



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



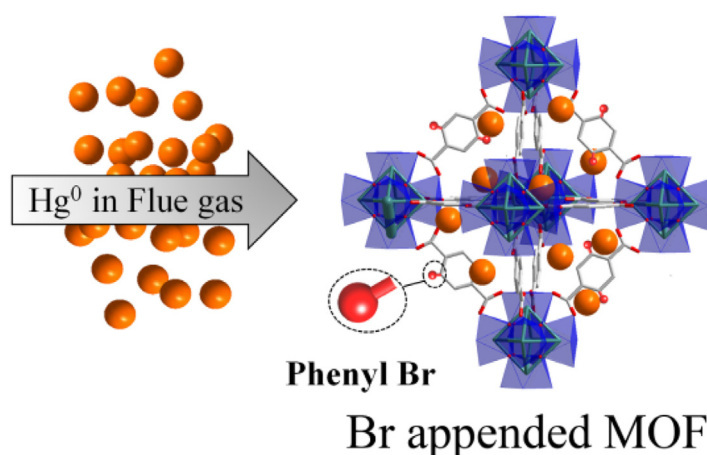
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## HIGHLIGHTS

- Facilitation of photocatalysis using simple metal-halides as VB hole scavengers.
- Recombination prevention by coupled valence and conduction band approaches.
- Determination of anions critical levels beyond which process retardation occurs.
- Determination of the photocatalytic process rate of reaction kinetics.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 13 June 2016

Received in revised form 17 August 2016

Accepted 29 August 2016

Available online 30 August 2016

### Keywords:

Alkali metals

Electron donors

Photocatalysis

Polychlorinated phenol

Oxidation

## 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.

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## 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]. Pentachlorophe-

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nol (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 [2,8,10,14–16]. 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 electron 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 electrons ( $e^-$ ) 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 ( $HO^\bullet$ ) 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  $O_2^{\bullet -}$  is the free charged oxygen specie.



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 electrons and valence band pairing holes. This can be achieved either by instantly and reactively utilising the promoted electrons ( $e^-$ ) 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 ( $CH_2O_2$ ), 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 (Schnellendorf, 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 quartz 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.

### 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<sup>-1</sup> 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

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