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Influence of the iron source on the solar photo-Fenton degradation of different classes of organic compounds

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Abstract

In this work the influence of two different iron sources, $Fe(NO_3)_3$ and complexed ferrioxalate (FeOx), on the degradation efficiency of 4-chlorophenol (4CP), malachite green, formaldehyde, dichloroacetic acid (DCA) and the commercial products of the herbicides diuron and tebuthiuron was studied. The oxidation of 4CP, DCA, diuron and tebuthiuron shows a strong dependence on the iron source. While the 4CP degradation is favored by the use of $Fe(NO_3)_3$, the degradation of DCA and the herbicides diuron and tebuthiuron is most efficient when ferrioxalate is used. On the other hand, the degradation of malachite green and formaldehyde is not very influenced by the iron source showing only a slight improvement when ferrioxalate is used. In the case of formaldehyde, DCA, diuron and tebuthiuron, despite of the additional carbon introduced by the use of ferrioxalate, higher mineralization percentages were observed, confirming the beneficial effect of ferrioxalate on the degradation of these compounds. The degradation of tebuthiuron was studied in detail using a shallow pond type solar flow reactor of 4.5 L capacity and 4.5 cm solution depth. Solar irradiation of tebuthiuron at a flow rate of $9\,L\,h^{-1}$, in the presence of $10.0\,mmol\,L^{-1}$ H_2O_2 and $1.0\,mmol\,L^{-1}$ ferrioxalate resulted in complete conversion of this herbicide and 70% total organic carbon removal.

Keywords: Ferrioxalate; Tebuthiuron; Diuron

1. Introduction

The Advanced Oxidation Processes (AOP) have attracted considerable interest from academic and industrial sectors for the treatment of wastewaters, oxidation of contaminants present in the gas phase and remediation of soils (Gogate and Pandit, 2004; Mohseni and David, 2003; Watts et al., 1994). They are considered as promising alternatives to conventional processes due to the high efficiency for the oxidation of organic contaminants. The AOPs have been traditionally defined as based on the formation of hydroxyl radicals ($^{\bullet}OH$), although there are controversies about their participation in some degradation processes (Bossmann et al., 1998). The hydroxyl radical can be generated by the

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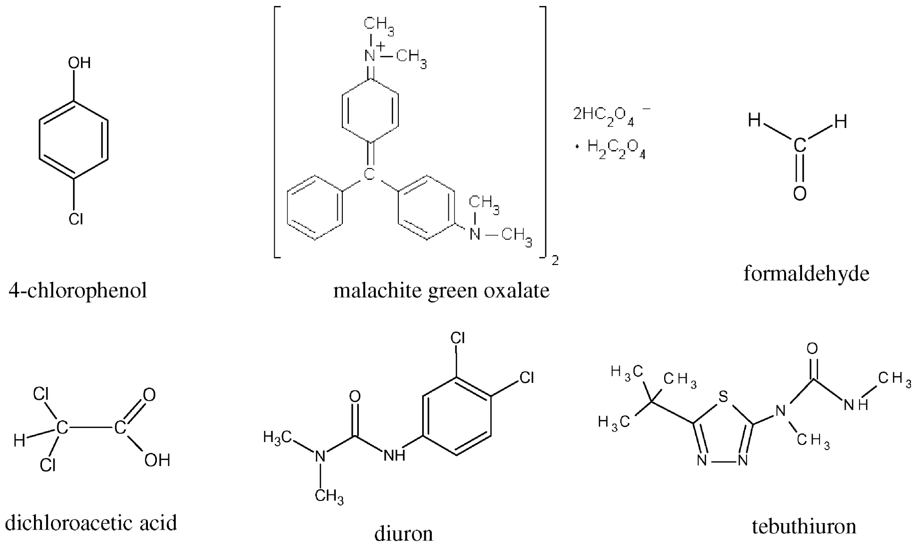

Fig. 1. Structural formula of the model compounds studied.

combination of oxidants such as ozone, or hydrogen peroxide with ultraviolet or visible irradiation and catalysts such as metal ions or semiconductors. Its high redox potential of 2.730 V ($^{\bullet}OH$, H^+/H_2O) (Wardman, 1989), permits the oxidation of many classes of organic compounds to CO_2, H_2O and inorganic ions from heteroatoms present, or at least the oxidation of contaminants to less harmful and biodegradable compounds (Legrini et al., 1993; Andreozzi et al., 1999; Benitez et al., 2000; Esplugas et al., 2002).

The light enhanced Fenton reaction, the so-called photo-Fenton process (Eq. (1)), is one of the AOP which has gained increasing attention in recent years due to its higher efficiency when compared to the dark process (Eq. (2)). The photoreduction of Fe(III) to Fe(II) shown in equation (1) is considered responsible for the enhancement of the oxidation effect. In a cyclical process, the regenerated Fe(II) can further react with H_2O_2 (Eq. (2)), besides of generating additional hydroxyl radical (Eq. (1)) (Pignatello, 1992; Zepp et al., 1992).

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \qquad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad (2)$$

The most important advantages of the photo-Fenton process are its simplicity of operation and the possibility to use the solar light, what can considerably reduce the operating costs (Bauer and Fallmann, 1997; Fallmann et al., 1999; Malato et al., 2002; Nogueira et al., 2002).

The improvement of the photo-Fenton degradation of contaminants such as toluene and 2-butanone by the use of the ferrioxalate complex compared to that of Fe^{3+}/H_2O_2 has been reported previously (Safarzadeh-Amiri et al., 1996) (Eqs. (3) and (4)).

$$[Fe(C_2O_4)_3]^{3-} + h\nu \rightarrow Fe^{2+} + 2C_2O_4^{2-} + C_2O_4^{-\bullet} \qquad (3)$$

$$C_2O_4^{-\bullet} + [Fe(C_2O_4)_3]^{3-} \rightarrow Fe^{2+} + 3C_2O_4^{2-} + 2CO_2 \qquad (4)$$

The high quantum yield of Fe(II) generation ($\Phi_{Fe(II)} = 1.24$ at 300 nm) (Hatchard and Parker, 1956) has been pointed out as one of the main reasons for the high efficiency of ferrioxalate in photo-Fenton process (Eqs. (3) and (4)) when compared to Fe^{3+}/H_2O_2 (Eq. (2)).

The photo-Fenton process mediated by ferrioxalate has been studied for destruction of several organic contaminants, using solar light (Nogueira and Guimarães, 2000; Nogueira et al., 2002; Emilio et al., 2002). The strong absorption of ferrioxalate up to 550 nm makes a large portion of the solar spectrum available for this process.

Despite of the beneficial effect when using ferrioxalate as source of iron in photo-Fenton process, the addition of oxalate has been considered as disadvantageous due to the increase of carbon load in the system. However, due to the complete conversion of oxalate to CO_2 no net increase of carbon is expected. On the other hand, a detrimental effect of ferrioxalate in relation to $Fe(NO_3)_3$ has been observed for the degradation of 4-chlorophenol with solar irradiation (Nogueira et al., 2004).

In this context, the objective of this work is to study the influence of the iron source, ($Fe(NO_3)_3$ and ferrioxalate complex (FeOx), on the photo-Fenton degradation efficiency of different classes of organic compounds under solar irradiation. The organic model compounds studied were: 4-chlorophenol, malachite green oxalate (triarylmethane basic green 4), formaldehyde, dichloroacetic acid and the commercial products of the