The impact of alkali metal halide electron donor complexes in the photocatalytic degradation of pentachlorophenol

Z. Khuzwayo, E.M.N Chirwa

Department of Chemical Engineering, Water Utilisation Division, University of Pretoria, Pretoria, 0002 South Africa. Tel.: +27793797619, E-mail: zack.khuzwayo@up.ac.za.

Abstract

The performance of photocatalytic oxidation of chemical pollutants is subjected to the presence of anion complexes in natural waters. This study investigated the influence of alkali metal (Na^+ (sodium), K^+ (potassium)) halides (Cl^- (chloride), Br^- (bromide), F^- (fluoride)) as inorganic ion sources in the photocatalytic degradation of pentachlorophenol (PCP) in batch systems. It was found that the exclusive presence of halides in the absence of an electron acceptor adequately facilitated the photocatalyst process below critical levels of anion populations, where beyond the critical point the process was significantly hindered. Below the determined critical point, the performance in some cases near matches that of the facilitation of the photocatalytic process by exclusive oxygen, acting as an electron scavenger. The coupling of halide ions and oxygenation presented significantly improved photo-oxidation of PCP, this was confirmed by the inclusion of formic acid as a comparative electron donor. The Langmuir-Hinshelwood kinetic expression was used to calculate the performance rate kinetics. The probable impact of the halide anions was discussed with regards to the process of electron hole pair recombination prevention.
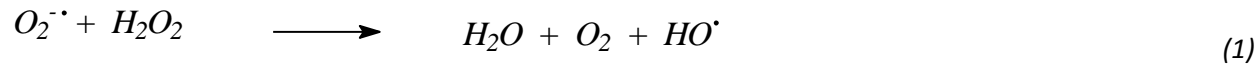
Keywords:

Alkali metals, electron donors, photocatalysis, polychlorinated phenol, oxidation

1. Introduction

Chlorophenols (CPs) are listed as priority pollutants in most water regulation authorities due to their ability to bioaccumulate in organisms, potential mutagenic and carcinogenic effects, and their ability to affect the quality of drinking water [1-6]. Pentachlorophenol (PCP) is the highest chloride-substituted phenolic compound, its widespread use was based on its highly effective biocide properties and wood preservation [4,7-9]. PCP has a high toxicity and is resistant to biological degradation processes, for this reason conventional water and wastewater treatment technologies are unable to remove or treat chlorophenols when dissolved in aqueous systems [10-12]. One type of technology that has been developed to treat these class of compounds is advanced oxidation processes (AOPs).

Photocatalysis is one of the advanced oxidation photochemical processes that is the most efficient nonselective chemical pollutant removal technology [13]. Various studies have been conducted on the application of photocatalysis in the treatment of PCP, its salts (notably sodium pentachlorophenate (PCP–Na) and other chlorophenols [2,8,10,14,15,16]. Most findings are in agreement that this technology is effective at removing most organic pollutants in aqueous mediums. Most research has subsequently shifted towards areas of improvement of the technology. One such drawback of the photocatalysis is that in natural water systems, it experiences impairment due to the deactivation of photocatalyst by the presence of inorganic ions [17], such as halide anions. Chloride inorganic ions have received plenty of attention, while limited research has focused on the rest. The presence of electron donor species such as halide anions can have both positive and negative influence on the photocatalyst performance. Studies amongst others by Caregnato et al. [18] on the chloride anion effect on the advanced oxidation processes and by Yang et al. [19] on the involvement of chloride ions in the photocatalytic process showed that, chloride anions present in polluted waters under certain conditions are able to scavenge the active oxidising radicals produced and slow down the rate of the degradation, while it may enhance the oxidation process under conditions of high anions concentration where due to the participation of chloride radicals. This is determined by the abundance ions, which above certain critical concentrations can retard semiconductor surface adsorption [19-20]. At conducive anion populations, they can act as and complement the surface radicals of activated sites by preventing the election hole pair recombination process. This study will focus on simple metal complexes for the delivery of anions in the investigation of their impact on the kinetic rate of photocatalytic reactions.

The photocatalyst semiconductor adsorption process is reported by various studies to follow a stepwise reactions scheme. Many of these studies including those by Rodriguez et al. [21], Salvador [22], Mills and Le Hunte [23], Hoffman et al. [24] and Turchi and Ollis [25] proposed similar surface adsorption mechanisms in the adsorption of organic compounds onto the semiconductor catalyst surface in aqueous systems. According to the reactions schemes, organic compounds at the catalyst surface are better oxidised due to the participation of the resultant positive holes (h^+) [21]. The energy activation of the oxide semiconductor particles results in the ejection of elections (e^-) from the low energy valence band state to a higher energy conduction band state. Remaining on the catalyst surface at the valence band edge is the resulting positive hole. The organic compound is adsorbed onto the photocatalyst surface, where a transition state radical charge is formed in the catalyst-compound moiety. Hydroxyl radicals (HO°) are formed on the TiO_2 surface by the h^+ reacting with adsorbed water (H_2O) molecules, surface titanol groups and hydroxide molecules that facilitate oxidation reaction pathways. Hydroxyl radical formation can typically lead to the formation of hydrogen peroxide (H_2O_2). This is achieved through the reaction of the valence band ejected electrons with the O_2 molecule in the presence of hydrogen (H^+) ions in solution, and by the reaction of H_2O molecules with hydrogen ions to form H_2O_2 and H^+. Hydrogen peroxide contributes to the oxidation of organic electron donors as it has properties that allow it to act as an electron acceptor and is also a direct source of hydroxyl radicals. Eqs.1-3 show the eventual steps in the hydroxyl radical formation process, and the reaction leading to the oxidation of the organic analyte, where $O_2^{-\circ}$ is the free charged oxygen specie.

2

$$O_2^{-\bullet} + H_2O_2 \longrightarrow H_2O + O_2 + HO^{\bullet} \qquad (1)$$

$$e^- + H_2O_2 \longrightarrow OH^- + OH^{\bullet} \qquad (2)$$

$$PCP + HO^{\bullet} \longrightarrow Products \qquad (3)$$

The photocatalytic process is primarily founded on the generation of reduction and oxidation source pathways. These pathways are maintained by prevention of the recombination process of the conduction band promoted elections and valence band pairing holes. This can be achieved either by instantly and reactively utilising the promoted elections (e^-) or by instantly and reactively occupying the trapping positive holes (h^+). The sorption of semiconductor catalyst surface electron acceptors and electron donors are an imperative step in the photodegradation process. The typical photocatalysed semiconductor systems are in aerated solutions, where O_2 performs the task of an electron acceptor thus discouraging the e^--h^+ recombination step. Photocatalytic efficiency can be improved by increases in hydroxyl radical concentrations, and through the generation of derivative oxidising compounds, Eqs.1 and 2 [26-27]. The application of electron acceptors and their properties in the facilitation of the photocatalytic process has been studied extensively and reported many times over in literature, this study focuses on the impact on simple low cost halide complexes that have been reported to potentially affect the photocatalytic process.

2. Experimental

2.1. Materials

Formic acid (CH$_2$O$_2$), sodium chloride (*NaCl*) 99.5%, potassium chloride (KCl) 99.5%, sodium bromide (*NaBr*) 99%, and sodium fluoride (*NaF*) 99% were purchased from Merck (South Africa). Pentachlorophenol (PCP) 97% and anatase 99.7% titanium dioxide (*TiO$_2$*) were purchased from Sigma-Aldrich Logistik GmbH (Schnelldorf, Germany). Phenol and GC grade methanol were purchased from Merck (South Africa). Ultra-pure (UP) water was dispensed by the Millipore Direct Q3 with pump instrument.

2.2. Reactors configuration

The photocatalytic process setup is presented in Fig.1. The reactor vessel had a 1 L capacity up to the solution level and it rested on a magnetic stirrer with an rpm setting of 200. 15 cm on either side of the vessel were quarts sleeved long-arc UV lamps (Phillips HOK 4/120 SE), Table 1. A fizzling oxygen tube was attached to a flow regular, a sensor probe (HQd MTC 101) was fitted on the top side, and a glass sampling tube was attached to precision pump tubing (Masterflex), and all were immersed in the solution. The setup was installed in a temperature regulated walk-in reactor room that is wall-connected to a cold-room of 4 °C set temperature, the wall connection has small port-openings that allow transfer of cooled air. The reactor room has a driven air-vacuum that constantly drives the cooling system.

3

2.3. Kinetic determinations

The Langmuir–Hinshelwood (L-H) adsorption isothermal equilibrium model was used to determine and calculate the PCP adsorption kinetic parameters. 30 mg L^{-1} equivalent mass concentration of TiO_2, and five point analyte mass ranges were used to determine equilibrium concentrations. The Langmuir equilibrium adsorption constant and the standard error were then used to determine and estimate the rate degradation kinetics by applying the Langmuir-Hinshelwood heterogeneous photocatalytic expression. Kinetic simulations and parameter estimations were performed using a Aquasim 2.0 computer program.

2.4. Experimental procedure

The reactor setup process included solution temperature determinations over the irradiation period, this was conducted by control pseudo-experimental runs using water. There was a relationship between the fractional increases in solution temperature and the distance of the radiation sources. Progressive increases in UV lamp distances were conducted to determine the distance when the solution temperature would remain relatively unchanged.
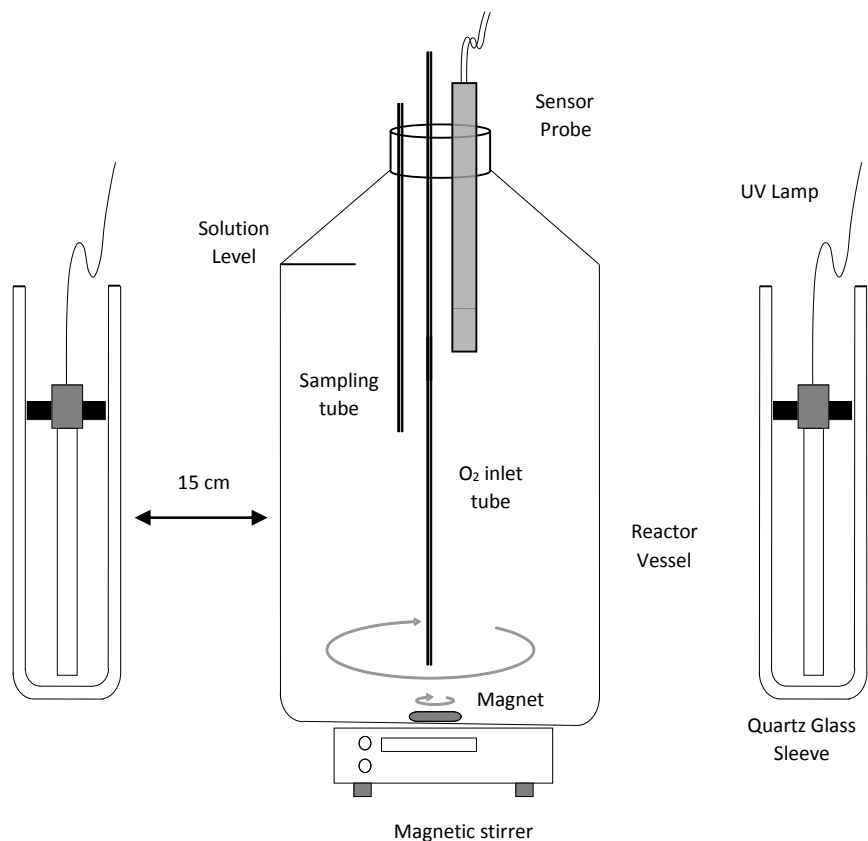

Fig.1 Schematic of the laboratory photocatalytic reactor setup

Table 1 Lamp properties used to configure the reactors system

Lamp	Length (mm)	Width (mm)	Radiation Details (W)			Voltage (V)
			Wattage	UVA	UVB	UVC	
HOK4/120	100	16	400	31	32	52	120

Table 2 Electron donor chemical compounds and their mass concentrations

[e donor] mg L^{-1}	Formic Acid	NaCl	KCl	NaBr	NaF
1 x	24.4	20	20	20	20
2 x	48.8	40	40	40	40
4 x	97.6	80	80	80	80

Analyte spiked solutions were prepared accordingly, catalyst dispensation (30 mg L^{-1} mass equivalent anatase *TiO$_2$*) took place after 30 minutes of solution stirring, the matrix solution was then sonication (8891 Cole-Parmer) for 10-15 minutes, followed by the application of the different halide salts and formic acid, Table 2. Oxygen flow (99.9999%)(20 mL min^{-1}) was initiated prior to solution transfer, and similarly to Argon (99.9999%) purging where relevant, UV irradiation was only started when the system was set and ready. 1.5 mL sample volumes were removed at predetermined intervals, centrifuged (Eppendorf minispin) for 20 minutes at 5000 rpm, the supernatant aliquot used for instrumental analysis through direct injection. Organic compound tracking was performed using a Gas Chromatography Mass Spectrometer (GCMS). All experiments conducted were repeated several times (minimum of three) and average values are reported.

3. Results

The primary aim of the study was to investigate the kinetic effects of the involvement of halide anions in the photocatalytic process and their influence to the e^--h^+ recombination step by applying simple low cost halide reactants. Fig.2a shows the summary of the experimental sets conducted on each of the identified halide salt electron donors and formic acid. It was with intention that an organic electron donor (formic acid) was identified, its inclusion was meant to provide insight and comparison to alkali metal-halogen salts complexes. Iguchi et al. [28] reported the applications of chloride anions in photocatalytic systems being used to scavenge valence band holes and improve performance. The addition of *NaCl* to their system enhanced performance significantly, it was also noted that other chloride salts such as *KCl*, *CsCl*, *MgCl$_2$* and *CaCl$_2$* imparted positive influence. Another study by Krivec et al. [29] reported that chloride ions that are formed as by-products in the photocatalytic process can react with photogenerated holes and influence oxidation. This study evaluated the kinetic behavioural profiles of the photocatalytic process under additions of halide salts and their impact on the rate of degradation in the presence of oxygenation in its absence and in combination with it.
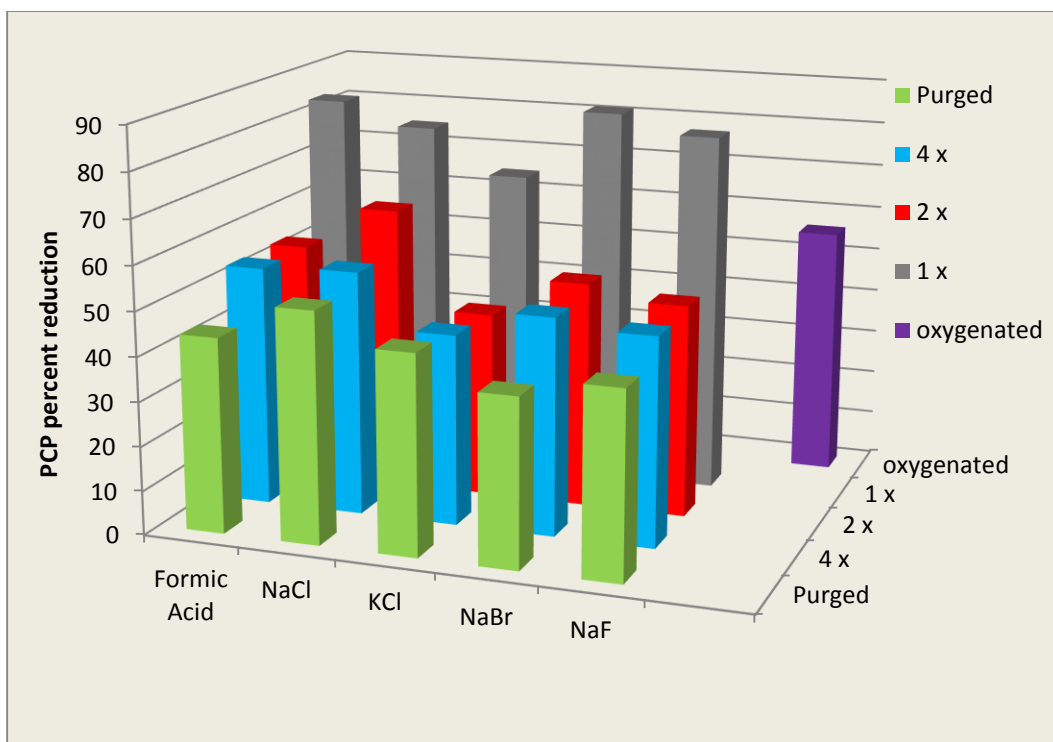
5

Fig.2a. Summary of the photocatalytic percentage reduction of PCP in various concentrations of electron donors and acceptors. [TiO_2] 30 mg L^{-1}, gas flow and purge 20 mL min^{-1}, [PCP]$_o$ 10 mg L^{-1}

The oxygenated set in Fig.2a simply refer to the photocatalytic degradation of pentachlorophenol in the presence of oxygen, where oxygen acted as an electron acceptor in the prevention of recombination. The purged sets refer to the continuous purging of argon gas into solution to void it of oxygen and related species that may be formed, to strictly analyse the system in an anaerobic state, where only the added electron donating species had impact on the rate of degradation of PCP, Fig.2b. The purged sets were with the addition of (1 x) mass concentrations of the electron donors, which were 20 mg L^{-1} for the salts and 24.4 mg L^{-1} for formic acid. All other columns presented in Fig.2a unless otherwise indicated, involved the combination of oxygenation and electron donor compounds. Each of the donor species identified will be discussed along with comparative analysis of their performances towards the oxidation of PCP. The discussion in this study will centre on the halide anions influence on the photocatalytic process in combinations with oxygenation where relevant. Fig.2b highlights the photocatalytic performance in the degradation of PCP in the absence of an electron scavenger on the conduction band edge. The oxidation process is facilitated by metal halide anions and formic acid in the various experimental sets towards prevention of the recombination step. The reduction in the presence of the electron donors exclusively ranged between 37 and 52 percent, while the reduction in the exclusive presence of the electron acceptor is 56 percent. This demonstrates that both the valence and conduction band edge recombination prevention approaches can be similarly efficient.
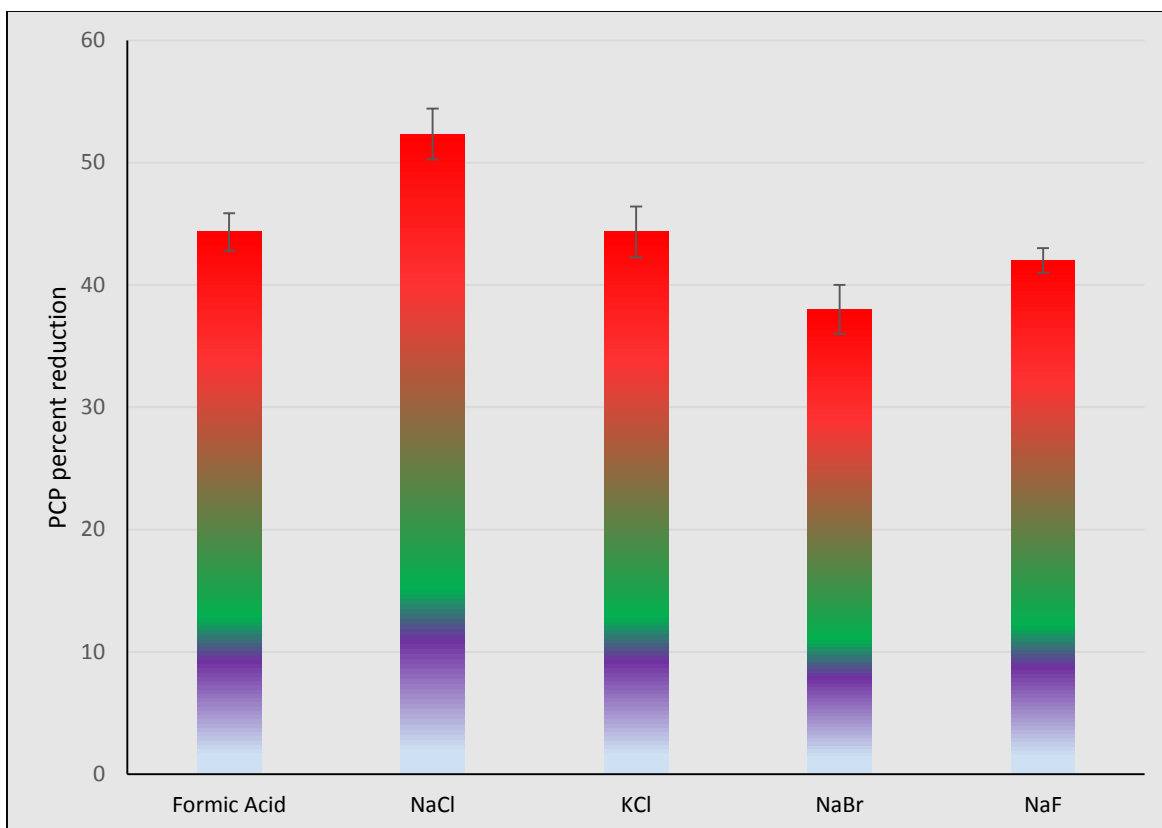
6

Fig.2b. Photocatalytic percentage reductions of PCP under isolated conditions of the highest performing halide anions sets. $[TiO_2]$ 30 mg L^{-1}, gas flow and purge 20 mL min^{-1}, $[PCP]_o$ 10 mg L^{-1}

The combination of the electron acceptor and each electron donor recorded a reduction range between 69 and 85 percent, where the combination with *KCl* is the least efficient at the 20 mg L^{-1} for all metal halides and formic acid in 120 minutes of irradiation, as evident in Fig.2a.

3.1. The effect of halide ions in the photocatalytic process

In the photocatalytic process, the photogenerated active holes react with surface hydroxyl groups or water molecules to form trapping sites. The formed radicals oxidise organic pollutant molecules via radical mediated mechanisms. The radical-surface complex can be influenced by the presence of chloride ions [19], and by theoretical extension, can be influenced by other halide ions. Chloride ions can act as hole blockers by scavenging the oxidising radical species and completing with contaminant molecules. They influence the oxidation process through e^-h^+ recombination prevention as a competitive surface blocker at the valence band level, but can also be detrimental to the oxidation process when excess numbers are present in solution. The blocking mechanism of chloride ions is suggested to have positive influences on reductive pathways generation through recombination prevention at the conduction band level, and this has been reported in various studies [30-33]. The influence of *Cl* ions have also been reported to be pH

7

dependent in aqueous systems, Yang et al. [19] found that at the point of zero charge (pH$_{pzc}$) very little influence was made by Cl^- to the photoreduction of chlorobiphenyls, the reason suggested by Wang et al. [34] is that chloride concentrations near the TiO_2 surface are lower than that in bulk solution. The current study's optimal pH values were recorded between 5.2 and 5.6. Given that this range is lower than that of pH$_{pzc}$ it can be expected that there is a possibility of elemental interference by the chloride ions present in solution. This is expected to be in the form of competition for generated active surface sites against matrix soluble organic compounds, namely PCP and the generated hydroxyl radicals. Eq.4 shows the surface hole and chloride reaction that leads to site blocking at the valence band level.

$$HO^{\bullet} + Cl^- \longrightarrow ClOH^{\bullet}$$

(4)

Piscopo et al. [35] found that when the concentration of chloride ions was increased there were fewer HO° radicals generated and greater photocatalytic inhibition was experienced. Yang et al. [19] though in agreement with Piscolo et al.'s findings noted that a different event may occur at high chloride ion concentrations that may be of contrast, which is that chloride ligands may be able to form inner-sphere surface complexes resulting in TiCl formation. The reaction reported that explains the inner-sphere complex is given in Eq.5.

$$TiOH + Cl^- + H^+ \overset{k_{Cl^-}}{\rightleftharpoons} TiCl + H_2O$$

(5)
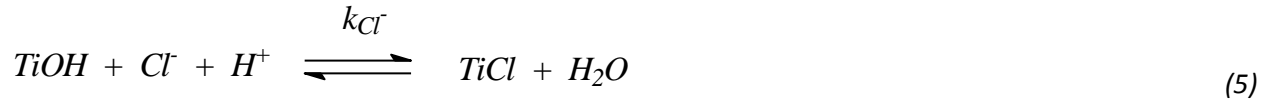
Kormann et al., [36] reported that the reaction presented in Eq.5 only takes place at low pH values, sighting a pH > 6.2 to be negligible to $TiCl$ complex formation. Yang et al. [19] working at a pH region between 5 and 6 reported that the formation of inner-sphere complexes are considerable, this is within the pH range measured in the current study.

$$TiCl + h^+ \longrightarrow TiCl^{\bullet}$$

(6)

$$TiCl^{\bullet} + Cl^{\bullet} \rightleftharpoons TiCl_2^{\bullet\bullet}$$

(7)

Yamazaki et al. [37] documented that the chloride facilitated titanium hole scavenging process becomes prominent once the initial titanium monochloride complex is formed, the follow-up reactions to Eq.5 take the forms of Eqs.6 and 7. Hirakawa and Nasaka [38] suggested that with a potential of + 2.47, the formed chloride radicals can in principle oxidise organic chemical compounds, however no evidence of this was reported in this paper. Yang et al., [19] found that the formed chloride radicals were unsuccessful in the photocatalytic oxidation of methyl blue, and suggested that this may be an organic class specific process as they found that the electropositive molecules could not be transported to the inner surface with methyl blue.

8

Fig.3 shows the degradation rate constants (k) of PCP with increases in *NaCl* dosages of 20 mg L^{-1} increments. The oxygenated data sets in isolation recorded k of 0.025 mg L^{-1} min L^{-1}. The photocatalytic sets voided of an electron scavenger (*O$_2$*) in combination with sodium chloride performed the least efficient, but the highest of these (20 mg L^{-1}) still performed well enough to remove almost 50% of PCP. Though this was not implausible, it was surprising that such a significant amount of degradation took place, Fig.2. This suggests that the reliance of the photocatalytic principle to oxygenation for recombination prevention in isolation is overstated in literature or that the importance of the alternative recombination prevention processes is underemphasised. A more efficient semiconductor photocatalysis promotion method would be to manage the e$^-$-*h$^+$* recombination prevention steps from both the conduction and valence band edges. 56 percent of PCP was oxidised under conditions of just oxygenation, coincidentally this value is not too far from the performance of the addition of the salt in the absence of oxygenation that registered 52 percent.

Fig.3 shows that the 20 mg L^{-1} salt addition recorded the most efficient degradation of pentachlorophenol. When the salt concentration were doubled, the degradation of PCP was compromised, and adding four-times the concentration of salt made negligible difference to that recorded in 40 mg L^{-1}. These findings are consistent with those obtained by Krivec et al. [29] where they confirmed that when a certain critical concentration of chloride ions has been reached, the system cannot initiate further. Doubling the salt mass concentrations from 40 to 80 mg L^{-1} slightly impeded the already severely compromised performance, and registered efficiencies worse than those in the complete absence of sodium chloride. The overall findings with regards to *NaCl* suggest that there is impairment in the photocatalytic ability to oxidise PCP with increased concentrations beyond 20 mg L^{-1}. Which means that whatever electron donor induced improvements to the recombination prevention process made at the 20 mg L^{-1} concentration levels are negatively matched by the excess chloride ions present.

A point of interest might be that photocatalytic performance does not deteriorate equitably and systematically with increased salt additions. The nature of process inhibition through surface hole competition and eventual blocking suggests that more chloride ions means more unavailable oxidation sites on the semiconductor catalyst, which can in principle lead to total inhibition of the photocatalytic process, however that is not what has been experienced in this study. The majority of published papers on this subject including those by Guillard et al. [30] and Chen et al. [31] are of the opinion that increases in chloride ions should lead towards total inhibition of the photocatalytic process. There is perhaps an equilibrium reaction taking place on the surface of the titania complex to explain the findings in the current study, this is proposed and represented in Eq.8.
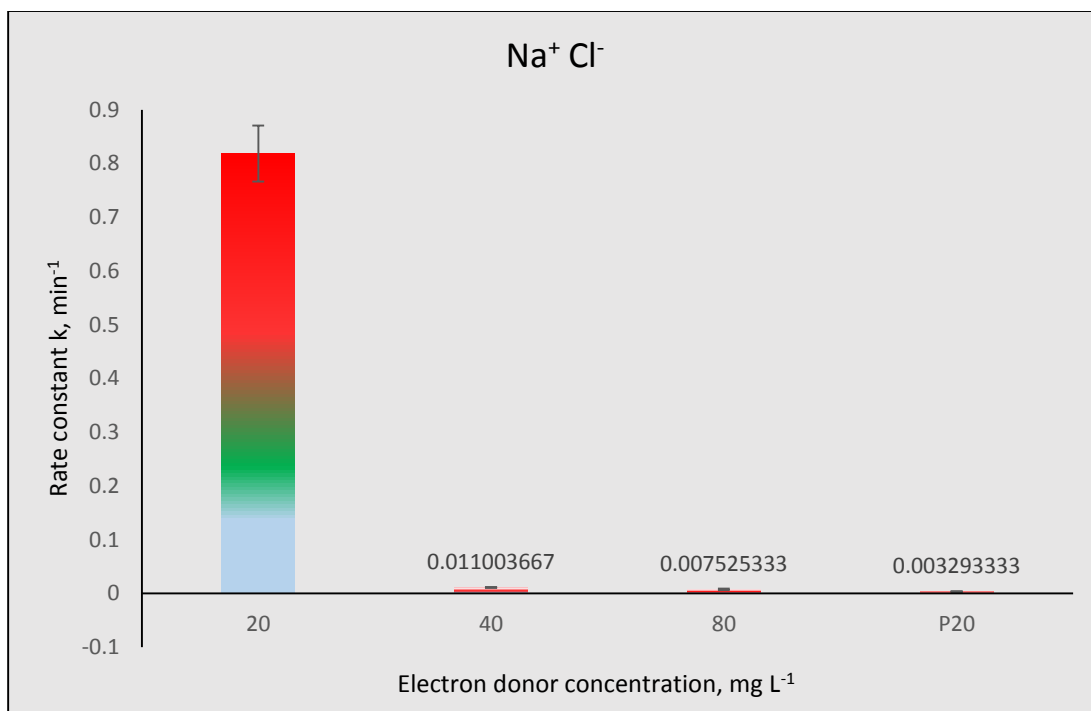
Fig.3. The influence of chloride ions in the form of NaCl to the photocatalytic degradation kinetics of PCP. [TiO$_2$] 30 mg L^{-1}, gas flow and purge 20 mL min^{-1}, C$_o$ 10 mg L^{-1}
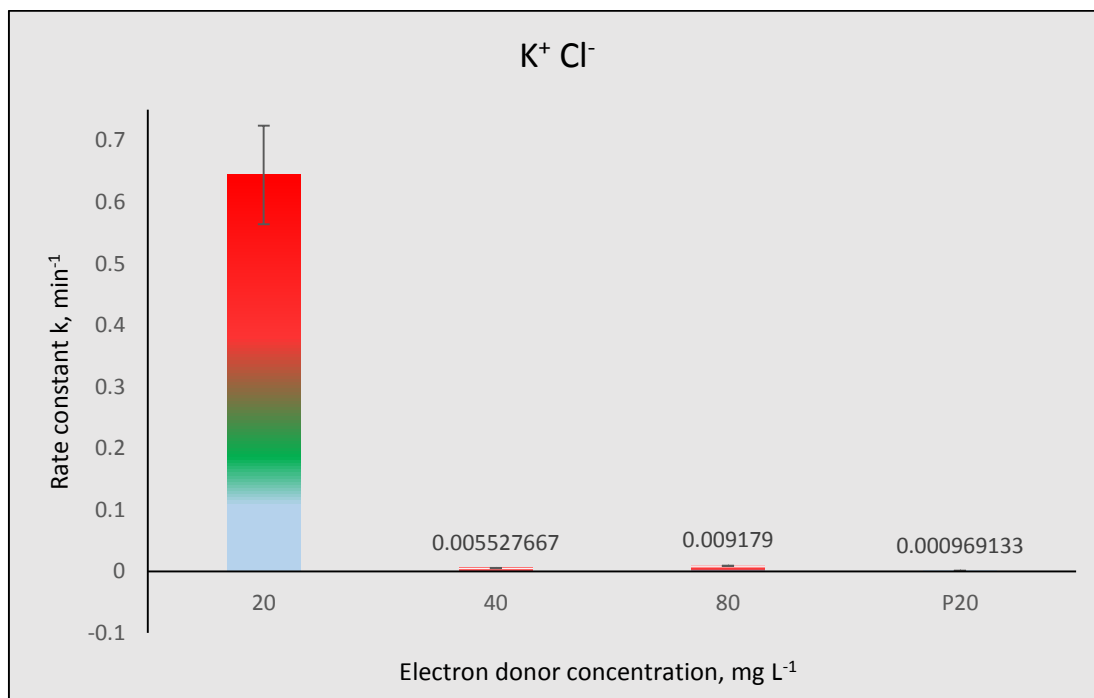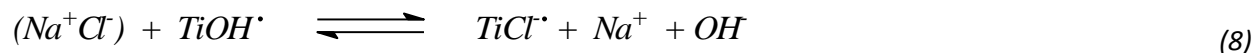

Fig.4. The influence of chloride ions in the form of KCl to the photocatalytic degradation kinetics of PCP. [TiO$_2$] 30 mg L^{-1}, gas flow and purge 20 mL min^{-1}, C$_o$ 10 mg L^{-1}

10

$$(Na^+Cl^-) + TiOH^\bullet \rightleftharpoons TiCl^\bullet + Na^+ + OH^- \tag{8}$$

Eq.8 is similar to the inner-sphere complex reaction in Eq.5 explaining an alternative mechanism of chloride ions complexes acting as degradation side products that undermine the photocatalytic ability to oxidise organic compounds. Another point of interest may pertain to whether the *NaCl* concentration of 20 mg L^{-1} is the ideal or the critical level at which the abundance of chloride ions favour the photocatalytic process. Reproducibility of measurements at mass ranges below 20 mg were a challenge for reactors designed to hold solution volumes not in excess of 1000 mL. Singular grains or simple agglomeration resulted in statistical uncertainties, even two mass factor increases in salt concentrations still resulted in non-absolute rate constants differentiation beyond 20 mg L^{-1}, it is thus reasonable to assume that the 20 mg L^{-1} is the critical concentration level. It is interesting to note that there is little qualitative difference between the rate constants profiles derived between sodium chloride and potassium chloride, Fig.3 and Fig.4. The main difference between the alkali metals, with the exception of size is their reactivity towards water molecules, the product of these reactions are metal hydroxides (Metal-OH) and the release of gaseous hydrogen (H_2). Potassium reacts to water in a much fiercer manner than sodium, releasing more energy. A proposed explanation for the lesser efficiency oxidation when using *KCl* as an electron donor in comparison to *NaCl* may be that the dissociated metal (*K*) aggressively forms potassium hydroxide (*KOH*), thus discouraging the formation of free hydroxyl radicals that result from the conduction band electron acceptance. Eq.8 proposes that an equilibrium reaction takes place on the surface of the titania complex in *NaCl* applications, this equilibrium process may be impaired in the presence of a much stronger alkali metals such as potassium.

The abundance of the favourably released dissociated chloride ions from potassium chloride molecules may behave as rate limiting step at higher concentrations and possibly enhance the oxidation process at lower concentrations. The project also attempted to determine whether there was an influential difference in the performance of other halogens elements that were bonded to the alkali metals in the photocatalytic oxidation of pentachlorophenol in aqueous systems. The halogen group constitutes of fluoride (*F*), chloride, bromine (*Br*), iodine (*I*) and astatine (*At*), and forms part of group 17 of the periodic table. Displacement reactions are experienced when a more reactive halogen dislodges a less reactive halogen. This phenomenon may be something to ponder with regards to photocatalytic oxidation of polyhalogenated organic compounds such as pentachlorophenol in aqueous systems, this may not be empirically falsifiable using current data but deductive reasoning may be fruitful. Figs.5 and 6 show the photocatalytic reduction rate constants of pentachlorophenol in the presence of *NaBr* and *NaF*, respectively. The overall photocatalytic reduction percentages of PCP in Fig.2 shows little significant difference in the values between sodium chloride, sodium bromide and sodium fluoride, where 79, 85 and 81 percent reductions took place respectively in the 20 mg L^{-1} experimental sets.
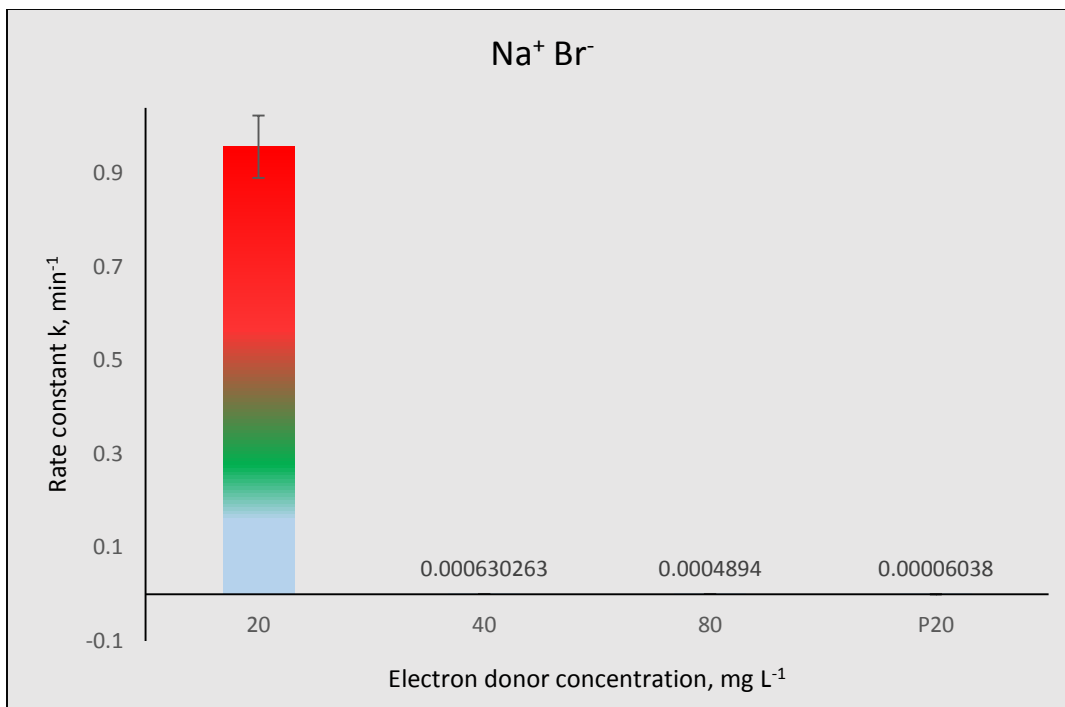
11

Fig.5. The influence of halide ions in the form of NaBr to the photocatalytic degradation kinetics of PCP. [TiO$_2$] 30 mg L^{-1}, gas flow and purge 20 mL min^{-1}, C$_o$ 10 mg L^{-1}
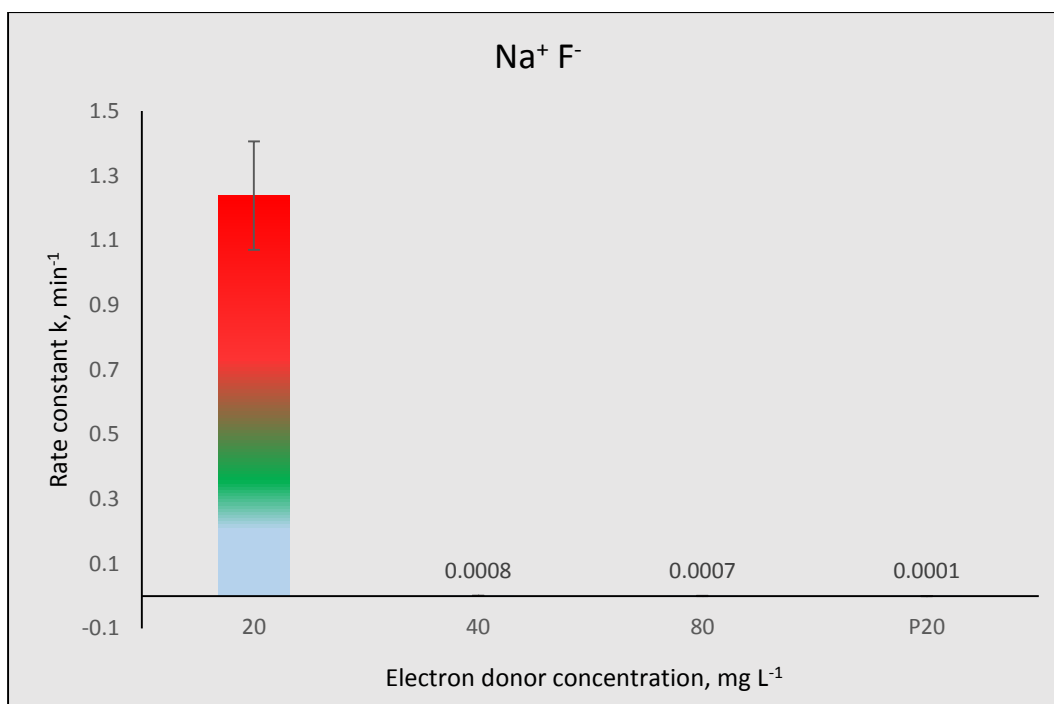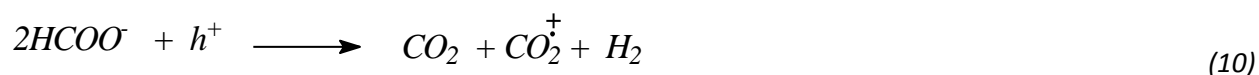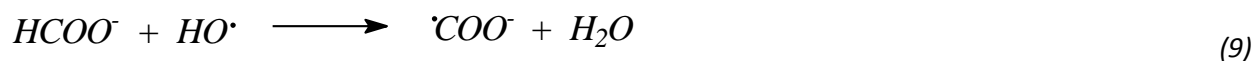

Fig.6. The influence of halide ions in the form of NaF to the photocatalytic degradation kinetics of PCP. [TiO$_2$] 30 mg L^{-1}, gas flow and purge 20 mL min^{-1}, C$_o$ 10 mg L^{-1}

Increases in concentration of both *NaBr* and *NaF* beyond the 20 mg L^{-1} similarly to *NaCl* and *KCl* resulted in photocatalytic deficiencies, this is evident in Figs.5 and 6. The concentration was not linearly reduced nor recorded to be regressive, similarly to *NaCl*, there seemed to be little correlation between increases in applied concentrations and the impairment to photocatalytic process. The performances of the higher salts concentrations compromised the oxidation process to a point significantly less than that of just oxygen in isolation acting as an electron scavenger. An important observation of Figs.5 and 6, and complementary results is that the higher reaction potential halide species of bromide and fluoride achieved improved rate of PCP photocatalytic degradation constants than the chloride anions. The increased salts concentration of 40 and 80 mg L^{-1} masses also registered significantly impaired efficiencies, which showed that there was no systematic correlation between increases in salt concentration and photocatalytic performance beyond the critical level. This is attributed to the strengths of the semiconductor surface moieties and the dissociated chargers bond's in solution. Though the formed complexes of higher reaction potential anion species may be stronger, there still must exist an equilibrium state facilitated by an unidentified mechanism that maintains the free chargers responsible for the continual degradation of pentachlorophenol, however limited the rate of oxidation.

The mechanistic pathways discussed with regards to halide ions, their substitution propensities, and the possibility of direct oxidation to lower level chlorosubstituted phenols from the higher complex pentachlorophenol compound means that there is a high probability of significant numbers of chloride ions dissociated in aqueous matrix or trapped on the surface hole. The addition of electron donors in the form of metal halide salts would most probably reactively disrupt the surface-chloride ion radicals represented in Eq.6 and Eq.7. When fluoride is the added halide ion electron donor, a chloride displacement reaction would be experienced as fluoride has a higher reaction potential in comparison to the solution present chloride ions oppose to bromide where the reverse may occur. There is thus a possibility of semiconductor catalysis adsorption selectivity amongst group 17 elements. This was not investigated in this study, there was however a comparative compound reactivity determination conducted, where formic acid as an organic compound was analysed for its effects as an electron donor.

3.2. The effect of formic acid in the photocatalytic process

Formic acid is the simplest dissociated carboxylic acid and has been used in many studies for its properties as an election donor. Tan et al. [39] studied the effects of organic hole scavengers on the photocatalytic reduction of selenium anions, they found formic acid to be the most effective scavenger amongst the group selected. The formic acid surface reaction as proposed by Tan et al. is given in Eq.9. Rengaraj and Li [40] proposed that a simple reaction and conversion can be achieved as evident in Eq.10 resulting in stronger reactive $CO_2^{\circ+}$ species than conventional CO_2 [41].

$$HCOO^- + HO^\bullet \longrightarrow {}^\bullet COO^- + H_2O \tag{9}$$

$$2HCOO^- + h^+ \longrightarrow CO_2 + CO_2^{\bullet+} + H_2 \tag{10}$$

13

The equations above show the formate reaction with surface holes resulting in H_2O production from the release of the H^+ ions, this would essential render the surface hole inaccessible by the ejected electron in the conduction band. Formic acid also exhibited the highest hydrogen production enhancement ability in a study by Puangpetch et al., [41] where it outperformed methanol, acetic acid, propanoic acid, hydrochloric acid, and sulphuric acid. The formic acid oxidation to carbon dioxide is straight-forward and involves minimal intermediate products.
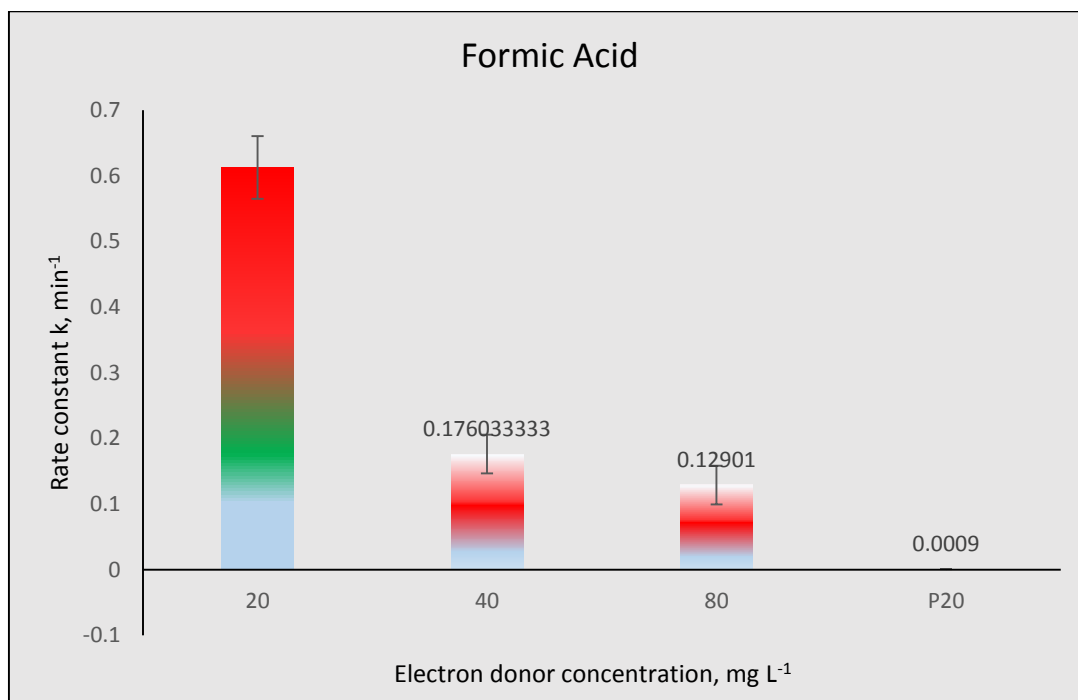

Fig.7. The influence of formic acid to the photocatalytic degradation kinetics of PCP. [TiO_2] 30 mg L^{-1}, gas flow and purge 20 mL min^{-1}, C_o 10 mg L^{-1}

Fig.7 shows the kinetic effects of progressive increases in formic acid concentrations in the degradation of pentachlorophenol. The argon purged degradation profile noticeably and expectedly recorded the least efficiency, what is also important to note is that though there was no involvement of an electron scavenger, 44 percent reduction was recorded. This can deductively be attributed to the presence of formic acid. There is a significant different in the 24.4 mg L^{-1} profile that is coupled with oxygenation and in its absence, an improvement of 28 percent was recorded in betterment to that of exclusive oxygenation. Fig.7 shows that increases in formic acid concentrations do not have notable positive impact on the performance of the photocatalytic process beyond the 24.4 mg L^{-1} concentration, there is however an indication that this increase in concentration may lead to oxidation hindrance. This is in line with findings by Li et al., [43] where at low formic acid concentrations the reduction of analytes was influenced by increment changes of the organic electron donor concentrations. This was the difference between the application of formic acid and metal halide complexes, where there are systematic effects in the increase

14

of the electron donor concentration and the inhibition of the photocatalytic process, where-as this phenomena did not occur or was significantly minimised in the application of sodium halides. Organic compounds behave differently depending on many factors including the functional groups of compounds. The photocatalyst surface adsorption element is pivotal to the oxidation process, as the radical hydroxyl species diversity and abundance can result from multiple process, and free hydroxyl charges behave less stringently than the hydrogen-halide complexes that are formed in halide rich matrices.

4. Conclusion

The study investigated the impacts of the involvement of different metal halide complexes and formic acid in the photocatalytic process as reaction promoters in the presence and absence of oxygen acting as an electron accepting scavenging molecule. The exclusively oxygenated and exclusively sodium halide electron donating complexes and formic acid experimental sets all performed near equally in isolation, while the coupled recombination blocking steps performed far better in combination. Progressive increases in electron donor concentrations near-completely halted the photocatalytic process when sodium halides were applied in excessive concentrations, while the organic formic acid electron donor registered a negative kinetic relationship with excessive increases in concentration. It was determined that beyond a specific electron donor concentration which may be uniquely specific to each configured system, the photocatalytic process is compromised.

15

5. References

[1] W. Wang, S. Wang, J. Zhang, Z. Hu, X. Zhang, J.M. Sierra, Degradation kinetics of pentachlorophenol and changes in anaerobic microbial community with different dosing modes of co-substrate and zero-valent iron, International Biodeterioration & Biodegradation. 113 (2016) 126-133.

[2] M. Antenopoulou, D. Vlastos, I. Konstantinou, Photocatalytic degradation of pentachlorophenol by N-F-TiO2: identification of intermediates, mechanism involved, genotoxicity and ecotoxicity evaluation, Photochemical and Photobiological Sciences. 14 (2015) 520-527.

[3] L.J. Xu, J.L, Wang, Degradation of chlorophenols using a novel Fe^0/CeO_2 composite, Applied Catalysis B: Environmental. 142-143 (2013) 396-405.

[4] K.C. Christoforidis, M. Louloudi, Y. Deligiannakis), Complete dechlorination of pentachlorophenol by a heterogeneous SiO2-Fe-porphyrin catalyst. Applied Catalysis B: Environmental. 95 (2010) 297-302.

[5] J. Michałowicz, W. Duda, Phenols - sources and toxicity, Polish Journal of Environmental Studies. 16 (2007) 347–362.

[6] H.L. Chang, L. Alvarez-Cohen, Model for cometabolic biodegradation of chlorinated organics, Environmental Science and Technology. 29 (1995) 2357-2367.

[7] K. Govindan, M. Raja, M. Noel, E.J. James, Degradation of pentachlorophenol by hydroxyl radicals and sulfate radicals using electrochemical activation of peroxomonosulfate, peroxodisulfate and hydrogen peroxide, Journal of Hazardous Materials. 272 (2014) 42-51.

[8] M. Pera-Titus, V. García-Molina, M.A. Baños, J. Giménez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, Applied Catalysis B: Environmental. 47 (2004) 219-256.

[9] M. Sung, S. Z. Lee, H. L. Chan, Kinetic modelling ring byproducts during ozonation of pentachlorophenol in water, Separation and Purification Technology. 84 (2012) 125-131.

[10] M. Aslam, S.M. Tahir, M.I.I. Iqbal, N. Salah, M.A. Gondal, A. Hameed, Sunlight mediated removal of chlorophenols over tungsten supported ZnO: Electrochemical and photocatalytic studies, Journal of Environmental Chemical Engineering. 3 (2015) 1901-1911.

[11] N. Wang, X. Li, Y. Wang, X. Quan, G. Chen, Evaluation of bias potential enhanced photocatalytic degradation of 4-chlorophenol with TiO_2 nanotube fabricated by anodic oxidation method, Chemical Engineering Journal. 146 (2009) 30–35.

[12] E. da Costa, P.P. Zamora, A.J.G. Zarbin, Novel TiO_2/C nanocomposites: synthesis, characterization, and application as a photocatalyst for the degradation of organic pollutants, Journal of Colloidal and Interface Sciences. 368 (2012) 121–127.

[13] J. Ângelo, L. Andrade, L.M. Madeira, A. Mendes, An overview of photocatalysis phenomena applied to NOx abatement, Journal of Environmental Management. 129 (2013) 522-539.

[14] X. Chang, G. Ji, Q. Sui, G. Yu, Rapid photocatalytic degradation of PCP–Na over $NaBiO_3$ driven by visible light irradiation, Journal of Hazardous Materials. 166 (2009) 728-733.

[15] X. Chang, J. Huang, Q. Tan, M. Wang, G. Ji, S. Deng, G. Yu, Photocatalytic degradation of PCP-Na over BiOI nanosheets under simulated sunlight irradiation, Catalysis Communications. 10 (2009) 1957-1961.

[16] M. Antonopoulou, I. Konstantinou, Environmental Science and Pollution Research. 22 (2015) 9438-9448.

[17] K. Wang, Y. Hsieh, C. Wu, C. Chang, The pH and anion effects on the heterogeneous photocatalytic degradation of o-methylbenzoic acid in TiO_2 aqueous suspension, Chemosphere. 40 (2000) 389-394.

[18] P. Caregnato, J.A. Rosso, J.M. Soler, A. Arques, D.O. Martire, M.C. Gonzalez, Chloride anion effect on the advanced oxidation processes of methidathion and dimethoate: Role of Cl^{2-} radical, Water Research. 47 (2013) 351-362.

[19] S.Y. Yang, Y.X. Chen, L.P. Lou, X.N. Wu, Involvement of chloride anion in the photocatalytic process, Journal of Environmental Science. 17 (2005) 761-765.

[20] M.L. Dell'Arciprete, J. Soler, L. Santos-Juanes, A. Arques, D.O. Mártire, J. Furlong, M.C. Gonzalez, Reactivity of neonicotinoid insecticides with carbonate radicals, Water Research. 46 (2010) 3479-3489

[21] E.M. Rodríguez, G. Márquez, M. Tena, P.M. Álvarez, F.J. Beltrán, Determination of main species involved in the first steps of TiO_2 photocatalytic degradation of organics with the use of scavengers: The case of ofloxacin, Applied Catalysis B: Environmental. 178 (2015) 44-53.

[22] P. Salvador, On the nature of photogenerated radical species active in the oxidative degradation of dissolved pollutants with TiO 2 aqueous suspensions: A revision in the light of the electronic structure of adsorbed water, J. Phys. Chem. C. 111 (2007) 17038-17043.

[23] A. Mills, S. Le Hunte, An overview of semiconductor photocatalysis, Journal of Photochemistry and Photobiology A. 108 (1997) 1-35.

[24] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental Applications of Semiconductor Photocatalysis, Chemical Reviews. 95 (1995) 69-96.

[25] C.S. Turchi, D.F. Ollis, Photocatalytic Degradation of Organic Water Contaminants: Mechanisms Involving Hydroxyl Radical Attack, Journal of Catalysis. 122 (1990) 178-192.

[26] S.J. Armakovic, S. Armakovic, N.L. Fincur, F. Sibul, D. Vione, J.P. Setrajcic, B.F. Abramovic, Influence of electron acceptors on the kinetics of metoprolol photocatalytic degradation in TiO_2 suspension. A combined experimental and theoretical study, RSC Advances. 54589.

[27] M. Muruganandham, M. Swaminathan, Photocatalytic decolourisation and degradation of Reactive Orange 4 by TiO_2-UV process, Dyes and Pigments. 68 (2006) 133-142.

[28] S. Iguchi, K. Teramura, S. Hosokawa, T. Tanaka, Effect of the chloride ion as a hole scavenger on the photocatalytic conversion of CO_2 in an aqueous solution over Ni-Al layered double hydroxides, Physical Chemistry Chemical Physics. 17 (2015) 17995-18003.

[29] M. Krivec, R. Dillert, D.W. Bahnemann, A. Mehle, J. Strancar, G. Drazic, The nature of chlorine-inhibition of photocatalytic degradation of dichloroacetic acid in a TiO_2-based microreactor, Physical Chemistry Chemical Physics. 16 (2014) 14867-14873.

[30] C. Guillard, H. Lachheb, A. Houas, M. Ksibi, E. Elaloui, J. Herrmann, Influence of chemical structure of dyes, of pH and of inorganic salts on their photocatalytic degradation by TiO_2 comparison of the efficiency of powder and supported TiO_2, Journal of Photochemistry and Photobiology A. 158 (2003) 27-36.

[31] J. Chen, D. Ollis, W.H. Rulkens, H. Bruning, Photocatalyzed Oxidation of Alcohols and Organochlorides in the Presence of Native TiO_2 and Metallized TiO_2 Suspensions. Part 2: Photocatalytic Mechanism, Water Research. 33 (1999) 669-676.

[32] B. Zhu, L. Zou, Trapping and decomposing of color compounds from recycled water by TiO_2 coated activated carbon, Journal of Environmental Management. 90 (2009) 3217-3225.

[33] M. Abdullar, G.K.C. Low, R.W. Mathews, Effects of common inorganic anions on rates of photocatalytic oxidation of organic carbon over illuminated titanium dioxide, Journal Physical Chemistry. 94 (1990) 6820-6825.

[34] Y.B. Wang, C.S. Hong, F. Fang, Effect of Solution Matrix on TiO_2 Photocatalytic Degradation of 2-Chlorobiphenyl, - Environmental Engineering Science. 16 (1999) 433-440.

[35] A. Piscopo, D. Robert, J.V. Weber, Influence of pH and chloride anion on the photocatalytic degradation of organic compounds: Part I. Effect on the benzamide and para-hydroxybenzoic acid in TiO_2 aqueous solution, Applied Catalysis B: Environmental. 35 (2001) 117-124.

[36] C. Kormann, D.W. Bahnemann, M.R. Hoffmann, Photolysis of chloroform and other organic molecules in aqueous titanium dioxide suspensions, - Environmental Science Technology. 25 (1991) 494-5010.

[37] S. Yamazaki, T. Tanimura, A. Yoshida, Reaction Mechanism of Photocatalytic Degradation of Chlorinated Ethylenes on Porous TiO_2 Pellets: Cl Radical-Initiated Mechanism, - Journal of Physical Chemistry A. 108 (2004) 5183-5188.

[38] T. Hirakawa, T. Nasaka, Properties of $O_2^{\bullet-}$ and $OH^{\bullet}$ Formed in TiO_2 Aqueous Suspensions by Photocatalytic Reaction and the Influence of H_2O_2 and Some Ions, Langmuir. 18 (2002) 3247-3254.

[39] T.T.Y. Tan, D. Beydoun, R. Amal, Photocatalytic Reduction of Se(VI) in Aqueous Solutions in UV/TiO_2 System: Kinetic Modeling and Reaction Mechanism, Journal of Physical Chemistry B. 107 (2003) 4296-4303.

18

[40] S. Rengaraj, X.Z. Li, Enhanced photocatalytic reduction reaction over Bi_3^+-TiO_2 nanoparticles in presence of formic acid as a hole scavenger, Chemosphere. 66 (2007) 930-938.

[41] Y. Li, F. Wasgestian, Photocatalytic reduction of nitrate ions on TiO_2 by oxalic acid, Journal Photochemistry Photobiology A. 112 (1998) 255-259.

[42] T. Puangpetch, S. Chavadej, T. Sreethawong, Hydrogen production over Au-loaded mesoporous-assembled SrTiO3 nanocrystal photocatalyst: effects of molecular structure and chemical properties of hole scavengers, Energy Conversion and Management. 9 (2011) 2256-2261.

[43] L. Li, F. Jiang, J. Liu, Y. Wan, S. Zheng, Enhanced photocatalytic reduction of aqueous Pb(II) over Ag loaded TiO_2 with formic acid as hole scavenger, Journal of Environmental Science and Health, Part A. 47 (2012) 327-336.