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# Treatment technologies and degradation pathways of glyphosate: A critical review

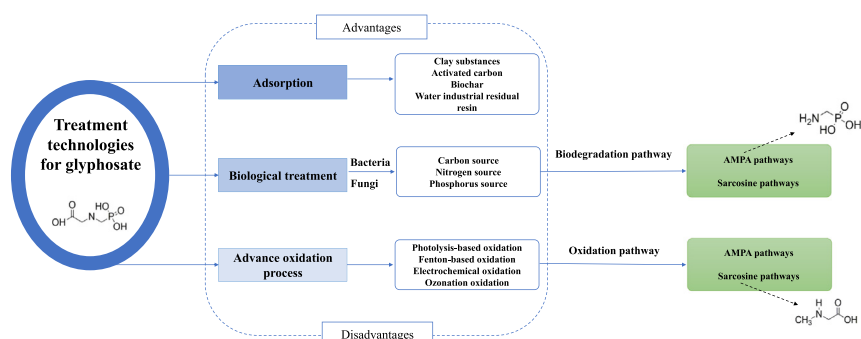
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## HIGHLIGHTS

- Adsorption, biological and oxidation processes for glyphosate in wastewater are compared.
- Degradation pathways of glyphosate to AMPA and sarcosine are proposed and discussed.
- Combined processes are expected to be interesting technology for glyphosate treatment.
- Insights into future research for glyphosate treatment by different technologies are discussed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Glyphosate is one of the most widely used post-emergence broad-spectrum herbicides in the world. This molecule has been frequently detected in aqueous environment and can cause adverse effects to plants, animals, microorganisms, and humans. This review offers a comparative assessment of current treatment methods (physical, biological, and advanced oxidation process) for glyphosate wastewaters, considering their advantages and drawbacks. As for other molecules, adsorption does not destroy glyphosate. It can be used before other processes, if glyphosate concentrations are very high, or after, to decrease the final concentration of glyphosate and its by-products. Most of biological and oxidation processes can destroy glyphosate molecules, leading to by-products (the main ones being AMPA and sarcosine) that can be or not affected by these processes. This point is of major importance to control process efficiency. That is the reason why a specific focus on glyphosate degradation pathways by biological treatment or different advanced oxidation processes is proposed. However, one process is usually not efficient enough to reach the required standards. Therefore, the combination of processes (for instance biological and oxidation ones) seems to be high-performance technologies for the treatment of glyphosate-containing wastewater, due to their potential to overcome some drawbacks of each individual process. Finally, this review provides indications for future work for different treatment processes to increase their performances and gives some insights into the treatment of glyphosate or other organic contaminants in wastewater.

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## 1. Introduction

Glyphosate (N-(phosphonomethyl)glycine, C<sub>3</sub>H<sub>8</sub>NO<sub>5</sub>P) is a post-emergence and nonselective broad-spectrum herbicide to control many annual and perennial weeds. It is one of the most used herbicides for agricultural, forestry, and urban setting in the world, due to its low toxicity to non-target organisms. The total amount of glyphosate used for agricultural and non-agricultural applications reached 126 million kilograms in 2014 (Benbrook, 2016). Glyphosate stops aromatic amino acid biosynthesis in plants through inhibiting the enzymes 5-enolpyruvylshikimate-3-phosphate synthase or 3-deoxy-D-arabinoheptulosonate-7-phosphate synthase, which is a precursor for aromatic amino acids, ultimately hormones, vitamins and other important metabolites for plants (Kataoka et al., 1996).

Due to intensive use and accumulation of glyphosate in the environment, some harmful effects have been reported for plants, animals, and human health, such as weakening plant systems, disrupting the metabolism of terrestrial and aquatic animals and causing endocrine disruption to human (Mesnage et al., 2015; Tarazona et al., 2017; Van Bruggen et al., 2018). In 2015, the International Agency for Research on Cancer classified glyphosate as “probably carcinogenic to humans”, while authors disagree on this conclusion, which requires further research (Andreotti et al., 2018).

Furthermore, after spreading, glyphosate-containing herbicides may contaminate the environment. Through spraying, glyphosate can directly enter the atmosphere environment, with concentrations in rain waters up to 0.48 g.L<sup>-1</sup> (Villamar-Ayala et al., 2019). Then, glyphosate reaches the target organisms by foliar contact. Without degradation in the plant, the large roots of some weeds transport glyphosate into deep soil layers. A part of glyphosate is adsorbed into organic matter and clay of soils, resulting in its accumulation in soils over time (Van Bruggen et al., 2018). Meanwhile, glyphosate can be transferred into water because of runoff. Therefore, due to the extensive use of glyphosate, it has been frequently detected in the aqueous environment. For instance, the concentration of glyphosate in surface or groundwater is in the range of 2–430 µg.L<sup>-1</sup> in the USA (Mahler et al., 2017), higher than in Europe: 0.59–165 µg.L<sup>-1</sup> (Villeneuve et al., 2011). These values exceed the maximum contaminant level goal of 0.7 µg.L<sup>-1</sup> for drinking water (Saunders and Pezeshki, 2015).

Glyphosate can also contaminate the aqueous environment from industrial effluents of glyphosate synthesis industries or some textile industries through using glyphosate as raw materials for textile additives (Baylis, 2000). Three major industrial synthesis methods are used for glyphosate production: hydrocyanic acid, diethanolamine, and glycine process. These processes reject a large amount of industrial wastewater and other environmental pollutions. To obtain 1 ton of glyphosate, about 5–6 tons of crystallised mother liquid is generated with ~1% glyphosate, 1–4% formaldehyde and other by-products (Xing et al., 2018). Most of glyphosate is recovered from the mother liquor through nanofiltration, while 200–3000 mg.L<sup>-1</sup> glyphosate remains in the nanofiltration permeate wastewater in China. It has also been reported that the glyphosate concentration in industrial effluents could achieve up to 2560 mg.L<sup>-1</sup> (Xing et al., 2017). Therefore, it is necessary to develop processes capable of degrading glyphosate contained in urban and industrial wastewaters.

Aminomethylphosphonic acid (AMPA) is the most important metabolite of glyphosate from microorganisms degradation. It shows

similar characteristics to glyphosate (Jönsson et al., 2013). However, AMPA is more persistent than glyphosate with a half-life of 119–985 days (Assalin et al., 2009). In addition, except glyphosate, AMPA can be transferred from other organic phosphonates, used as adjuvants in detergents and as stabilisation agents in cooling waters. Sarcosine is another important intermediate for glyphosate degradation. It can be detected when glyphosate served as a source of phosphate for microorganisms during phosphate deprivation (Shushkova et al., 2016).

Several review papers have been published on the treatment technologies of glyphosate. Jönsson et al. (2013) and Villamar-Ayala et al. (2019) both reviewed the treatment of glyphosate through using physical treatment processes, biological treatment, and advanced oxidation processes (AOPs) and briefly compared their advantages and disadvantages. However, these review papers not summarised glyphosate degradation pathways. Sviridov et al. (2015) only focused on some metabolic pathways of glyphosate in microorganisms. A comprehensive summary of degradation pathways of glyphosate contained in water by different treatments is not well-reviewed until now. Furthermore, almost no literature has reviewed these glyphosate treatment technologies against their disadvantages. Thus, this paper is expected to offer a comparative assessment of current treatment methods used to remove glyphosate from aqueous environment, considering benefits and limits, as well as degradation pathways and mechanisms. Meanwhile, this review will focus on the potential improvement of these technics.

## 2. Treatment technologies for glyphosate-containing wastewater

Conventional methods, such as adsorption or biological treatments, have been applied to treat glyphosate-containing wastewater. Advanced oxidation processes (AOPs) have also been proposed as alternative treatment technologies for glyphosate-containing wastewater. All these treatment technologies are described below.

### 2.1. Adsorption

Adsorption is widely used in large-scale biochemical and purification for wastewater treatment due to simple design, non-toxic, low-cost adsorbents, and high efficiency. Removal of glyphosate from aqueous environment by adsorption has been studied for several decades. Table 1 summarised different studies on this subject. Several materials have been used as adsorbents to remove glyphosate from synthetic wastewater or simulated real wastewater under different conditions, such as clay substances, activated carbon, biochar, industrial residual, resins, etc.

Synthesised clay substances, such as hydrotalcites, have a low glyphosate maximum adsorption capacity of 0.004 mg.g<sup>-1</sup> at a concentration less than 25 mg.L<sup>-1</sup> (Villa et al., 1999). However, layered double hydroxides (LDH), known as hydrotalcite-like anionic clays substances, such as MgAl-layered double hydroxides, presented better performance for glyphosate adsorption than hydrotalcites with glyphosate maximum adsorption capacity up to 184.5 mg.g<sup>-1</sup>, due to its relatively large surface areas and high charge density. However, this process is usually considered as ineffective in practice, due to the existence of competition for adsorption sites between glyphosate and the original anions of wastewater, such as Cl<sup>-</sup> (Li et al., 2005).

**Table 1**  
Removal of glyphosate from synthetic wastewater by adsorption.

Reference	Adsorbent	Conditions	Glyphosate (mg.L <sup>-1</sup> )	Adsorption capacity (mg.g <sup>-1</sup> )	Adsorption mechanisms
Clays (Villa et al., 1999) (Li et al., 2005)	Hydrotalcites MgAl-layered	20 °C 25 °C; 24 h; pH: 5.6–13.1	5–25 0–608	0.001–0.004 27.4–184.5	Coordination bonds External surface adsorption and interlayer anion exchange
Activated carbon (Nourouzi et al., 2010) (Salman et al., 2012)	From waste newspaper From palm oil fronds	28 °C; 3 d; pH:2.0–9.0 30 °C; 22 h; pH:2.0–12.0	5–100 25–250	48.4 104	– External surface adsorption and electrostatic attraction
Biochar (Herath et al., 2016) (Mayakaduwa et al., 2016) (Jia et al., 2020) (Hu et al., 2011)	From rice husk From woody Nano-CuFe <sub>2</sub> O <sub>4</sub> modified Residual from industrial water	20 °C; 3 h; pH:3.0–9.0 20 °C; 4 h; pH:3–8 25 °C; 4 h; pH:4 22 °C; pH:4.3–9.0	0–100 20 50–600 50–500	123.03 44 269.4 From 85.9 to 113.6	Pore diffusion, π-π electron donor-acceptor interaction. π-π electron donor-acceptor interaction. Electrostatic attraction and coordination bonding –
Resin (Chen et al., 2016) (Jia et al., 2017) (Xiao and Meng, 2020) (Rissouli et al., 2017)	D301 Supported hydroxyl iron oxide D151 preloaded with Fe <sup>3+</sup> Chitin and chitosan	35–45 °C 20–40 °C; 24 h 10–40 °C; 24 h 18–38 °C; pH: 3.09–9.81	400 500–1100 1–30	400–833 396.8–401.1 481.85 Chitin: 14 Chitosan: 35.08	– Electrostatic attractions Coordination bonding Electrostatic interaction

Activated carbon is mainly used for wastewater purification due to its microporous structure, huge surface area, and high efficiency. However, a limited number of relevant research papers have been reported about activated carbon as an adsorbent to remove glyphosate (Table 1). The high cost of activated carbon materials is still an important problem that limits its practical industrial applications. Recently, waste-derived activated carbon appears as an effective method to decrease the production cost for contaminants adsorption, like glyphosate (Hadi et al., 2015). The adsorption capacity of glyphosate could be achieved up to 48 and 104 mg.g<sup>-1</sup> with activated carbon derived from waste newspaper and palm oil fronds, respectively (Nourouzi et al., 2010; Salman et al., 2012).

Biochar, a universal adsorbent like activated carbon, has drawn more attention because of its low cost and highly aromatic and porous structure, which contributes to the high removal efficiency of biochar. The maximum adsorption capacity of glyphosate of 44 mg.g<sup>-1</sup> was obtained by woody biochar (Mayakaduwa et al., 2016), comparable (48 mg.g<sup>-1</sup>) to that reported by Nourouzi et al. (2010) for activated carbon, while lower than that for husk derived engineered biochar (123 mg.g<sup>-1</sup>) (Herath et al., 2016). Furthermore, the chemical modification method can effectively modify biochar surface properties to obtain high adsorption performance. Jia et al. (2020) found a higher maximum adsorption capacity of glyphosate of 269 mg.g<sup>-1</sup> by nano-CuFe<sub>2</sub>O<sub>4</sub> modified biochar prepared by a coprecipitation method.

Aluminium sludge, an inevitable residual from water treatment using aluminium sulphate as primary coagulant, presents the potential to be reused as an efficient and low-cost adsorbent. Dewatered and liquid aluminium sludges were reported to have a maximum glyphosate adsorption capacity of respectively 86 mg.g<sup>-1</sup> and 113 mg.g<sup>-1</sup>, with the comparable capacity to LDH and activated carbon. Aluminium sludge is economic and available due to its local, easy, and large availability in global scale. However, LDH and activated carbon have to be artificially synthesised or produced (Hu et al., 2011).

Due to unique porous structure and surface chemistry, resin exhibits better adsorption affinity to glyphosate in aqueous solutions compared to other adsorbents, with a maximum adsorption capacity of 833 mg.g<sup>-1</sup> (Chen et al., 2016). However, due to the low selectivity of the

resin when inorganic salts coexist with glyphosate, its application in wastewater treatment is limited. Jia et al. (2017) developed a synthetic double valent iron composite resin to improve selectivity for glyphosate treatment. However, in the presence of phosphate or Cl<sup>-</sup>, a significant decrease of the adsorption capacity of glyphosate onto this adsorbent was also found. Cl<sup>-</sup> could compete with glyphosate anion for the anion exchange sites of resins, which limits its application for real wastewater treatment. This is because, in the mother liquor of glyphosate, Na<sub>2</sub>HPO<sub>3</sub> (1.2–2.6% wt) and NaCl (about 10–20 wt%) co-exist with glyphosate (Xie et al., 2010). In order to solve this disadvantage, Xiao and Meng (2020) applied D151 resin preloaded with Fe<sup>3+</sup> as an adsorbent for glyphosate from synthetic wastewater, in the presence of 16% NaCl. They found that NaCl exhibited no significant effect on glyphosate adsorption with the maximum adsorption capacity of 481.8 mg.g<sup>-1</sup>. It is much higher than that of other reported adsorbents in the presence of Cl<sup>-</sup>.

Biopolymers, such as chitin and chitosan, are cheap and eco-friendly adsorbents for glyphosate at low concentration with excellent regeneration performance (Rissouli et al., 2017). However, they have lower adsorption capacity compared to layered double hydroxides, activated carbons, biochars, and resins. It will be interesting to improve its performance in further works before applying it in practice.

The pH is one of the most important factors that affect glyphosate adsorption process, through modifications of the surface charge of the adsorbents and the degree of ionisation and speciation of the adsorbate. It can be observed that glyphosate presents amphoteric characteristics with its carboxyl, phosphonate, and amine groups and negatively charged at higher pH. Acidic condition was reported to be more favourable to glyphosate adsorption by different adsorbents. Furthermore, it is reported that when the pH value of solute is below the point of zero charge, the adsorbents become positively charged and glyphosate is negatively charged. Then the adsorption of glyphosate increases with the pH due to the enhancement of electrostatic forces between adsorbents and glyphosate. However, when the pH value of the solute is above the point of zero charge, the adsorption of glyphosate decreases with the pH of the solution due to the repulsive force between adsorbents and glyphosate (Herath et al., 2016; Nourouzi et al., 2010).

Multiple mechanisms have been proposed to control glyphosate adsorption by different adsorbents. It is suggested that coordination bonds, external surface adsorption, and interlayer anion exchange exist in clay substance. External surface adsorption and electrostatic attraction are involved in activated carbon. Electrostatic attractions and coordination bonding predominate in resins. Compared to other adsorbents, biochar has the most complex mechanisms for glyphosate adsorption, including pore diffusion,  $\pi$ - $\pi$  electron donor-acceptor interaction, H-bonding, electrostatic attraction, and coordination bonding. Although glyphosate has been effectively removed by different adsorbents, the mechanism is still unclear, which needed to be further studied. Moreover, to quantify the individual contributions of these mechanisms is a challenging task (Li et al., 2005; Villa et al., 1999).

To conclude, adsorption is an efficient method for glyphosate treatment. However, some drawbacks exist, which limits its practical application for real wastewater. The requirement of the acidic condition is a major drawback as it is not recommended to change dramatically the pH of wastewater which is not compatible with release to the environment. The other point is that no adsorbent is selective with respect to glyphosate. This is also a major drawback, as wastewater contains many other pollutants, many of them at higher concentrations than glyphosate. Even if the affinity of glyphosate with some of the adsorbents is quite good, it seems difficult to use this technology as a primary treatment, except to decrease large initial concentrations of glyphosate if other pollutant concentrations are not very high. It is probably recommended to use adsorption as a possible secondary treatment when all pollutants concentration has decreased. Finally, the disposal of the residue after adsorption remains a problem which also needs further research.

## 2.2. Biological treatment

Biodegradation of organic compounds is known as an efficient and eco-friendly method to remove organic pollutants from the aqueous environment. In biodegradation process microorganisms metabolism results in the breaking down of glyphosate into smaller molecules. Enzymatic reactions involved in these processes generally lead to harmless molecules. Literature shows that high glyphosate removal could be obtained by biodegradation process under a wide range of glyphosate concentrations (Table 2). However, biological treatment could not achieve high mineralization efficiency because of the generation of by-products such as AMPA or sarcosine. Furthermore, this process requires long residence time and suitable microorganisms' growth conditions to achieve high removal efficiency. The reported glyphosate-degrading strains are usually isolated from glyphosate-contaminated sources (soils, wastewater, etc) or selected from laboratory collections.

Considering glyphosate-degrading microorganisms, bacteria have been more studied than fungi. This can be explained by the fact that the C-P lyase enzyme systems for glyphosate biodegradation are widespread among bacteria (Hove-Jensen et al., 2014). The most commonly isolated bacteria for glyphosate biodegradation are *Pseudomonas* spp. (Manogaran et al., 2017). Most of reported species use glyphosate as the sole phosphorus source. Few exceptions use glyphosate as nitrogen or carbon source. In the common process, microorganisms are cultivated in carbon, nitrogen and phosphate free media containing glyphosate. The induction of glyphosate metabolic enzyme system increases their glyphosate utilization efficiency. It is reported that glyphosate serves as a better phosphorous source for microorganisms than as a carbon source (Moneke et al., 2010). However, during the growth and metabolism process of microorganisms, the demand for carbon source is much higher than that for nitrogen or phosphorus sources. Thus, microorganisms that can use glyphosate as carbon source could lead to removal processes with higher efficiency. However, improving this process needs to develop further research. Propositions, based on the current state of the art, are made in the following paragraphs.

To assess the glyphosate-degradation performance of microorganisms, it is necessary to optimise the culture conditions, including culture temperature, initial pH, glyphosate concentration, inoculation biomass and incubation time (Zhan et al., 2018). The most used culture conditions are a temperature of 25–37 °C, pH of 6–7.5 and aerobic medium, depending on different microorganisms. Only Obojska et al. (2002) observed a thermophilic bacteria, *Geobacillus caldoxylosilyticus* T20, which could achieve more than 65% of glyphosate removal at 60 °C with initial glyphosate concentration of 169 mg.L<sup>-1</sup>. Kryuchkova et al. (2014) found a facultative anaerobic strain, *Enterobacter cloacae* K7, which could utilize glyphosate as sole phosphorus source and obtain 40% degradation with glyphosate initial concentration of 845 mg.L<sup>-1</sup>. These two examples indicate that glyphosate degradation could be improved.

Two major degradation pathways exist for glyphosate-degrading microorganisms as proposed in Fig. 1 (Zhan et al., 2018). One pathway is the conversion of glyphosate to stoichiometric quantities of AMPA (aminomethylphosphonic acid) and glyoxylate through the cleavage of C-N bond by the glyphosate oxidoreductase, the product of the cloned *gox* gene (Hove-Jensen et al., 2014; Zhan et al., 2018). Glyoxylate usually enters the tricarboxylic acid cycle as a convenient energy substrate for most glyphosate-degrading bacteria (Sviridov et al., 2015). Three pathways are proposed for AMPA: (i) AMPA releases to the environment, and has potential toxicity to the environment (Jacob, 1988; Lerbs et al., 1990); (ii) AMPA is further metabolized to methylamine and phosphate, catalysed by C-P lyase (Jacob, 1988; Pipke et al., 1987; Pipke and Amrhein, 1988); (iii) a phosphatase pathway, i.e. AMPA is first metabolized to phosphonoformaldehyde by transaminase and then transformed to phosphate and formaldehyde for further metabolism by phosphatase (Sviridov et al., 2014). This last pathway is still a hypothesis as none of its enzymes have been isolated nor characterized (Hove-Jensen et al., 2014), which needs further research.

The second degradation pathway is the metabolization of glyphosate to phosphate and sarcosine through the direct cleavage of the C-P bond, catalysed by C-P lyase (Firdous et al., 2017). Phosphate can be further metabolized by other species of the microbial community unable to break down the C-P bond of glyphosate (Sviridov et al., 2012). Sarcosine can be used as growth nutrient (carbon and nitrogen source) for microorganisms and is further metabolized to glycine and formaldehyde by sarcosine-oxidase. Glycine is further metabolized by microorganism and formaldehyde enters the tetrahydrofolate-directed pathway of single-carbon transfers to generate CO<sub>2</sub> and NH<sub>4</sub><sup>+</sup> (Borggaard and Gimsing, 2008). In this case, final products are no more toxic to the environment.

It is reported that under natural conditions and in waste treatment facilities, the main biodegradation pathway is AMPA's one. Sarcosine pathway is the main route observed under isolated conditions (Villamar-Ayala et al., 2019). In the AMPA and sarcosine pathways, C-P lyases have an important role (Sviridov et al., 2012; Tang et al., 2019). C-P lyases commonly exist in microorganisms, however, not all such enzymes can attack glyphosate or AMPA, but specific C-P lyases induced by exposure to glyphosate. The frequency of these two pathways is quite similar when glyphosate is used as a phosphorus source. However, when glyphosate is used as carbon or nitrogen source, the information is limited. Compared to sarcosine, AMPA is less biodegradable. Thus, further efforts should focus on the improvement of AMPA degradation capability of microorganism and/or find new microorganisms which could simultaneously effectively degrade glyphosate and AMPA.

To continue in this research direction, some reports indicate that AMPA and sarcosine pathways simultaneously exist in some bacteria, such as *Bacillus cereus* CB4, *Ochrobacterium anthropic* GPK3, and *Pseudomonas* sp. LBr (Fan et al., 2012; Jacob, 1988; Sviridov et al., 2012). However, this type of research is still rare. Glyphosate biodegradation by microorganisms appears to be regulated by the inorganic phosphorus supply (Hove-Jensen et al., 2014). The AMPA pathways is not generally subjected to inorganic phosphorus concentration. However, glyphosate conversion to sarcosine strongly depends on the concentrations of

**Table 2**  
Glyphosate-degrading microorganisms reported in the literature.

Microorganism	Origin	Source	Culture conditions	Degradation pathway	Comments	References
<b>Bacteria</b>						
<i>Acetobacter</i> sp., <i>P. fluorescens</i>	Glyphosate-contaminated rice field	Carbon or phosphorus	30 °C; aerobic	Not shown	Bacteria could tolerate up to 250 mg.ml <sup>-1</sup> glyphosate	(Moneke et al., 2010)
<i>Bacillus subtilis</i> Bs-15	Rhizospheric soil of a pepper plant		35 °C; pH: 8; aerobic		65% glyphosate removal	(Yu et al., 2015)
<i>Comamonas odontotermitis</i> P2	Glyphosate-contaminated soil in Australia		29.9 °C; pH: 7.4; aerobic		Complete degradation (1.5 g.L <sup>-1</sup> ) within 104 h	(Firdous et al., 2017)
<i>Achromobacter</i> sp. Kg 16	Glyphosate-contaminated soil	Phosphorus	28–30 °C; pH: 6.0–7.5; aerobic	Acetylgllyph-osate	A new pathway of glyphosate utilization: acetylation	(Shushkova et al., 2016)
<i>Achromobacter</i> sp. MPK 7A			28–30 °C; pH: 7; aerobic	Sarcosine	About 60% glyphosate (500 mg. L <sup>-1</sup> ) removal	(Ermakova et al., 2017)
<i>Achromobacter</i> sp. MPS 12A	Alkylphosphonates-contaminated soil		28 °C; pH: 6.5–7.5; aerobic	Sarcosine	Glyphosate consumption: 124 μmol g <sup>-1</sup> biomass	(Sviridov et al., 2012)
<i>Agrobacterium radiobacter</i>	Sludge from waste treatment plant		30 °C; pH: 7; aerobic	Sarcosine	No data for glyphosate removal efficiency	(Wackett et al., 1987)
<i>Alcaligenes</i> sp. GL	Non-axenic cultures of <i>Anacystis nidulans</i>		28 °C; pH: 7.5; aerobic	Sarcosine	50–80% glyphosate (5 mM) removal	(Lerbs et al., 1990)
<i>Arthrobacter atrocyaneus</i> ATCC 13752	Collection of microorganisms and cell cultures, Germany		Room temp.; pH: 7.2; aerobic	AMPA	Capable of degrading glyphosate without previous culture selection	(Pipke and Amrhein, 1988)
<i>Arthrobacter</i> sp. GLP-1	Mixture culture with <i>Klebsiella pneumoniae</i>	Phosphorus	Room temp.; pH: 7; aerobic	Sarcosine	Capable of degrading glyphosate without previous culture selection	(Pipke et al., 1987)
<i>Bacillus cereus</i> CB4	Glyphosate-contaminated soil		35 °C; pH: 6; aerobic	AMPA and sarcosine	94% degradation (6 g.L <sup>-1</sup> ) in 5 days	(Fan et al., 2012)
<i>Bacillus cereus</i> 6 P	Glyphosate-exposed orange plantation site		28 °C; pH: 7; aerobic	Not shown	38% glyphosate (1 mM) removal	(Acosta-Cortés et al., 2019)
<i>Burkholderia vietnamiensis</i> AO5–12 and <i>Burkholderia</i> sp. AO5–13	Glyphosate contaminated sites in Malaysia		30 °C; pH: 6; aerobic	Not shown	91% and 74% glyphosate (50 mg. L <sup>-1</sup> ) degradation for AQ5–12 and AQ5–13, respectively	(Manogaran et al., 2017)
<i>Enterobacter cloacae</i> K7	Rhizoplane of various plants in Russia		30–37 °C; pH: 6.8–7; Facultative anaerobic	Sarcosine	40% glyphosate (5 mM) degradation	(Kryuchkova et al., 2014)
<i>Flavobacterium</i> sp. GD1	Monsanto activated sludge		25 °C; pH: 6.8–7; aerobic	AMPA	Complete degradation of glyphosate (0.02%)	(Balthazor and Hallas, 1986)
<i>Geobacillus caldxylosilyticus</i> T20	Central heating system water		60 °C; pH: 7; aerobic	AMPA	>65% glyphosate (1 mM) removal	(Obojska et al., 2002)
<i>Ochrobacterium anthropic</i> GPK3	Glyphosate-contaminated soil		28 °C; pH: 6.5–7.5; aerobic	AMPA and sarcosine	Glyphosate consumption: 284 μmol g <sup>-1</sup> biomass	(Sviridov et al., 2012)
<i>Ochrobactrum</i> sp. GDOS	Soil		30 °C; pH: 7; aerobic	AMPA	Complete degradation (3 mM) within 60 h	(Hadi et al., 2013)
<i>Pseudomonas pseudomallei</i> 22	Soil		28 °C; aerobic	AMPA (putative)	50% glyphosate (170 mg.L <sup>-1</sup> ) degradation in 40 h	(Peñaloza-Vazquez et al., 1995)
<i>Pseudomonas</i> sp. 4ASW	Glyphosate-contaminated soil		29 °C; pH: 7.2; aerobic	Sarcosine	100% glyphosate (0.25 mM) removal	(Dick and Quinn, 1995)
<i>Pseudomonas</i> sp. GLC11	Mutant of <i>Pseudomonas</i> sp. PAO1 on selective medium	Phosphorus	37 °C; pH: 7; aerobic	Sarcosine	Capable of tolerating up to 125 mM glyphosate	(Selvapandiyam and Bhatnagar, 1994)
<i>Pseudomonas</i> sp. LBr	A glyphosate process waste stream		Room temp.; pH: 7; aerobic	AMPA and sarcosine	Capable of eliminating 20 mM glyphosate from growth medium	(Jacob, 1988)
<i>Pseudomonas</i> sp. PG2982	<i>Pseudomonas aeruginosa</i> -ATCC 9027		Room temp.; aerobic	Sarcosine	No data for glyphosate removal efficiency	(Kishore and Jacob, 1987)
<i>Rhizobiaeae meliloti</i> 1021	Spontaneous mutation of a wild-type strain		28–32 °C; pH: 7; aerobic	Sarcosine	50% glyphosate (0.5 mM) removal	(Liu et al., 1991)
<i>Achromobacter</i> sp. LW9	Activated sludge from glyphosate process waste stream	Carbon	28 °C; pH: 7; aerobic	AMPA	100% glyphosate (0.1%, w/v) transformation to AMPA	(McAuliffe et al., 1990)
<i>Bacillus subtilis</i> , <i>Rhizobium leguminosarum</i> , <i>Streptomyces</i> sp.	Soils		35 °C; pH: 6	AMPA and sarcosine	About 87% glyphosate (250 mg. L <sup>-1</sup> ) degradation	(Singh et al., 2019)
<i>Ochrobactrum intermedium</i> Sq20	Glyphosate-contaminated soil		Room temp.; pH 7; aerobic	Sarcosine	Complete degradation (500 mg. L <sup>-1</sup> ) within 4 d	(Firdous et al., 2018)
<i>Pseudomonas</i> spp. strains GA07, GA09 and GC04	Glyphosate-contaminated soil in China		33 °C; pH: 7; aerobic	AMPA and sarcosine	Glyphosate (500 mg.L <sup>-1</sup> ) removal: 54%–81%	(Zhao et al., 2015)
<i>Salinicoccus</i> spp.	Qom Hoze-Soltan Lake in Iran		Salt conc.: 5%–10%; 30 °C; pH: 6.5–8.2; aerobic	Not shown	The native halophilic isolates could biodegrade glyphosate	(Sharifi et al., 2015)
<i>Streptomyces</i> sp. StC	Activated sludge from a municipal sewage treatment plant	Phosphorus, and/or nitrogen	28 °C; pH: 7.2; aerobic	Sarcosine	60% degradation (10 mM) within 10 d	(Obojska et al., 1999)
<b>Fungi</b>						

(continued on next page)

**Table 2** (continued)

Microorganism	Origin	Source	Culture conditions	Degradation pathway	Comments	References
<i>Aspergillus niger</i> , <i>Scopulariopsis</i> sp., <i>Trichoderma harzianum</i>	Soil	Phosphorus	28 °C; pH: 6; aerobic	AMPA	No data for removal efficiency	(Krzyśko-Lupicka et al., 1997)
<i>Fusarium oxysporum</i>	Sugar cane		30 °C; pH: 6; aerobic	Not shown	41% glyphosate (50 mg.L <sup>-1</sup> ) removal	(Castro et al., 2007)
<i>Penicillium notanum</i>	Spontaneous growth on hydroxyfluorenyl-9-phosphate	Phosphorus	28 °C; pH: 7.2; aerobic	AMPA	Capable to degrade glyphosate at sublethal doses (<0.5 mM)	(Bujacz et al., 1995)
<i>Aspergillus oryzae</i> sp. A-F02	Sludge from a glyphosate manufacture	Carbon	30 °C; pH: 7.5; aerobic	Not shown	87% degradation (1000 mg.L <sup>-1</sup> ) within 7 d	(Wu et al., 2010)
<i>Penicillium chrysogenum</i>	Soil	Nitrogen	Dark at 28 °C; pH:7.0; aerobic	AMPA (putatively)	40% degradation (5 mM) after 15 d	(Klimek et al., 2001)

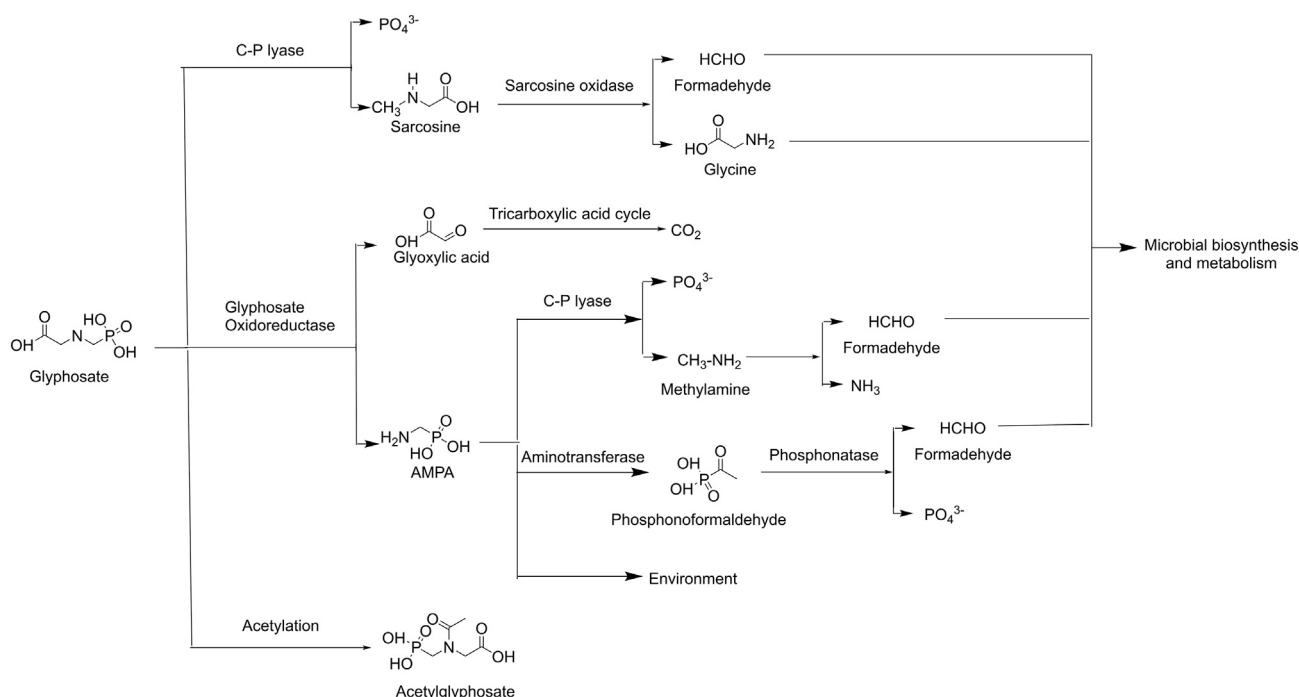
exogenous and endogenous inorganic phosphorus, which rarely occurs in natural environments (Sviridov et al., 2015). Borggaard and Gimsing (2008) explained that it is possible because C-P lyase activity which is commonly encoded by the *phn* or *htx* operon, generally induced under phosphate starvation conditions. However, the mechanism for this phenomenon is still unclear.

Actually, another degradation pathway was observed in *Achromobacter* sp. Kg16 which utilized glyphosate as sole phosphorus source, resulting in the production of acetylgliphosate (Shushkova et al., 2016). The physiological role of this pathway remains unknown. Moreover, acetylgliphosate cannot be utilized by *Achromobacter* sp. Kg16 as a phosphorus source, resulting in its poor growth. Although glyphosate biodegradation has been extensively studied, the accurate degradation mechanism and pathways are still not known.

Most reported studies have focused on the glyphosate biodegradation by pure culture of bacteria. Little research on glyphosate biodegradation was carried on mixed culture. Hallas and Adams (1992) reported glyphosate removal from wastewater effluent discharged from an activated sludge process in lab columns and found that more than 90% of glyphosate degradation was achieved for an initial concentration of

50 mg.L<sup>-1</sup>. Nourouzi et al. (2010) reported that 99.5% of glyphosate (300 mg.L<sup>-1</sup>) was converted to AMPA and 2% of AMPA was degraded into further metabolites by mixed bacteria isolated from oil palm plantation soil. The mixed cultures are more likely able to completely degrade contaminants, compared to pure culture due to the various enzymes available in mixed culture (Barbeau et al., 1997; Nourouzi et al., 2012). Moreover, due to the high requirements of pure culture, mixed culture processes are more suitable for industrial applications. Thus, it is interesting for further research to find the mixed culture which is effective to remove glyphosate from aqueous effluents.

To provide practical information for the design of processes, it is necessary to study the microbial degradation kinetics. Monod model is widely used in case of pure cultures, limited substrate, and non-inhibitory biomass growth (de Lucas et al., 2005; Singh et al., 2008; Tanyolaç and Beyenal, 1998). Due to substrate inhibition at high substrate concentrations, Monod model must be extended to Haldane model. Monod model could predict the kinetic of glyphosate consumption by mixed culture isolated from soils at high concentration (>500 mg.L<sup>-1</sup>) with the maximum specific cell growth rate ( $\mu_m$ ) of 0.18–0.87 h<sup>-1</sup>. Haldane model could predict the growth inhibition



**Fig. 1.** Biodegradation pathways of glyphosate in bacteria (Zhan et al., 2018).

kinetic of glyphosate with a low ratio of self-inhibition and half-saturation constants ( $<8$ ) (Nourouzi et al., 2012). A low ratio of self-inhibition and half-saturation constants (1.21) was also obtained to predict glyphosate growth inhibition kinetic by unacclimated activated sludge (Tazdaït et al., 2018). Besides, a first-order kinetic model is also used to evaluate biodegradation process to obtain degradation rate constant ( $k$ ) and half-life ( $t_{1/2}$ ).  $k$  and  $t_{1/2}$  with the range of 0.0018–0.0464  $\text{h}^{-1}$  and 14.9–385.7 h, respectively, were found for glyphosate biodegradation by pure culture, such as *Pseudomonas* spp. GA07, GA09 and GC04 (Zhao et al., 2015), *Ochrobactrum intermedium* Sq20 (Firdous et al., 2018), and *Bacillus cereus* 6 P (Acosta-Cortés et al., 2019). In addition, la Cecilia et al. (2018) reported glyphosate biodegradation in a vineyard and a wheat field in the Po Valley (Italy) with  $t_{1/2}$  of 84 and 157 d, respectively. However, almost no information is reported on the yield coefficient for glyphosate-degrading bacteria, which needs to be further studied. Although the biodegradation of glyphosate has been extensively studied, the information on glyphosate biodegradation kinetics, especially on the inhibitory effect, is still rarely studied. The inhibitory effect of herbicide on its own biodegradation is necessary to investigate, since the assessment of substrate inhibition to enzymatic reactions is becoming increasingly crucial in the treatment of general toxic compounds, particularly for pesticides degradation (Hao et al., 2002; Tazdaït et al., 2018).

Nevertheless, biological treatment is a promising method to treat glyphosate-containing wastewater, most research being conducted at lab-scale and focused on the isolation and identification of strains. The information to apply this technology to treat glyphosate-containing wastewater at an industrial scale is still rare. Furthermore, in order to know the precise pathways of glyphosate biodegradation, the research related to the structure of all of the intermediates and enzymes involved in glyphosate biodegradation, as well as procedures for chemical synthesis or isolation of these intermediates and enzymes should be investigated in the near future. This approach should be developed, as some bacteria can, specifically or not, use glyphosate as phosphorus or carbon source. It must be noticed that for bacteria degradation leading mainly to AMPA, this secondary compound is usually not well degraded. It seems probably necessary to achieve biological treatment in combination with another process treatment, to obtain a high degradation not only of glyphosate but also of its by-products.

### 2.3. Advanced oxidation processes (AOPs)

Table 3 summarizes AOPs tested for the treatment of glyphosate-containing wastewater. First, this table shows that photolysis-based oxidation can lead to high glyphosate and TOC removal efficiency up to 99.8% and 92%, respectively, at low concentration (less than 50  $\text{mg} \cdot \text{L}^{-1}$ ) from synthetic glyphosate wastewater. Moreover, the use of photocatalyst improves the photodegradation of glyphosate. Several parameters could affect the efficiency, such as illumination time, pH, type of photocatalyst. Chen and Liu (2007) found that the photodegradation efficiency of glyphosate increased with the increase of illumination time. Yang et al. (2018) reported that with the increase of pH from 3 to 9, the photo-degradation of glyphosate in goethite/UV and magnetite/UV systems both decreased, indicating that an acidic condition is favourable for glyphosate photo-degradation.  $\text{TiO}_2$  is a heterogeneous photocatalyst commonly used for glyphosate removal because of its stability, non-toxicity, and low cost. It is generally governed by both adsorption and photocatalytic reactions (Echavia et al., 2009). However, due to the  $\text{TiO}_2$  band-gap of 3.2eV, only 4% of the solar radiation can be utilized and the recombination of the photogenerated electron-hole pairs takes place quickly on a time scale of  $10^{-9}$  to  $10^{-12}$  s (Lin et al., 2012). These drawbacks limited its practical application. To improve its photocatalytic activity and inhibit the recombination of the photogenerated electron and hole, several attempts have been reported, such as non-metal doping (Echavia et al., 2009), metal doping (Xue et al., 2011) and metal/non-metal co-doping (Lin et al., 2012). Although

complete glyphosate removal has been achieved, mineralization efficiency is not high (less than 74%). Recently, bismuth tungstate ( $\text{Bi}_2\text{WO}_6$ ) has attracted more and more attention for photodegradation of organic contaminants due to its stability, chemical inertness, and good photocatalytic activity. However, the combined probability of photogenerated electrons and holes limits its photocatalytic activity. Lv et al. (2020) synthesised a novel hierarchical  $\text{CuS}/\text{Bi}_2\text{WO}_6$  p-n junction photocatalyst to improve its photocatalytic activity and obtained the highest glyphosate degradation of 85% for 3 h under 44 W light-emitting diode (LED) light irradiation. However, its production is complex and costly. In order to overcome the cost of photocatalyst production, the combination of hydroperoxide and UV radiation ( $\text{H}_2\text{O}_2/\text{UV}$ ) has been reported to treat glyphosate at higher concentrations (up to 90  $\text{mg} \cdot \text{L}^{-1}$ ). This process is quite simple and convenient (López et al., 2018; Manassero et al., 2010; Vidal et al., 2015). During  $\text{H}_2\text{O}_2/\text{UV}$  process, the  $\text{H}_2\text{O}_2$  concentration is an important parameter. When the  $\text{H}_2\text{O}_2$  concentration is too small, the initial step of  $\text{H}_2\text{O}_2$  decomposition is not fast due to its weak absorption coefficient. However, when the  $\text{H}_2\text{O}_2$  concentration is too high, it becomes a scavenger of hydroxyl radicals competing with glyphosate degradation reaction, resulting in a decrease of glyphosate reaction rate (Junges et al., 2013). Therefore, the optimum concentration of  $\text{H}_2\text{O}_2$  in the  $\text{H}_2\text{O}_2/\text{UV}$  process is necessary to be determined experimentally.  $\text{H}_2\text{O}_2/\text{UV}$  process induced a good degradation of glyphosate ( $>70\%$ ), but it requires a long treatment time (more than 5 h). Meanwhile, due to the high cost of electricity associated with using energy-consuming UV lamps (Echavia et al., 2009) and the low penetration of UV in the water body hamper the development of these photolysis-based processes at large scale application (Tran et al., 2017; Zhan et al., 2018). For the future work, the reuse of catalysts and the decrease of its cost production, the improvement of mineralization efficiency and the reduction of reaction time should be investigated.

Fenton oxidation has been reported to be a successful technology for glyphosate treatment. It has the advantages of simple operation, no mass transfer limitation, and easy implementation as a stand-alone or hybrid system (Bokare and Choi, 2014; Chen et al., 2007). 96% and 63% removal of total phosphate and chemical oxygen demand (COD), respectively, have been achieved by the conventional Fenton process (Liao et al., 2009). However, several drawbacks exist in the conventional Fenton process: the continuous loss of oxidants and iron ions, the formation of solid sludge and the high costs and risks associated with handling, transportation, and storage of reagents (Zhang et al., 2019). In order to overcome these shortcomings, combination coupling are proposed, i.e. electro-Fenton and photo-Fenton processes. They have both been reported to achieve complete glyphosate removal and good mineralization at low concentrations (Balci et al., 2009; Souza et al., 2013). Electro-Fenton process overcomes the limitations of the accumulation of iron sludge, the high costs and risks. It is reported that 91.9% glyphosate removal and 81.6% TOC removal have been achieved by electro-Fenton oxidation through using a carbon fibre cathode (Tran et al., 2019). However, this process consumes extensive anode. Photo-Fenton process can reduce iron sludge production. Souza et al. (2013) reported that under optimised conditions (pH 2.8, 0.27  $\text{mmol} \cdot \text{L}^{-1}$   $\text{Fe}^{2+}/\text{Fe}^{3+}$ , 10.3  $\text{mmol} \cdot \text{L}^{-1}$   $\text{H}_2\text{O}_2$  and 1.13  $\text{mmol} \cdot \text{L}^{-1}$  oxalate), complete glyphosate removal and 74% TOC have been obtained by photo-Fenton process. But it faces several challenges, such as short working life span, high energy consumption and economic costs (Aramyan, 2017; Zhang et al., 2019). Moreover, Fenton based process needs an acidic reaction condition (pH at 2–4), which, as mentioned before, is not convenient to treat high quantities of wastewater. Thus, Fenton-based processes are generally used in a synthetic and low concentration glyphosate wastewater rather than real wastewater from the glyphosate production. Meanwhile, to obtain high mineralization efficiency, an excess of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  is needed. Thus, for an actual application, a post-treatment of the effluent would be necessary to treat the excess iron. Furthermore, the following questions remain to be further



**Table 3**  
AOPs reported to be used for glyphosate treatment.

Reference	AOPs type	Wastewater <sup>a</sup>	Conditions	Glyphosate conc. (mg.L <sup>-1</sup> )	Remarks <sup>b</sup>
(Chen et al., 2007)	Photo degradation	S	T: 22 °C; pH: 3.5–6; illumination time: 3 h; presence of Fe <sup>3+</sup> and C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	5.0	$\eta_G = 63\%$
(Chen and Liu, 2007)	Photocatalytic degradation;	S	T: 30 °C; pH: 2–12; illumination time: 0.5–3.5 h	0.042	$\eta_G = 92\%$
(Assalin et al., 2009)	Catalyst: TiO <sub>2</sub>		illumination time: 0.5 h	42	$\eta_{\text{TOC}} = 92\%$
(Echavia et al., 2009)			T: 22 °C; illumination time: 2 h	17	$\eta_G = 100\%$ ; $\eta_{\text{TOC}} = 74\%$
(Xue et al., 2011)			pH: 7; illumination time: 1 h	23	$\eta_G = 76\%$
(Lin et al., 2012)			illumination time: 1.3 h	50	$\eta_G = 99.8\%$
(Yang et al., 2018)	Photocatalytic degradation	S	Catalyst: Goethite or magnetite; T: 20 °C; pH: 3–9; illumination time: 2 h	10	$\eta_G = \text{from } 92\% \text{ to } 99\%$
(Lv et al., 2020)			Catalyst: hierarchical CuS/Bi <sub>2</sub> WO <sub>6</sub> p-n junction photocatalyst; illumination time: 3 h	16.9	$\eta_G = 85.9\%$
(Manassero et al., 2010)	H <sub>2</sub> O <sub>2</sub> /UV	S	T: 25 °C; pH: 3.5–10; illumination time: 5 h	27–91	$\eta_G = 70\%$ ; $\eta_{\text{TOC}} = 29\%$
(Junges et al., 2013)			T: 20 °C; pH: 5.2; illumination time: 2–6 h	50	$\eta_G = 90\%$ ; $\eta_{\text{TOC}} = 70\%$
(Vidal et al., 2015)			T: 25 °C; pH: 5.2; reaction time: 12 h	30–73	$\eta_G = 80\%$ ; $\eta_{\text{TOC}} = 70\%$
(López et al., 2018)			T: 25 °C; pH: 3–10; reaction time: 8 h	30	$\eta_G = 71\%$
(Liao et al., 2009)	Fenton	R	T: 90 °C; pH: 3–4; reaction time: 2 h; $n(\text{H}_2\text{O}_2)/n(\text{Fe}^{2+}) = 4:1$	–	$\eta_G = 96\%$ ; $\eta_{\text{COD}} = 63\%$
(Zhang et al., 2011)	Adsorption-Fenton		Adsorbent: nano-tungsten/D201 resin; pH: 2–4	258	$\eta_G = 60\%$
(Balci et al., 2009)	Electro-Fenton	S	Mn <sup>2+</sup> as catalyst; T: 23; pH: 3; anode: Pt cylindrical mesh; cathode: carbon felt; electrolyte: 0.05 M Na <sub>2</sub> SO <sub>4</sub>	17	$\eta_{\text{TOC}} = 82\%$
(Lan et al., 2016)			20 °C; pH 3–6; anode: RuO <sub>2</sub> /Ti mesh; cathode: activated carbon fibres; electrolyte: 0.1 M Na <sub>2</sub> SO <sub>4</sub>	17–253	$\eta_G = 85\%$ ; $\eta_{\text{COD}} = 72\%$
(Tran et al., 2019)			room temperature; pH 2–6; anode: Pt gauze; cathode: carbon felt; electrolyte: 0.01 M Na <sub>2</sub> SO <sub>4</sub>	8.5–67.6	$\eta_G = 91.9\%$ ; $\eta_{\text{TOC}} = 81.6$
(Huston and Pignatello, 1999)	Photo-Fenton	S	T: 25 °C; pH: 2.8; reaction time: 2 h; H <sub>2</sub> O <sub>2</sub> : 0.01 M; Fe <sup>3+</sup> : 5.0 × 10 <sup>-5</sup> M; UV irradiation: 300–400 nm	0.034	$\eta_{\text{TOC}} = 35\%$
(Souza et al., 2013)			T: 40 ± 2 °C; pH 2.8 ± 0.2; reaction time: 2 h; H <sub>2</sub> O <sub>2</sub> : 10.3 M; Fe <sup>2+</sup> /Fe <sup>3+</sup> : 0.27 M; UV irradiation: 320–400 nm	100	$\eta_G = 100\%$ ; $\eta_{\text{TOC}} = 74\%$
(Aquino Neto and de Andrade, 2009)	Electrochemical oxidation	S	Anode: RuO <sub>2</sub> and IrO <sub>2</sub> DSA®; T: 25 ± 1 °C; pH: 3; current density: 50 mA cm <sup>-2</sup> ; electrolyte: NaCl	1000	$\eta_{\text{COD}} = 91\%$
(Lan et al., 2013)			Anode: RuO <sub>2</sub> and IrO <sub>2</sub> DSA®; room temperature; pH: 5.0; current density: 10 mA.cm <sup>-2</sup> ; MnO <sub>2</sub> dosage: 0.25 mM; reaction time: 2 h; electrolyte: Na <sub>2</sub> SO <sub>4</sub>	17	$\eta_G = 40\%$ and 80% for electrochemical and electro-MnO <sub>2</sub> process
(Kukurina et al., 2014)			Anode: PbO <sub>2</sub> ; room temperature; current density: 0.12 A.cm <sup>-2</sup> ; reaction time: 4 h; electrolyte: H <sub>2</sub> SO <sub>4</sub>	17	$\eta_G = 100\%$
(Rubí-Juárez et al., 2016)			Anode: Born doped diamond (BDD); 20 °C; current density: 10–100 mA.cm <sup>-2</sup>	100	$\eta_G = 100\%$ in NaCl media
(Farinos and Ruotolo, 2017)			Anode: PbO <sub>2</sub> and BDD; T: 30 °C; current density: 30 mA.cm <sup>-2</sup> ; reaction time: 8 h	150	$\eta_{\text{TOC}} = 95\%$
(Tran et al., 2017)			Anode: Ti/PbO <sub>2</sub> ; pH: 3–10; current intensity: 4.55–90.9 mA.cm <sup>-2</sup> ; reaction time: 6 h; electrolyte: Na <sub>2</sub> SO <sub>4</sub>	4.3–33.8	$\eta_G = 95.5\%$
(Speth, 1993)	O <sub>3</sub>	S	Gas flowrate: 0.62 L.min <sup>-1</sup> ; O <sub>3</sub> : 1.0–2.9 mg.L <sup>-1</sup>	0.8–1	$\eta_G = 100\%$
(Assalin et al., 2009)			O <sub>3</sub> : 14 mg.L <sup>-1</sup> ; pH: 6.5 and 10; reaction time: 0.5 h	42.2	$\eta_{\text{TOC}} = 97.5$
(Jönsson et al., 2013)	O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>		T: 15 °C; O <sub>3</sub> : 0.5–1.0 mg.L <sup>-1</sup> ; H <sub>2</sub> O <sub>2</sub> : 0.5 and 1.0 mg.L <sup>-1</sup>	0.00259–0.00365	$\eta_G = 99\%$
(Tan et al., 2019)			Room temperature; O <sub>3</sub> : 48.72 mg.L <sup>-1</sup> ; pH: 9.0	100	$\eta_{\text{TOC}} = 68.3\%$

<sup>a</sup> S means “Synthetic glyphosate wastewater” and R “Real wastewater containing glyphosate”.

<sup>b</sup>  $\eta_G$ : glyphosate conversion;  $\eta_{\text{TOC}}$ : TOC conversion;  $\eta_{\text{COD}}$ : COD conversion.

investigated: the regeneration and recycling of Fe<sup>2+</sup> process and the reduction of the sludge.

Electrochemical oxidation is one of the cleanest technologies to effectively degrade glyphosate compared to other AOPs. It offers high energy efficiency without the addition of chemicals. It has been reported to treat effluents with glyphosate concentration ranging from 17 to 1000 mg.L<sup>-1</sup> and complete glyphosate mineralization has been

achieved at glyphosate concentration less than 100 mg.L<sup>-1</sup>. High mineralization (91%) was also obtained with concentrations up to 1000 mg.L<sup>-1</sup> on PuO<sub>2</sub> and IrO<sub>2</sub> dimensionally stable anode. PbO<sub>2</sub>, born doped diamond, and Ti/PbO<sub>2</sub> has been also used as anode for electrochemical oxidation of glyphosate (Farinos and Ruotolo, 2017; Kukurina et al., 2014; Rubí-Juárez et al., 2016; Tran et al., 2017). PuO<sub>2</sub> and IrO<sub>2</sub> offer a mechanical resistance and successful scale-up in the

electrochemical industry (Aquino Neto and de Andrade, 2009). Electrochemical degradation could be affected by several parameters: pH, glyphosate initial concentration, supporting electrolyte nature and concentration, electronic composition, electrolysis, and current density. It is reported that the acidic pH is generally more favoured for glyphosate oxidation due to the decrease of the oxygen evolution reaction at low pH values (Aquino Neto and de Andrade, 2009; Farinos and Ruotolo, 2017; Lan et al., 2013). NaCl is the most attractive supporting electrolyte for glyphosate electrochemical oxidation due to the formation of some powerful oxidising species, such as chlorine radical, hypochlorous acid and hypochlorite ion during electrolysis. An increase in current density generally leads to an increase in oxidation of glyphosate (Aquino Neto and de Andrade, 2009; Kukurina et al., 2014; Lan et al., 2013; Rubí-Juárez et al., 2016). However, some drawbacks exist during electrochemical oxidation process: the high costs related to the electrical supply, the addition of electrolytes required due to the low conductance of wastewaters, the loss of activity and the short lifetime of electrode by fouling due to the deposition of organic compounds on the surface of electrode (Sirés et al., 2014). Future research should focus on the reuse of these electrodes by understanding the passivation/reactivation mechanisms and incorporating strategies to apply this technology in water treatment. Furthermore, electrochemical reactions are limited by mass transfer of contaminants to the electrode surface, which could affect its performance (Chaplin, 2018). Thus, it is interesting to find a new device for electrochemical oxidation to reduce mass transfer limitation, such as microfluidic devices. Recently, they have drawn increasing attention for wastewater treatment due to their high mass transfer efficiency, high product yield selectivity, and quite easy to scale up (Pérez et al., 2017; Scialdone et al., 2010, 2011). However, they are currently too expensive for large scale applications. Thus, it is interesting to find a cheaper and effective alternative in the further research.

Compared to other AOPs, ozonation oxidation can effectively treat glyphosate-containing wastewater in the shortest time under low concentration. Two glyphosate oxidation mechanisms are involved in ozonation: direct oxidation by ozone or indirect oxidation by hydroxyl radicals. Complete glyphosate degradation has been obtained by ozonation oxidation (Assalin et al., 2009; Speth, 1993). Both high removal efficiencies of glyphosate (>99%) and AMPA (85%) were achieved with simultaneous use of  $O_3$  and  $H_2O_2$  under a short reaction time (Jönsson et al., 2013). Moreover, in order to reduce the capital and operation costs, Tan et al. (2019) studied the in situ generations of  $H_2O_2$  using multi-walled carbon nanotube aluminium composite in  $O_3/H_2O_2$  process for glyphosate degradation. They obtained a removal efficiency of TOC and total phosphorus of 68.35% and 73.27%, respectively. However, there are several drawbacks for ozonation which hinders its application into practice: (1) ozone is unstable under normal conditions; (2) due to its low solubility in water, special mixing techniques are needed; (3) ozone water treatment is much expensive due to the high service and maintenance; (4) the mass transfer of  $O_3$  limits its performance.

In addition, Barrett and McBride (2005) obtained 71% and 47% of glyphosate and AMPA removal efficiency by manganese oxidation. Feng et al. (2020) applied an autoclave reactor for glyphosate degradation by wet air oxidation with a temperature of 423–523 K and under a total pressure of 15 MPa and obtained maximum glyphosate and TOC removal of 100% and 54%, respectively, at 523 K after 60 min from synthetic wastewater with glyphosate concentration of 1000 mg.L<sup>-1</sup>. Recently, combined processes became potential technologies for organic contaminants treatment, including glyphosate. Several combined processes have been reported for glyphosate removal from wastewater. Zhang et al. (2011) combined adsorption treatment and Fenton oxidation using the nano-metal/resin complexes as the adsorbent to treat the industrial wastewater containing glyphosate. They found that the maximum degradation rate of glyphosate was enhanced by up to 60%. Xing et al. (2018) reported that 100% glyphosate removal and over 93% organic phosphorus removal for real glyphosate wastewater (containing 200–3000 mg.L<sup>-1</sup> glyphosate) was achieved by catalytic wet

oxidation using modified activated carbon as a catalyst in a co-current up flow fixed bed reactor through combining AOPs and adsorption. Recently, among different combined process, combining AOPs and biological treatment is a very promising method for wastewater treatment contaminated by organic pollutants. AOPs as a pre-treatment can convert the initial persistent organic compounds into more biodegradable intermediates, which could subsequently be treated by biological treatment to increase performance and decrease cost (Oller et al., 2011). The combined AOPs-biotreatment technology has been used for the treatment of wastewater containing pesticides or herbicides, textile wastewater, paper mill wastewater, olive mill wastewater, etc., to obtain effectively treatment performance (Oller et al., 2011). Thus, it could be also a potential method for glyphosate-containing wastewater treatment. However, no literature has been reported for glyphosate-containing wastewater treatment through combining AOPs and biological treatment, which can be further studied.

Fig. 2 summarizes the possible oxidation pathways for glyphosate under different AOPs. It shows that, as for biological mechanisms, glyphosate oxidation generally follows two mechanisms related to the cleavage of C-P and C-N bonds attributed to hydroxyl radicals. Glyphosate is attacked by hydroxyl radicals to yield sarcosine and  $PO_4^{3-}$  or AMPA and glycolic acid. The two mechanisms can exist alone or together during glyphosate oxidation process.

The glyphosate photo-degradation is often related to both AMPA and sarcosine pathways. However, only sarcosine pathway for photo-degradation is presented by Yang et al. (2018). This is because the formation of Fe-O-P bond in the presence of iron oxide would change the electron density distribution around the phosphorus centre of glyphosate, and potentially induce the C-P bond more assailable to reactive oxygen species generated in goethite and magnetite suspension under UV irradiation. Furthermore, few studies have shown the direct formation of glycine at high pH without the formation of sarcosine in  $TiO_2/UV$  process (Manassero et al., 2010; Muneer and Boxall, 2008). The mechanism for this phenomenon is still unclear and further research is needed. The single sarcosine pathway is also been reported in the electrochemical and manganese oxidation of glyphosate (Barrett and McBride, 2005; Lan et al., 2013). AMPA pathway is found in electro-Fenton and catalytic wet air oxidation process of glyphosate (Balci et al., 2009; Xing et al., 2018). Assalin et al. (2009) have detected AMPA during glyphosate degradation by ozonation oxidation. Sarcosine could be further oxidized to glycine, formaldehyde, or formic acid. Glycine could be transferred to methylamine, formaldehyde, and  $NH_4^+$  or oxidized to oxalic, glycolic acid and N-contained intermediates which can be further oxidized to acetic acid,  $NH_4^+$  and  $NO_3^-$ . AMPA may be further converted to formaldehyde,  $NH_4^+$ ,  $NO_3^-$  and  $PO_4^{3-}$  through the cleavage of C-P bond. Other small organic compounds may also exist in the glyphosate oxidation processes, such as acetic acid and glycolic acid. Even though the possible oxidation pathways of glyphosate have been abundantly reported, the precise mechanisms are still unknown which is needed further studies due to the complex and various by-products formed during glyphosate oxidation by different AOPs.

Although glyphosate-containing wastewater has been reported to be effectively treated by these above technologies, which are mostly conducted at a lab-scale, detailed studies are necessary to scale-up to an industrial scale. An advantage of these processes is that they can oxidise glyphosate and most of its by-products like AMPA, sarcosine, etc., as well as other polluting molecules. To decrease its cost, it could be interesting to use these technologies after a first process that can decrease the pollution concentration.

### 3. Conclusions and perspectives

Glyphosate, a most extensively used herbicide in the world, could accumulate and transfer in the environment, which could cause potential threats to the environment and human health. This study reviews several treatment technologies for glyphosate in wastewater reported

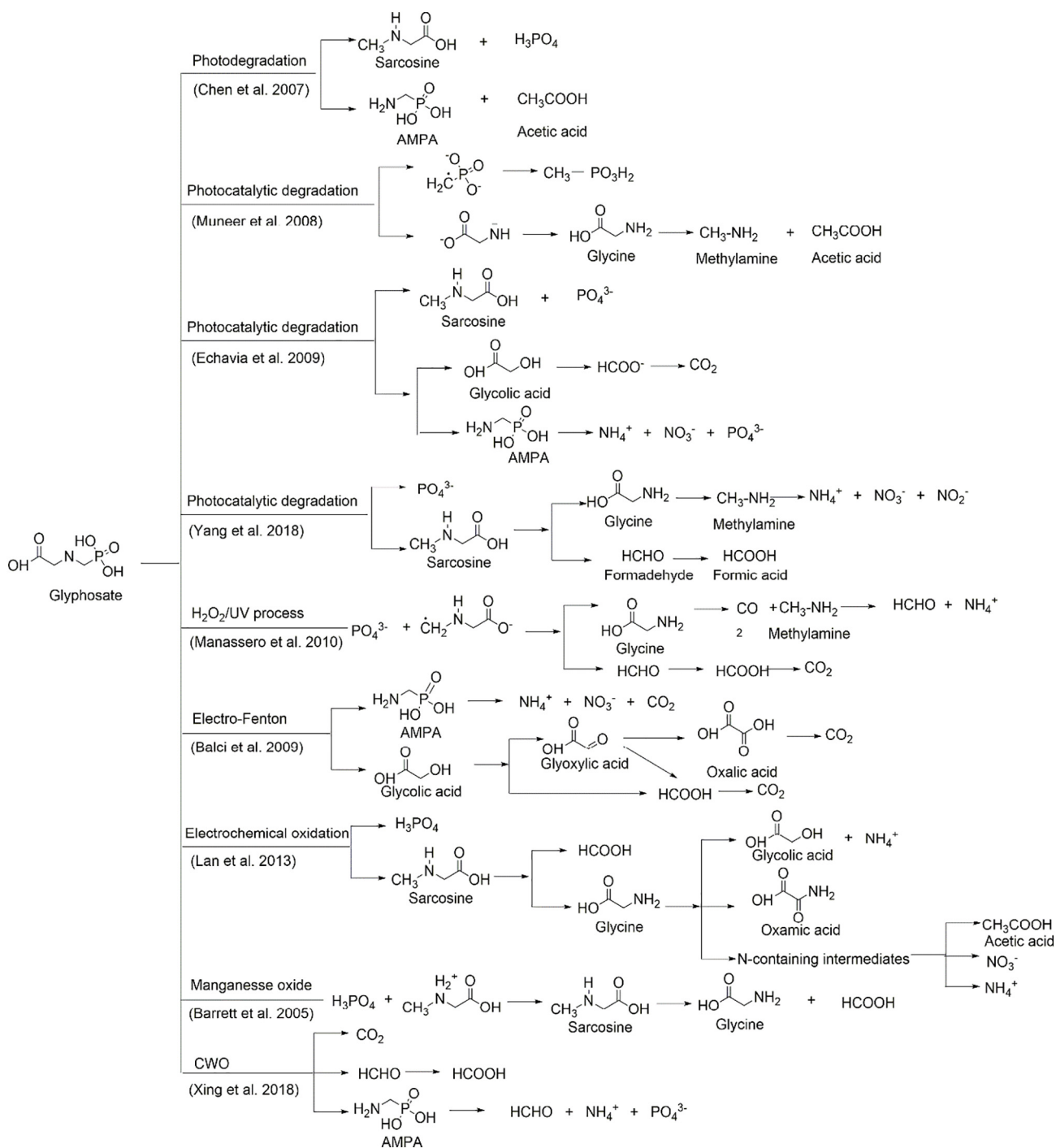


Fig. 2. Potential oxidation pathways of glyphosate under different processes.

in the literature by evaluating their performances and highlighting their advantages, disadvantages, and limitations. A comparative discussion is summarised in Table 4.

Adsorption is a simple technology that could effectively remove glyphosate from wastewater with maximum adsorption capacity up to 833 mg.g<sup>-1</sup>, but it requires post-treatment. Adsorption using biochar or resin is recommended for glyphosate wastewater treatment when just considering glyphosate removal efficiency and low cost, without considering the mineralization efficiency.

Although biological treatment is a low-cost and eco-friendly technology for glyphosate treatment, it is inefficient for real glyphosate

wastewater due to the existence of other constituents which could be toxic to biological treatment. It requires long residence time for complete glyphosate degradation and needs pre-treatment steps to reduce the toxicity of the wastewater. For glyphosate biodegradation, two main degradation pathways exist, i.e. AMPA and sarcosine pathways. Biological treatment is recommended to be used as a post-treatment after other treatment technologies to obtain higher degradation performance.

AOPs techniques (e.g. photolysis-based, Fenton-based, electrochemical, and ozonation oxidation) are effective for glyphosate degradation. They could treat glyphosate with a short time compared to adsorption

**Table 4**  
Summary of main advantages and disadvantages of glyphosate removal techniques.

Removal techniques	Main advantages	Main disadvantages
Adsorption	Simple and easy to operate Cost-effective and low secondary pollution risk High efficiency at low concentration	Difficult to regenerate, recycle and reuse of adsorbents The existence of competition adsorption New solid residue produced for subsequent treatment
Biological treatment	Low cost and eco-friendly Excellent handle in high level of wastewater	Time-consuming Pre-treatment needed to reduce the toxicity of wastewater
Photolysis-based oxidation	Excellent handle in low level of wastewater	Low penetration of UV in the water body Difficult to be commercialised
Fenton-based oxidation	Simple operation No mass transfer limitation High efficiency at low concentration	Sludge produced An acidic pH needed Difficult to regenerate and recycle the ferrous ions Further treatment needed
Electrochemical oxidation	Cleanest Excellent handle in high level of wastewater	Relative high energy consumption Short lifetime of electrode
Ozonation oxidation	Shortest reaction time High efficiency at low concentration	Limited by mass transfer Difficult to maintenance
Combined process	Overcome intrinsic limitation associated with individual treatment techniques	Limited by mass transfer of O <sub>3</sub> Limited research

and biological treatment. However, their drawbacks limit their application. Photolysis-based oxidation seems to be effective for glyphosate degradation in wastewater at low concentrations below 50 mg.L<sup>-1</sup>. However, the disposal of catalysts and difficulties to control the conditions hamper the application of photolysis-based oxidation. Fenton-based oxidation is an effective method to degrade glyphosate at low concentrations below 258 mg.L<sup>-1</sup> without mass transfer limitation, but it generates sludge and requires further treatment. In electrochemical oxidation, glyphosate degradation may be limited by the low mass transfer rate, resulting in low current efficiency. Ozonation oxidation could generate harmful disinfection by-products. Furthermore, complete mineralization of glyphosate could not be obtained by AOPs and various intermediates generate, which cannot achieve a safe discharge standard into the environment. Photolysis-based oxidation and ozonation oxidation is suitable to be carried out for glyphosate treatment under natural aqueous conditions at low glyphosate concentration. Fenton-based oxidation is interesting to treat urban wastewater containing glyphosate with relative low concentration under acidic conditions. Electrochemical oxidation is recommended for the treatment of urban and industrial wastewater with a wide range of glyphosate concentrations at relatively small quantities due to the limitation of cost. Wet air oxidation (catalytic or not) and the combined process is recommended to treat real glyphosate industrial wastewater at high concentrations.

Combined processes seem to be the most potential technology for the treatment of glyphosate in industrial wastewater containing 200–3000 mg.L<sup>-1</sup> glyphosate to obtain 100% glyphosate removal and over 93% organic phosphorus removal due to their benefits to overcome intrinsic limitations of individual processes, which should be further studied. Especially, combined AOPs with biological treatment will be a very promising technology for glyphosate treatment, which have been successfully used for the treatment of other contaminants in wastewater (Azabou et al., 2010; Minière et al., 2017; Pariente et al., 2008; Yan

et al., 2010; Yongrui et al., 2015). The main idea of this coupling is that glyphosate is first treated by AOPs to generate small molecular intermediates to increase the biodegradability of effluent, thus achieving the possibility of subsequent biological treatment for the complete degradation of glyphosate. The research for this coupling is worth to be investigated. One can also propose to first make a biological treatment to decrease the glyphosate concentration, followed by an oxidation process to destroy remaining glyphosate and non-biodegradable by-products formed during the biological treatment. In all cases, it could be interesting to finish with an adsorption process, as a tertiary treatment able to stop toxic molecules to reach rejection standards. Obviously, to conclude on the best treatment, an energetic and economical study is necessary, which must also consider the local treatment possibilities as well as energy costs.

Most of the processes were conducted at the lab scale. Further researches are still needed to study the practical application of these technologies to real glyphosate wastewater through considering how to overcome the drawbacks of each technology. The energy consumption and cost of these technologies also need to be systematically analysed. Meanwhile, the biodegradation pathway of glyphosate needs deeper investigation, through studying the structure of all of the intermediates and enzymes involved in glyphosate biodegradation, as well as procedures for chemical synthesis or isolation of these intermediates and enzymes. For glyphosate oxidation pathway, the analysis of more intermediates and the extent of each step is still needed further research to know more precise mechanisms during glyphosate oxidation process.

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