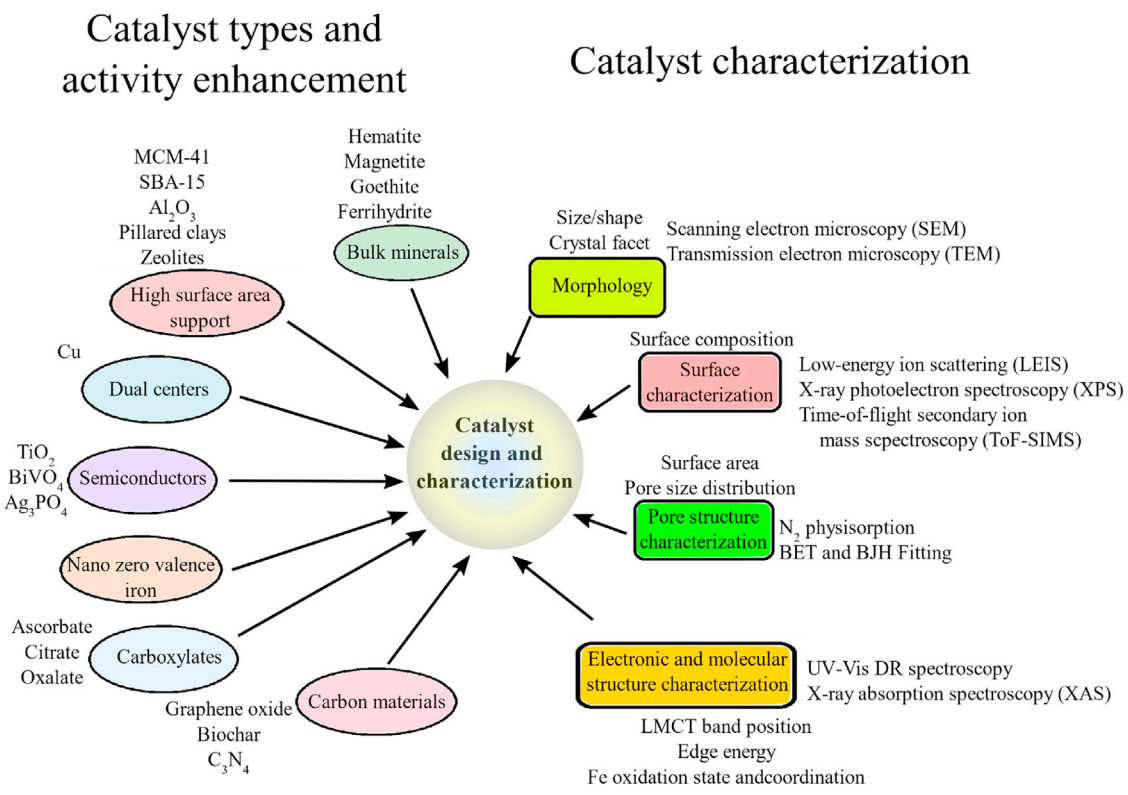

Fig. 2. Catalyst design considerations and characterization methods for heterogeneous photo-Fenton-like catalysts.

Table 2
Literature reported catalysts, process conditions and the resulting conversions of Fenton and Fenton-like processes used for the treatment of organophosphates.

Catalyst	Method and process conditions	Target organophosphate(s) (Conversion)	Source
$Fe(II)_{(aq)}$	Homogeneous Photo-Fenton (100 < λ < 280 nm, room temperature, 50 ppm contaminant concentration, COD:H_2O_2 = 1:2.1, 30 min reaction time)	Fenitrothion (86.9 %)Diazinon (56.7 %) Profenofos (89.7 %)	(Badawy et al., 2006)
$Fe(II)_{(aq)}$	Homogeneous Electro-Fenton (carbon cathode and Pt anode, 0.05 M – 0.4 M glyphosate, pH 2–6)	Glyphosate (91.9 %)	(Tran et al., 2019)
$Fe(II)_{(aq)}$	Homogeneous Photo-Fenton (295 < λ < 815 nm, pH = 2.8, 40□, 100 ppm glyphosate)	Glyphosate (~100 %)	(Souza et al., 2013)
$Fe(II)_{(aq)}/Fe(III)_{(aq)}$	Homogeneous Photo-Fenton (solar radiation ~3 mW/cm^2, 25□, pH = 2.8)	Glyphosate (~100 %)AMPA (70 %–80 %)	(Serra-Clusellas et al., 2019)
$Fe(III)_{(aq)}$	Homogeneous Photo-Fenton-like (300 < λ < 400 nm, 25□, pH = 2.8, contaminant concentration 0.0002 M)	Malathion (94 %, TOC loss 0 %)	(Huston and Pignatello, 1999)
$Fe(III)_{(aq)}/C_2O_4^{2-}$	Homogeneous Photo-Fenton-like (λ ≥ 365 nm, 22 □, pH = 3.5, concentration =5 ppm)	Glyphosate (60 % PO_4^{3-} release)	(Chen et al., 2007)
Goethite (FeOOH)	Heterogeneous Photo-Fenton-like (Power 20.8 mW/cm^2, 390 < λ < 800 nm, 25 □, pH = 3.5, contaminant concentration 10 ppm)	Glyphosate (39.7 %)	(Zhang et al., 2019)
Goethite (FeOOH) and Magnetite (Fe_3O_4)	Heterogeneous Photo-Fenton-like (UV: 275 nm, Visible: 350–1100 nm)	Glyphosate (Goethite 69 % and Magnetite 76 %)	(Yang et al., 2018)
Ag/Fe_2O_3 mesocrystals	Heterogeneous Photo-Fenton-like (Xenon lamp λ ≤ 420 nm)	Glyphosate (50 %)	(Chen et al., 2016)
MIL-101(Fe)	Heterogeneous Photo-Fenton-like (20.8 mW/cm^2,15 □ – 35 □)	tris(2-chloroethyl) phosphate (90 %)	(Hu et al., 2019)

et al. demonstrated the use of goethite and magnetite for glyphosate degradation using a 10 ppm glyphosate concentration with a 400 ppm catalyst loading (Yang et al., 2018). At pH 9, goethite and magnetite were reported to have initial dissolved iron concentrations of 14 and 87 ppb, respectively, while the same catalysts at pH of 3 resulted already in 53 ppb and 198 ppb iron leaching out (Yang et al., 2018). This shows that basic conditions are indeed preferable to minimize iron loss even though dissolved iron can enhance the reaction rate. The case of goethite and oxalate reported degrading glyphosate showed that a significant amount of Fe(II) was released into the solution due to the low pH of 3.5, which enhanced the reaction rate (Zhang et al., 2019). This dissolution is problematic since the degradation process in turn adds Fe(II) ions to the wastewater. The study of goethite and magnetite utilization for glyphosate degradation showed that heterogeneous catalysts can result in relatively high contaminant conversion with no detectable iron leaching (Yang et al., 2018). Using computational methods, authors showed that the C−P bond is readily cleaved by ROS when glyphosate adsorbs on the iron oxide surface. Magnetite was shown to have significantly higher reaction rates due to the presence of both Fe(II) and Fe (III), in contrast to goethite, which is primarily Fe(III). Chen et al. reported hematite mesocrystals promoted with Ag for glyphosate degradation with 50 % PO_4^{3-} liberation into the solution (Chen et al., 2016). The study compared unpromoted hematite mesocrystals with promoted mesocrystals to show that the PO_4^{3-} liberation can increase from 22 % to 50 % and

that after 2 h of reaction only 0.2 wt% of iron leached out (Chen et al., 2016). However, this material exhibits low surface area (17.9 m^2/g) which could limit its efficiency due to the low dispersion of the catalytic sites. Finally, the metal-organic framework MIL-101(Fe) has been reported as a highly effective catalyst for glyphosate degradation (Hu et al., 2019). The MIL-101(Fe) catalyst showed low iron leaching at pH 3.0 but higher leaching behavior at higher pH values (Hu et al., 2019). This special behavior in MOFs consisted of carboxylate ligands can be attributed to their lower stability in basic conditions (Hu et al., 2019; Yuan et al., 2018). This catalyst degraded 90 % of TCEP in deionized water but, due to radical scavenging species present in actual effluents, the efficiency was reduced for TCEP in real wastewater (Hu et al., 2019). This report shows the importance of testing both in deionized water as a controlled environment to understand the catalyst and the need for the real effluent studies to provide reaction condition optimization for real-world applications. The effect of dissolved organic matter (DOM) on this reaction is of particular importance due to the composition of real-world wastewater (Gonsior et al., 2011; Imai et al., 2002). Previous literature has discussed the inhibition of hydroxyl radical reactions with aromatics in water containing DOM, indicating that pure water studies would lead to optimal H_2O_2 and catalyst doses that are lower than the optimal conditions for real-world wastewater, and that the require reaction times would also be longer (Lindsey and Tarr, 2000). Previous studies show that Fenton processes that do not achieve full mineralization lead to significant changes in the DOM species distribution, showing that the operating conditions of the Fenton process should be tailored to achieve full oxidation or produce a known distribution of products aimed at a secondary treatment process such as biological or adsorption treatment (He et al., 2015; Mantzavinos and Psillakis, 2004).

Two key steps in the mechanism of heterogeneous photo-Fenton-like processes discussed in the literature are adsorption of the contaminant on the catalyst surface and subsequent reaction with ROS (Zhang et al., 2019). In a study utilizing goethite and oxalate ions, the authors claimed that adsorbed tetracycline was easily degraded while adsorbed glyphosate was not easily degraded (Zhang et al., 2019). However, the lack of clear experimental evidence from spectroscopic methods poses the issue of decoupling the effects of adsorption and degradation. For organic molecules that only contain C, H, and O, the products are CO_2 and H_2O, provided sufficient ROS are generated. In the case of organophosphates, P leads to the production of PO_4^{3-}. Materials, such as glyphosate, that also contain N can lead to the production of NO_3- or NH_4^+, as shown using computational methods (Yang et al., 2018). At higher pH values, the liberated PO_4^{3-} may adsorb on the catalyst due to the affinity of iron oxides to adsorb PO_4^{3-} ions (Wang et al., 2018), potentially affecting the overall process performance. The soluble ions, such as NO_3-, do not adsorb on the catalyst but pose an additional challenge of removal when present a low concentration ppb level.

Future research directions

The growth in the industrial manufacturing process scale, increased in population and urbanization, as well as the growth in agricultural outputs, has caused significant detrimental effects on the environment. Organophosphates destroy aquatic ecosystems, as well as present long-term issues to human health *via* water and soil exposure. Encroachment of organophosphates in the food chain suggests the need of exploring viable and effective treatment routes to reduce the organophosphate concentrations entering the watershed (Li et al., 2020b; Melgar et al., 2010; Pagliuca et al., 2006; Salas et al., 2003). With wastewater facilities transitioning away from discarding the wastewater and towards reusing and recovering water and nutrients contained therein, developing highly efficient AOPs becomes a research avenue of vital importance. To facilitate reuse of the wastewater for irrigation or gardening, it is critical that no harmful intermediates are produced during the AOP process and this problem has not been fully addressed when using photo-Fenton-like degradation of organophosphates (Vilé, 2020). As discussed in this review, the use of heterogeneous photocatalysts can be viewed as advantageous due to milder process conditions than the homogeneous process, better catalyst reusability, and lack of sludge production. While quite a few heterogeneous catalysts have been reported for dye and model contaminant molecule degradation under ideal conditions, there is a need for research utilizing wastewater feedstocks that are representative of real-world conditions, as well as for the measured reaction kinetics for the organophosphates reported in this review. Furthermore, by utilizing these kinetic insights, pilot-scale process design work must also begin *de novo* with environmental sustainability and economic feasibility in mind. Recent mechanistic studies have been performed to provide molecular insights of the heterogeneous photo-Fenton-like process using Density Functional Theory calculations, which indicates that computational methods are only recently emerging tool of paramount importance in understanding molecular-level insights for the degradation process of these complex molecules (Li et al., 2020a; Vorontsov, 2019). Therefore, this field offers a wide variety of opportunities to (a) improve the catalytic material design and characterization, (b) obtain further mechanistic insights, and (c) design large-scale processes with life-cycle assessment and techno-economic analysis.

Declaration of Competing Interest

The authors declare no conflicts of interest.

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