



Catalytic wastewater treatment: Oxidation and reduction processes. Recent studies on chlorophenols

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ABSTRACT

Although the water resource is not exhaustible, the water quality must be preserved. It does represent a major challenge for the coming decades. Since water is used for many different industrial, agricultural and domestic applications, a wide variety of waste effluents is being produced. Since conventional wastewater treatment plants, mainly based on biological processes, are poorly efficient for the treatment of toxic and/or non-biodegradable and/or highly concentrated effluents, new solutions are being looked for. Many different approaches have been investigated and catalytic processes may play a crucial role. Both oxidation and reduction processes for the treatment of chlorophenols have been reviewed. The principle of each of those processes is being described, the key parameters are identified and subsequently the major challenges to be overcome both in terms of material science and/or catalytic efficiency (activity and selectivity) are highlighted to offer a general but homogenized overview of the state-of-the-art in the different fields. Finally, the most recent developments in each field are shortly discussed.

1. Introduction

From the end of the 20th century, with an increasing social and political concern on the environment, the associated health risks and the possible harmful effects of the hazardous organic substances present in many industrial effluents, the removal of toxic organic compounds from aqueous wastewater (but also surface and ground waters) has drawn a lot of attention [1–5].

Among the many different pollutants encountered in the industrial wastewaters, chlorophenols (CPs) are very important chemical compounds and intermediates in several chemical industries, such as the production of sanitizers, germicides, precursors of pesticides and dyes. They are also in use in the wood industry as preservative agents and in the paper and cosmetic (Personal Care Products, PCPs) industries. Because most CPs are toxic, known or suspected as endocrine disrupting compounds (EDCs), possibly carcinogenic, mutagenic or teratogenic, hardly biodegradable and very difficult to remove from the environment (persistent, bioaccumulation), they constitute a particular group of priority toxic pollutants listed in both the US EPA Clean Water Act and the European Decision 2455/2001/EC [1,6]. They are also listed in the 2000 OECD List of High Production Volume Chemicals [7]. Moreover, an additional threat comes from the fact that chlorinated compounds are also known as precursors of dioxins and furans [8]. The maximum allowable concentration of 2-CP in drinking water was

fixed at $10 \mu\text{g L}^{-1}$ [1].

Therefore, to protect the environment, it was necessary to develop some highly efficient techniques for the treatment of such chlorinated organic-containing wastewaters. Among the different techniques applied for the elimination of CPs, both oxidation and reduction processes have been investigated, such as the photocatalytic degradation [9,10], the supercritical water oxidation [11], the Fenton process [12], the ozonation [13], the microwave irradiation [14], the sonochemical degradation [15], the wet air oxidation (WAO) [16–22] and the hydrodehalogenation.

In the following, the very latest developments in the field of catalytic oxidation and reduction processes for the elimination of chlorophenols from water are briefly reviewed. After a short presentation of the principle of each technology and some mechanistic insights, the key issues for each process were identified and, finally, the results of the latest research directly accessible in the open literature were summarized.

2. Oxidation processes

Oxidation processes are probably the most numerous for dealing with wastewater treatment. Many different type of oxidants have been evaluated. These different oxidants might be classified from the most powerful one – the hydroxyl radical – to the less reactive one –

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Table 1
Standard oxidation potential (eV, kJ mol^{-1}) of the most common oxidants involved in oxidation processes.

Oxidant	Standard oxidation potential	
	eV	kJ mol^{-1}
$\cdot\text{OH}$	2.80	270
O_3	2.07	200
H_2O_2	1.77	171
KMO_4	1.67	161
HClO	1.49	144
ClO_2	1.27	123
O_2	1.23	119

molecular oxygen, depending on their oxidation potential. As a general rule, the higher the oxidation potential, the stronger the oxidant. The most common oxidants are listed in Table 1.

Depending on the oxidant which is used and the operating conditions, the oxidation processes might be classified into two main groups: the processes operated under (near) ambient conditions, and the other processes operated at higher temperature and/or pressure. In the first category, one may find (i) the advanced oxidation processes (AOPs) whenever the reactive oxygen species is an hydroxyl radical (e.g. photocatalysis, sonocatalysis, Fenton) and (ii) the chemical oxidation technologies using directly a strong oxidant such as ozone or hydrogen peroxide. In the second one, the most developed process is the catalytic wet air oxidation.

Generally speaking, the first type of processes, operated under very mild reaction conditions, will be limited to the treatment of effluents with a low concentration in pollutants; typically with a Chemical Oxygen Demand (COD) lower than 5 g L^{-1} . On the opposite, wet air oxidation might be valuably used for the treatment of wastewater with a COD in the range $20\text{--}100 \text{ g L}^{-1}$.

2.1. Photocatalysis

Photocatalysis is an AOP. It has been widely investigated in the last decades, especially for gas phase applications. The (photo)catalyst has to be a semi-conductor. Upon irradiation with light of the appropriate energy, i.e. an energy higher than the band gap of the semi-conductor, an electron from the valence band might be excited to the conduction band. As a result, a pair of hole (h^+ in the valence band) and electron (e^- in the conduction band) is created. This hole-electron pair is very unstable and if they do not recombine, these two species might be responsible for subsequent oxidation and reduction reactions, respectively. Upon reaction with oxygen or water at the surface of the semi-conductor, different oxidative species will be generated such as hydroxyl radicals, hydroperoxyl radicals, superoxide radicals, etc. These species are directly responsible for the reactivity of the (photo) catalyst.

The efficiency of the process has been demonstrated to depend on many different parameters. The type of photocatalyst has a direct impact on the type of light to be used. The most common photocatalyst is certainly titanium dioxide, with a band gap ca. 3.2 eV in the case of anatase. Consequently, only UV light with a wavelength lower than ca. 388 nm can be efficiently applied. Another parameter to be taken into consideration is the amount of catalyst introduced in the reactor. An optimum photocatalyst loading always exists. Above this optimum, the opacity of the solution may prevent light diffusion and absorption down to the bulk of the solution. Light diffusion into the bulk of the liquid and absorption by the photocatalyst might also be hindered if the light might be absorbed elsewhere, for example if the active photocatalytic phase would be deposited on a black body such as a carbon type of support. Similarly, the radiant flux, i.e. the flux of photons, needs to be optimized. If more and more hole-electron pairs will be generated as the

radiant flux increases, above the optimum, the probability for direct recombination between electron and hole will also increase sharply. Consequently, above the optimum, shining more light over the photocatalyst is totally inefficient. As far as light irradiation is concerned, the angle of incidence of the light with respect of the photocatalyst surface is also of importance. The reactor design should be adapted so that this angle is close to 90° . Reactor design optimization is also crucial to avoid any mass transfer limitation, especially the oxygen transport into the bulk of the solution. Aeration has to be optimized to insure uniform mixing. It will also contribute to some extent to prevent recombination between holes and electrons. On the reaction side, a number of parameters are also of importance. The type of pollutant as well as the concentration of the pollutant have to be considered. If the pollutant would absorb light too strongly (e.g. some dyes), the photo-activation of the catalyst might be hindered. In parallel, if the concentration in pollutant is too high, strong adsorption of the pollutant on the photocatalyst surface may occur. The photocatalyst surface might get saturated with the pollutant and the generation of the reactive species from the reaction between hole, electron, oxygen and water might be hindered. Moreover, the reaction temperature will have a direct impact on the adsorption of the reactant and subsequently on the catalysis. Adsorption is an exothermic phenomenon, so that adsorption will progressively decrease as the reaction temperature increases. In addition, the pH of the solution might also have an impact on the adsorption and so, on the reaction. Depending on the speciation of the pollutant in water (pK_A) and the overall surface charge of the photocatalyst (pH_{ZPC}) as a function of pH, electrostatic interactions might be involved. Electrostatic attraction will favor adsorption, while electrostatic repulsion will hinder the adsorption and subsequently the reaction. Finally, when looking at real wastewater, the presence of ionic species in the effluent, such as carbonates, hydrogenocarbonates, Cl^- , etc. may perturb the reaction. Some would act as radical traps, other as competitors, etc. Generally, the best and optimum conditions have to be determined for each photocatalyst.

Considering the photo-activation mechanism as mentioned in the introduction of this section and looking at better performances, the most recent research works focused on the development of improved photocatalytic materials, with two major lines aiming at (i) better charge separation and better charge migration and (ii) visible-light driven photocatalysis. In the first case, researchers alternatively looked for lower electron-hole recombination rates, long-lived electrons or quick photo-excited electron transfer to the reaction site. In the second case, with the objective of sustainable development, solar photocatalysis is extensively studied. For that, new materials are tentatively developed, playing with Z-scheme, surface plasmon resonance or quantum size effects. Selected examples, combining in most cases both objectives, are reviewed in the following (Table 2).

To improve the photocatalytic activity, metal nanoparticles supported on semiconductors have been used to act as trapping centers in order to avoid recombination. Zhu et al. prepared a series of silver nanoparticles supported on a spinel like MFe_2O_4 ($\text{M} = \text{Co, Zn, Cu, Ni}$) oxide [23]. The support was prepared via a modified chemical co-precipitation method while the silver nanoparticles were introduced on the support via impregnation. The $\text{Ag/CoFe}_2\text{O}_4$ photocatalyst demonstrated the best performances in the oxidation of 4-chlorophenol (20 mg L^{-1} 4-CP, $0.01 \text{ g photocatalyst}$). Simultaneously, visible light absorption by the photocatalyst was improved.

Alternatively, Huerta Aguilar et al. developed different materials where Au or Ag nanoparticles are supported on a core-shell $\text{TiO}_2\text{-Fe}_3\text{O}_4$ type of hybrid material [24]. Benefiting from quantum size effect, metal NPs were used to allow visible light absorption but also fast electron transfer and storage, through the reduction of the TiO_2 band gap (additional electronic states within the band gap), the increase of the charge separation and the subsequent inhibition of hole-electron recombination. The Fe_3O_4 core was introduced to facilitate the separation of the photocatalyst from the effluent upon completion of the

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