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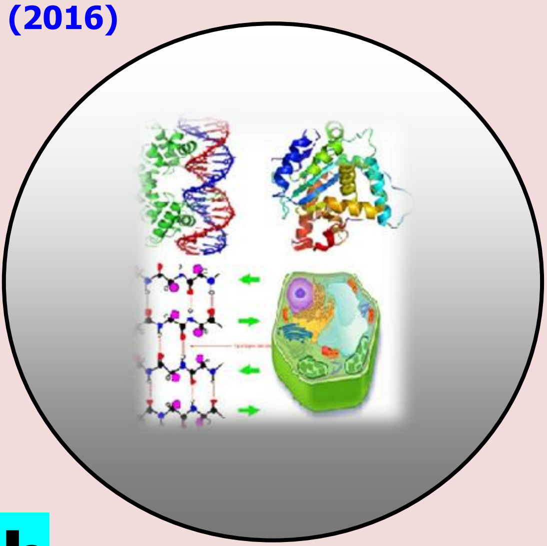

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RESEARCH PAPER

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Potential Application of Wood Ash for Organophosphates Degradation in a Large Scale Advanced Oxidation Process – A Review

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ABSTRACT

Wide application of organophosphates loads harmful effect to the environment that forces search for detoxification. Several degradation techniques such as biodegradation, hydrolysis, photolysis, and advanced oxidation process (AOPs) are used but they have their own limitations. Biodegradation is slow and begins with hydrolysis which forms more toxic intermediates while advanced oxidation process is effective but applied only in a small scale. Wood ash is an alkaline substance composed of semiconductor metal oxides such as SiO_2, Fe_2O_3, TiO_2 , MnO,Cr_2O_3, CuO , ZrO_2 , ZnO etc. having photo-catalytic nature. Alkalinity also enhances catalytic activity of wood ash. This review targets to assess potential application of wood ash for large scale AOPs of organophosphates.

Key words: Organophosphates, Wood Ash, Semiconductor Metal Oxides, Valence Band Hole and Conduction Band Electron.

INTRODUCTION

Organophosphates (OPPs)are esters analogous derivatives of phosphoric (Kumar *et al.,* 2013), phosphorothioic, or phosphonic acids, or their anhydrides, halides or amides (Lanjewar *e t al.*, 2014) which exist either as thionate; containing P = S bond or oxonate; having P = O group (*Lee et al.,* 2007; Obare *et al.,* 2010) (Figure 1). Oxonates are mostly likely oxidation metabolite of the thionates (Konstantinou *et al., 2001*).

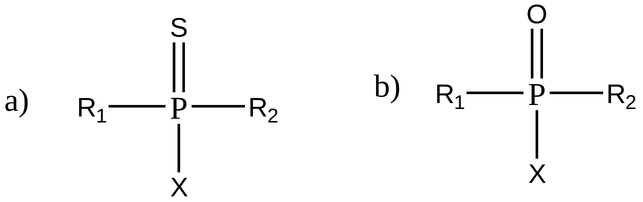


Figure 1: General structure of organophosphates, a) thionates b) Oxonates, where R_1, and R_2 are substituents on phosphorus atom; may be alkoxy, aryloxy and thioalkoxy groups while X is leaving group (Obare *et al.,* 2010).

Organophosphates widely used in agriculture primarily on vegetable and cotton farms (Williamson *et al.,* 2008) as they considered to degrade easily in the environment (Uygun *et al.,* 2007; Sanagi *et al.*, 2011). However, they are highly toxic and responsible for tremendous morbidity and mortality worldwide, killing approximately

300,000 people annually (Jackson *et al.,* 2014). Organophosphates suspected to accumulate in aquatic organisms like fish, soil and water (Ezemonye *et al*., 2008). Hence, in order to minimize their harmful effect, there should be means of quick removal techniques.

Previous literatures reported that organophosphates can be degraded by microbes (Harish *et al.,* 2013), hydrolysis, photolysis, and advanced oxidation process (AOPs) (Gatidou and Iatrou, 2011; Petsas *et al.,* 2013) but these techniques have their own limitations. Bio-degradation is slow and always begins with hydrolysis which results more harmful intermediates (Uygun *et al.,* 2005; Yang *et al.*, 2006; Gatidou and Iatrou, 2011; Liu *et al.,* 2015*)* which are potential environmental concern (Aydin *et al.,* 2011). The reported advanced oxidation process (AOPs) is effective (Derbalah and Ismail, 2013), and occurs in any hydroxyl free radical forming process such as Fenton reaction (Badawy *et al.,*2006; Papoutsakis *et al.,* 2016) or photo catalysis process. Photo-catalysis takes place on the surface of semiconductor metal oxides such as TiO_2 (Konstantinou *et al.*,2001; Shifu and Yunzhang, 2007; Wei *et al.,*2009; Petsas *et al., 2013;* Assalin *et al.,*2016), ZnO nanoparticle (Khan *et al*.,2015), silica gel immobilized TiO_2 (Echavia *et al.,*2009) and MnO_2/C nano-composites (Wang *et al.,*2016),TiO_2/Fe_2O_3 (Mirmasoomi *et al.,*2017) but applied only on a small scale (Shrikant and Khambete, 2014). Hence, searching for quick, large scale and efficient environmental remediation techniques is the hottest research issue.

Meanwhile, wood ash is known to be rich in semiconductor metallic oxides such as, SiO_2, Al_2O_3 , K_2O, Fe_2O_3, MgO, TiO_2, MnO, Cr_2O_3, CuO, and ZrO_2 (Udoeyo *et al.* 2006) which can initiate different chemical reactions. In addition, wood ash is a waste (Siddique, 2012) and easily accessible in our country Ethiopia since (81.8%) of the population is using fire wood and charcoal as fuel (Akililu, 2003). This review was to assess the role of wood ash for large scale AOPs of organophosphates.

Chemical reactions and the fate of organophosphates

Organophosphates considered being less reactive as they persist in the environment. However, some reported literatures pointed out that OPPs rapidly dissipate during storage (Uygun *et al.,* 2004) and detectable amount of such compounds persist in the environment only for a short period of time measured in months which assure their reactivity. For example in soil under usual environmental conditions, 90% of diazinon transforms in to 2-isopropyl-6- methyl-4-pyrimidinol (Bavcon *et al.,* 2002). Arjmandi *et al., (*2010) reported non-availability of diazinon in sprayed rice after one month and the highest trace reported after one day of spraying 1.14 ppm which implies that the sprayed diazinon either vaporized or changed into metabolites. According to Uygun *et al.,(*2005) malathion and isomalathion degrade 65–72% during storage, about 95% in milling and about 82% in white bread baking which confirms some sort of reaction. Organophosphate degrade in several ways such as hydrolysis, oxidization (Bavcon *et al.,* 2002), photolysis (Kouloumbos *et al.,* 2003), rearrangement, protonation (Barr *et al.,* 2005), fermentation (Bo *et al.,* 2010).

Causes and effects of hydrolysis

Hydrolysis is a major organophosphates degradation route in water and soil (Bavcon *et al*., 2002) and which attacks all types of OPPs particularly carboxyesters or carboxyamidics. Anhydride or halide OPs are also the most labile while amides are the least (Lanjewar *et al*., 2014). Phoxim is the most hydrolysis sensitive organophosphate as it simultaneously undergoes photodegradation (Gatidou and Iatrou, 2011). Hydrophilic organophosphates are labile and hydrolyze completely in 3-10 days in organism (Newhart, 2016).

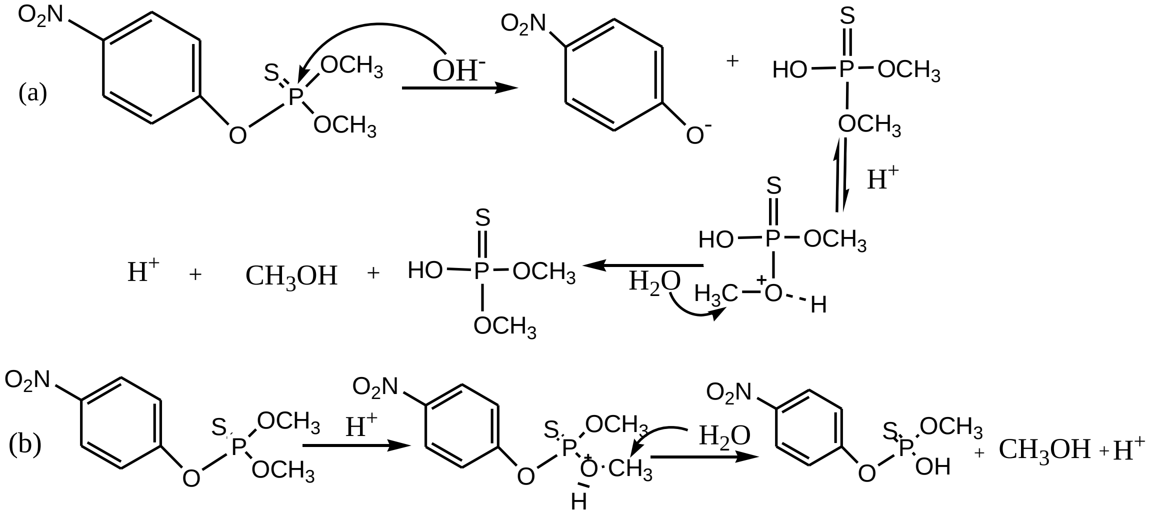
Hydrolysis strongly depends on pH and temperature (Lanjewar *e t al*., 2014). Except, diazinon which is susceptible in acidic medium, all other OPs hydrolyzed in alkaline medium (Kralj *et al.,* 2006). In alkaline aerobic condition, hydrolysis is too fast (Venugopal *et al*., 2011; Newhart, 2016) but extremely slow in acidic media (~at pH 6) up to 70 °C (Freed *et al.,* 1976). Liu *et al. (*2015) reported that at pH 13, 99% of methyl parathion was degraded but only 80% in the pH range 5-9 within 140 days. Some organophosphates like fenithion are totally passive to hydrolysis. Petsas *et al. (2013)* reported that combination of fenthion with TiO_2 in a covered bottle didn't show detectable change within 48hrs due to the absence of hydrolysis. Several chemical species such as metal ions and metal oxide nanoparticles initiate hydrolysis. Hydrolysis due to metal oxide depends on surface area, charge, morphology, and active site density. Any factors which enhance surface Lewis acidity of nanoparticles speed up hydrolysis. Example doping of TiO_2 nanoparticles with fluorine cause substitution of surface or lattice O and OH groups increased the Lewis acidity on the surfaces, owing to the stronger electronegativity and polarizing effect of fluorine so speeds up hydrolysis of organophosphous esters (Lee *et al.*,2007).

Hydrolysis forms a number of intermediates. Example: malathion converts to malaoxon, isomalathion (Uygun *et al.,2005*) or/ and dimethyl dithiophosphate (Venugopal et al., 2011), phoxim forms diethoxyphosphoyl thioimino-phenylacetonitrile, benzoic acid, α-hydroxy- iminophenylacetonitrile, N,N- [thio-bis (α-iminophenylacetonitrile)], and O,O,O-tetraethyldiphosphate (Gatidou and Iatrou ,2011), methyl parathion [O-metahyl O,O-dihydrogen phosphorothioate, O,O-dimethyl O-hydrogen phosphorothioate, Desmethyl methyl parathion and *p*-nirtophenol] (Liu *et al.,* 2015). However, hydrolysis of chlorpyrifos results 3, 5, 6-trichloro-2-pyridino l (Yang *et al.*, 2006).

Hydrolysis of some organophosphates

a) Hydrolysis of methyl parathion

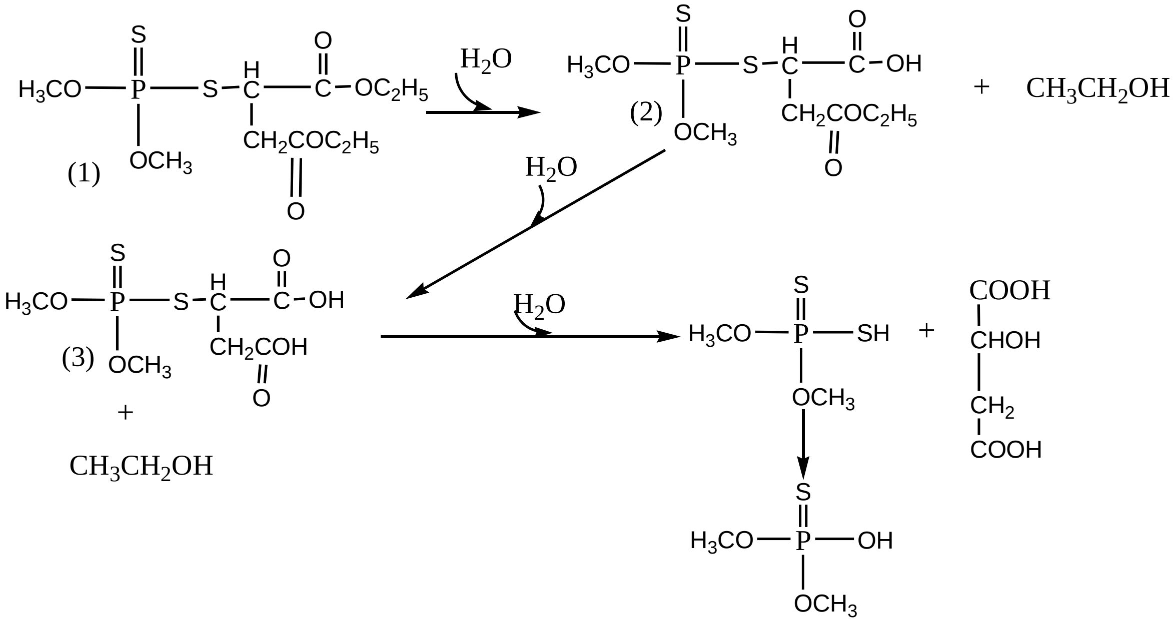
Liu *et al., (*2015) reported that methyl parathion undergo hydrolysis reaction both in acidic and basic media to form a number of intermediates.



Scheme 1: Hydrolysis of methyl parathion (a) in basic and (b) in acidic media

b) Hydrolysis of malathion

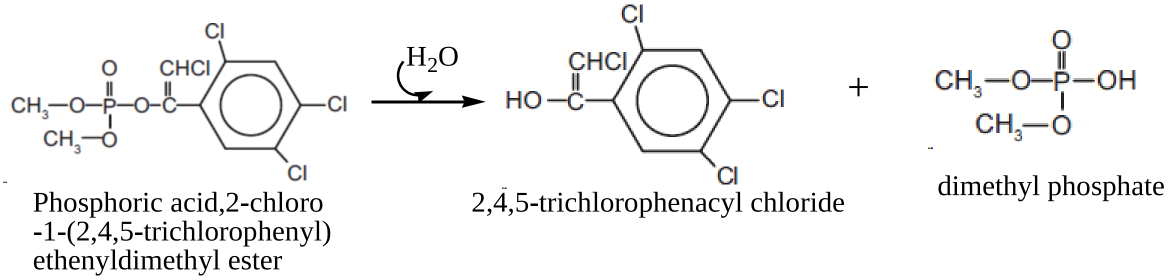
According to Newhart (20006) malathion undergoes hydrolysis to end up forming O,O-dimethyl O-hydrogen phosphorothionate and 2-hydroxysuccinic acid.



Scheme 2: Mechanism and hydrolysis by products of malathion.

c) Hydrolysis of tetrachlorvinphos

In water TCV undergoes hydrolysis and forms ester 2, 4, 5-Trichlorophenacyl chloride and dimethyl phosphate

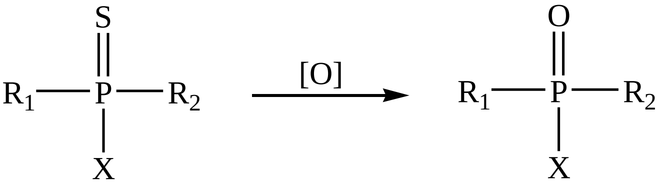


(Ortiz-Hernández and Sánchez-Salinas, 2010)

Scheme 3: Hydrolysis of tetrachlorvinphos and its reaction products

Causes and effects of oxidation

The most common organophosphates oxidation involves conversion of thionates oxon (Wu *et al.,* 2009). Thionates primarily oxidized to oxons, P=O (Kim et al., 2000; Kralj *et al.,* 2006; Lazarevic´-Pašti *et al.,* 2011).



$$R_1-\overset{\overset{\displaystyle S}{\|}}{\underset{\underset{\displaystyle X}{|}}{P}}-R_2 \xrightarrow{[O]} R_1-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle X}{|}}{P}}-R_2$$

Scheme 4: Partial oxidation of thionates to oxonate; where [O] is oxidant

The degree of oxidation and resulting products vary depending on length of reaction time, concentrations of organophosphate and oxidant (Bai *et al.,*2010), concentration of catalyst (Lazarevic´-Pašti *et al.,*2011), temperature (Shifu and Yunzhang, 2007) and pH (Kralj *et al.,*2006; Lazarevic´ -Pašti *et al.*,2011). Organophosphate may oxidize due to photolysis (Petsas *et al., 2013*), oxidants such as bromine (Kim *et al.*,2000), chlorine (Kamel *et al.,*2009), ozone (Wu *et al.,*2009) ,*N*-bromosuccinimide, hypochlorite,OCl^- (Kralj *et al.,*2006), hydrogen peroxide, peroxy disulfate, $S_2O_8^{2-}$ (Evgenidou *et al.*,2007; Lazarevic´ -Pašti *et al.*,2011), electrons and free radicals (Bai *et al.,* 2010). Ions such as Fe^{2+} (Catalkaya and Kargi *,* 2009), Fe^{3+}, Cu^{2+} and anions O_2^{2-}, $S_2O_8^{2-}$, BrO_3^- (Shifu and Yunzhang, 2007; Wei *et al.,* 2008) cause oxidation either by forming or facilitating free radical formation. When Fe^{2+} or Fe^{3+} reacts with H_2O_2 in the presence of UV light results $^{\cdot}OH$ and $^{\cdot}HO_2$ free radicals. While $S_2O_8^{2-}$ reacts with conduction band electron ,e^-CB or UV light to form $SO_4^{\cdot -}$ which in turn reacts with organic pollutants-to oxidize, water or e^-CB to form $^{\cdot}OH$ and SO_4^{2-}.The reaction of $SO_4^{\cdot -}$ with e^-CB blocks electron-hole(e^-/h^+) recombination (Pe´rez *et al.*,2006). Oxidant such as H_2O_2 (Petsas *et al., 2013)* and oxygen (Catalkaya and Kargi*,* 2009) may bring complete oxidation called mineralization can be enhanced by temperature (Shifu and Yunzhang, 2007). Organophosphates oxidation takes both in an acidic and alkaline media. Some organophosphates like diazinon oxidized faster in alkaline medium as high pH enhances efficiency of oxidants while others such as methyl parathion and parathion not affected by pH(Wu *et al.,* 2009). Some oxidants like *N*-bromosuccinimide, NBS are more efficient in acidic conditions while sodium hypochlorite is in alkaline (Kralj *et al.,* 2006). In addition, aqueous alkaline medium hydrolysis enhances oxidation (Gatidou and Iatrou, 2011; Liu *et al.,* 2015; Newhart, 2016).

Causes and effects of photolysis

Photolysis is a process in which compounds degrade due to exposure of light (Bavcon *et al.,* 2002). The rate of photolysis increases with pH (Usharani et al., 2012) photo-oxidation follows first-order kinetics (Petsas *et al., 2013).*

Causes and effects of photo Fenton reaction

Fenton process is a special form of AOP that mineralizes organic compounds due to $^{\bullet}OH$ (Huang *et al.,* 2012; Trovó *et al.,* 2013; Papoutsakis *et al.,* 2016) resulting from electrochemical process (Guivarch *et al.,* 2003). Fenton's reagent is a mixture of ferrous iron ions and hydrogen peroxide formed through simultaneously reducing O_2 and Fe^{3+} on carbon cathode in acidic medium (Guivarch *et al.,*2003). Several researchers reported that Fenton process mineralizes a variety of organic pollutants such as simazine (Catalkaya and Kargi, 2009), amoxycillin, acetaminophen, acetemiprid, caffeine, clofibric acid and carbamazepine (Bernabeu *et al*., 2012), melatonin (Xu *et al.,*2009), caffeine(Trovó *et al.,*2013), 4-nitrophenol(Chu *et al.,*2012), organophosphorus pesticides (Guivarch *et al*.,2003).

Fenton process can be carried out either in an open cylindrical reaction vessel (Bernabeu *et al.,* 2012) or an electrochemical cell (Guivarch *et al.,* 2003). It is highly affected by pH (Xu *et al.,* 2009) and more effective in an acidic pH ranges 2.8 to 3.5 (Catalkaya and Kargi, 2009; Bernabeu *et al.,* 2012). Xu *et al*. (2009) reported that the best pH value for the removal of melatonin in Fenton oxidation was 3.0.

Mechanism of Fenton reaction

In photo Fenton process mineralization of organic compounds stem from two routes namely direct photolysis and hydroxyl free radicals (Xu *et al.,* 2009). In the direct photolysis process, organic compounds oxidized by irradiation of compounds with photons in the UV region while in case of radical reaction organic pollutants oxidized by hydroxyl free radicals generated through photolysis of H_2O_2 (Scheme I) , $Fe(OH)^{2+}$ (Scheme III) and Fenton reaction(Scheme II) (Xu *et al.,*2009; Chu *et al.,*2012).

$$H_2O_2 \xrightarrow{hv} 2\,{}^{\bullet}OH \text{ ....(i)}$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \text{....(ii)}$$

$$[Fe(OH)(H_2O)_5]^{2+} \xrightarrow{hv} Fe^{2+} + 2\,\overset{\bullet}{O}H \text{ ......(iii)}$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + H\overset{\bullet}{O}_2^{-} + H^{+} \text{....(iv)}$$

Scheme 5: Reactions that form free radicals in photo-Fenton system

Causes and effects of photo-catalytic degradation

Photo-catalysis is a type of advanced oxidation process that can mineralize organic compounds on the surface of semiconductor transition metal oxides in the presence of light and usually oxidants. The photo-catalyst absorbs both oxidant and the target compound on its surface and serve as reaction medium (Affam and Chaudhuri , 2013). A number of literatures reported that several transition metal oxides such as TiO_2 (Konstantinou *et al.*,2001; Shifu and Yunzhang, 2007; Wei *et al.*,2009; Petsas *et al., 2013;* Assalin *et al.*,2016), ZnO nanoparticle combined with membrane filtration (Khan *et al*.,2015), silcagel immobilized TiO_2 (Echavia *et al.,*2009) and nano-composites such as MnO_2 /C(Wang *et al.,*2016),TiO_2/Fe_2O_3 (Mirmasoomi *et al.*,2017) have been used as photo-catalyst. Affam and Chaudhuri (2013) reported that photo-catalysis system containing TiO_2/H_2O_2 were effective against chlorpyrifos, cypermethrin and chlorothalonil. Photo-catalytic reaction takes place in any medium exposed to UV irradiation (Shifu and Yunzhang, 2007; Jafari *et al.,* 2014**)** or sunlight (Wang *et al.,* 2016).

Mechanism of photo-catalytic degradation

The efficiency of photo-catalysts primarily relays on their band gap energy and wave length of absorbed light that affect formation of electron-hole pairs (Mirmasoomi *et al.,* 2017). Electron-hole pairs formed only if energy of absorbed light is at least equal to the band gap of the photo-catalyst. Previous literatures reported that when light having greater or equal to band gap of the photo-catalyst absorbed, forces an electron to moves from valence band to conduction band that results hole in the valence band and energetic electron in the conduction band.

Valence band hole interacts with water or hydroxide ion (OH^-) to form hydroxyl free radical while conduction band electron e^-CB reacts with molecular oxygen O_2 adsorbed on the surface of photo-catalysts to form $O^{\cdot}{}_2^-$;oxidizes organic compounds(Wang *et al.,*2016). Free radicals (${}^{\cdot}OH$, ${}^{\cdot}O_2^-$ and ${}^{\cdot}HO_2$) are generally responsible for degradation of organic compounds (Wang *et al.,* 2016). However, in some conditions conduction band electron may fall back to the valence band hole the phenomenon referred “electron-hole recombination” minimizes degradation efficiency (Mirmasoomi *et al.,* 2017). However, the presence of some ions such as Fe^{2+} (Catalkaya and Kargi*,* 2009), Fe^{3+}, Cu^{2+} and anions O_2^{2-}, $S_2O_8^{2-}$, BrO_3^- (Shifu and Yunzhang, 2007; Wei *et al.,* 2008) prevent electron-hole recombination

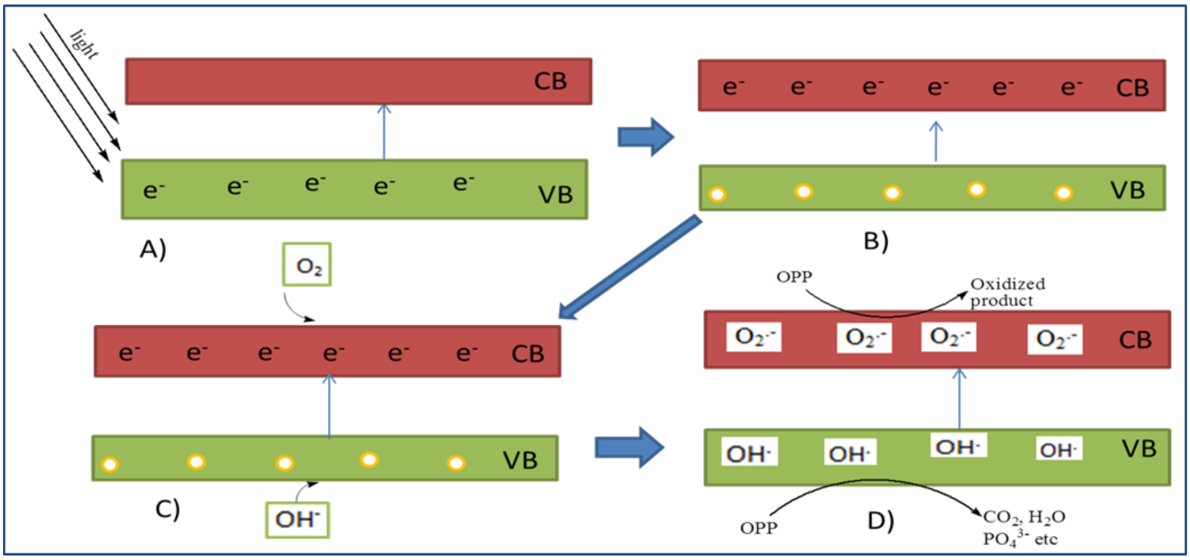


Figure: Systematic representation of free radicals formation and photo-catalyst; where CB is conduction band, VB, valence band, yellow spots valence band holes e^- ,conduction band electron and OPP, organophosphate (Shifu and Yunzhang, 2007; Wei *et al.* ,2009; Talebian and Nilforoushan, 2010; Affam and Chaudhuri, 2013; Wang *et al.,* 2016).

Ashes: Chemical compositions and reactions

Chemical compositions of ashes

Ash is an alkaline (Sharma *et al*., 2012) complex matter which results from composition of dry solid materials (Du *et al*., 2014); can be classified as wood ash (Serafimova *et al*., 2011; Scheepers and du Toit, 2016), coal fly ash (Singh, 2009; Alouani et al., 2017) and paper mill ash (Monosi et al., 2012) based on their origin and may vary in their constituents with the variation of temperature (Du et al., 2014). The main ingredients of wood ash is $CaCO_3$ followed by SiO_2 , MgO , K_2O, CaO as well as some metals Cd, Pb, Cr, Ni, Cu, Zn and As and anions such as P_2O_5 , NH_4^+ ,NO_3^-, Cl^- in the form of fine crystals (1-2 µm) which can agglomerate to nano-scale (Serafimova *et al*.,2011). Odlare, (2005) reported that wood ash could contain Cu, Fe and U as well as several other metals. The report of Udoeyo *et al. (*2006) showed that wood waste ash contains several metal oxides such as CaO, SiO_2, Al_2O_3, K_2O, Fe_2O_3,MgO, TiO_2, Na_2O, Zn, MnO, SrO, Cr_2O_3, CuO, ZrO_2, and Rb_2O as well as nonmetal like Cl and non-metal oxides like SO_3, and P_2O_5.

Madakson e*t al.(*2012) reported that coconut shell ash dominantly contains SiO_2, Al_2O_3, MgO and Fe_2O_3 as well as small amount of other metal oxides including CaO, K_2O, MnO and ZnO but free from radioactive materials. Singh (2009) suggested that SiO_2, Al_2O_3 and Fe_2O_3 are the main compositions of bituminous coal fly ash as well.

Possible chemical reactions in ash containing media

Although chemical composition of ash may vary due to its origin (Lima *et al.,*2008) and combustion temperature (Du *et al.,*2014), lots of reported literatures agreed that ash is alkaline substance (Sharma *et al*., 2012) with pH ranging to 12.6 (Serafimova *et al.*,2011) enriched with different semiconductor metal oxides such as SiO_2, ZrO_2, Cr_2O_3, Fe_2O_3 , MnO, ZnO and TiO_2 (Udoeyo *et al.,*2006) as well as anions like NO_3^-, Cl^-, SO_4^{2-} etc. Alkalinity of wood ash increases pH of the media (Laohaprapanon *et al.,*2010) which can bring rapid hydrolysis reaction on organophosphates (Venugopal *et al*., 2011; Newhart, 2016). On the other hand, semi-conductor metal oxides can result in effective photo catalytic degradation in the presence of UV-Visible light. If semiconductor metal oxides exposed to light, they eject electron from valence band to their conduction bands which results hole in the valence band and energetic electron in the conduction band (Shifu and Yunzhang, 2007). In alkaline media, since OH^- is highly concentrated, it has the greatest chance of combining with valence band hole to form high concentration of hydroxyl radicals. Anions like sulphate , SO_4^{2-} and carbonate CO_3^{2-} interact with photo-generated holes to form their corresponding free radicals (Wei *et al.,*2008) while cations like Fe^{3+}, Cu^{2+} and anions O_2^{2-} , $S_2O_8^{2-}$, BrO_3^- (Shifu and Yunzhang, 2007 ; Wei *et al.,*2008) and nitrates, NO_3^- (Gatidou and Iatrou,2011) initiate the formation of hydroxyl free radicals so speed up photo-catalytic degradation.

Reduction of Fe^{3+} photon in aqueous solution forms Fe^{2+} and $^{\cdot}OH$ (Shanthi *et al.*, 2013) while in alkaline condition photolysis of Fe^{3+} is also the source of additional •OH (Xu *et al.,* 2009). Shanthi *et al.* (2013) reported that under solar irradiation, ZnO is more efficient oxidant than H_2O_2 so can bring mineralization of organophosphates. However, Carbonate and hydrogen carbonate may harm photo- catalyic efficiency through scavenging hydroxyl free radicals but still they form free radicals which are responsible for oxidation of organic pollutants (Trovó *et al.,* 2013).

$$^{\cdot}OH + CO_3^{2-} \longrightarrow HO^{-} + CO_3^{2.-}$$

In addition, several literatures reported that varieties of ash species have been used as low cost adsorbent for various pollutants. Coal fly ash for metribuzin, metolachlor and atrazine (Singh, 2009), bagasse fly ash to remove methyl parathion pesticide (Akhtar *et al.,* 2007) suggested that is good adsorbent in aqueous solution. Laohaprapanon *et al.*(2010) removed COD, TOC, and BOD with efficiency of 23 to 37%, 15 to 30%, and 4 to 24%, respectively using wood fly ash as low cost adsorbent. Sharma *et al*.(2012) also reported that two sets of catalysts; Calcined wood ash catalyst, CWC and activated wood ash catalyst, AWC were prepared from wood ash through calcination of wood at different temperature and solid reaction method respectively. Calcined wood ash catalysts were prepared through dry ashing wood block followed by calcination at 500, 800, 1000 or 1200 °C while AWC were prepared through mixing wood ash with 0.25, 0.50 and 1.0 % K_2CO_3 or 0.5 % of $CaCO_3$ followed by calicination at 800 °C for 3 h .The catalytic activity of the newly prepared catalysts (CWC and AWC) were evaluated by the trans esterification of Jatropha oil with methanol. It was found that wood ash Catalysts obtained by calcination at 800 and 1000 °C (CWC800 and CWC1000) showed increased activity which gave 98.7% and 98.2% ester conversion respectively at 5 mass fraction percentage catalyst dosage while activated wood ash catalysts (A_KWC) showed ester conversion efficiency 97.5%, 99.0% and 99.0% with activated catalysts, AKWC 0.25, $A_KWC0.5$ and A_KWC_1 respectively at 5 mass fraction percentage catalyst dosage. And the authors suggested that the activity of the catalysts was due to their alkalinity but not surface area and particle size.

CONCLUSION

This review revealed that all conditions which generate hydroxyl radicals lead completely mineralization of organophosphates. Organophosphates also affected by chemical reaction such as hydrolysis, oxidation, photolysis, photo Fenton reaction and photo-catalytic degradation. The review showed that wood ash composed of varieties of semiconductor metal oxides that can generate hydroxyl free radicals. In addition, high alkalinity also indicates heterogeneous catalytic nature of wood ash. This showed that wood ash can be used for large scale advance oxidation process.

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