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Phenol oxidation kinetics in water solution using iron(3)-oxide-based nano-catalysts

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ABSTRACT

The influence of inorganic ions (HCO_3, $PO_4/HPO_4/H_2PO_4$, Cl, SO_4, Ca, Na and Mg) on the advanced chemical oxidation process of organic compounds dissolved in water is reported here. The catalytic behavior of iron(3)-oxide-based nano-particles was investigated together with inorganic ions and hydrogen peroxide concentrations, and pH level. Phenol was chosen as a typical organic contaminant for this study as a simulating pollutant. The limiting concentrations of radical scavengers making the oxidation process inefficient were identified. The strong effect of concentration of radical scavengers HCO_3, $PO_4/HPO_4/H_2PO_4$, the nano-catalyst and hydrogen peroxide concentrations, and pH on the phenol oxidation rate and lag time period before reaction starts was determined. It was shown that Cl, SO_4, Ca, Na and Mg ions had no significant effect on the kinetics of phenol oxidation.

1. Introduction

Drinking water, groundwater, domestic and industrial wastewater contain inorganic ions (HCO_3, $PO_4/HPO_4/H_2PO_4$, Cl, SO_4, Ca, Na, Mg, etc.) and often organic pollutants (De Laat et al., 2004). Traditional water treatment processes such as adsorption, coagulation, flocculation and membrane technologies achieve removal by separation by merely transferring the pollutants from one phase to another, producing concentrated sludge and leaving the problem of disposing of the transferred material (Catalkaya et al., 2003; Bali et al., 2003).

Organic and biological pollutions may be treated using suitable chemical oxidation processes (Bertanza et al., 2001). Biological treatment processes are usually slow, inefficient and somewhat limited in terms of the non-biodegradability and toxicity of some contaminants to microorganisms (Toledo et al., 2003).

A water treatment based on the chemical oxidation of organic compounds by Advanced Oxidation Processes (AOPs) that is useful for purifying surface water and groundwater and for cleaning industrial wastewater has been reported recently (Sigman et al., 1997; Yeber et al., 2000; Perez et al., 2002; Zelmanov and Semiat, 2008; Bach et al., 2008). AOPs have been used as a pre-treatment for biological systems when the dissolved organic matter is toxic, inhibitory or recalcitrant to microorganisms. The degradation and mineralization of organic pollutants in wastewater by AOPs are based on the generation of a very reactive free hydroxyl radical

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($OH^{\bullet}$). This radical is generated by the decomposition of hydrogen peroxide with ferrous iron (Fe^{+2}) (Walling, 1975; Neyens and Baeyens, 2003). The hydroxyl radical is highly reactive, non-selective and may be used to degrade a wide range of organic pollutants. It reacts with most organic compounds by adding to a double bound or by abstracting hydrogen atoms from organic molecules (Safarzadeh-Amiri et al., 1996, 1997; Buxton et al., 1988). The resulting organic radicals then react with oxygen, which leads to mineralization of CO_2, H_2O and mineral acids (Oliveros et al., 1997; Neyens and Baeyens, 2003). Fenton and Fenton-like systems ($Fe^{+2}/Fe^{+3}/H_2O_2$) are often used for industrial water treatment (Fenton, 1894; Neyens and Baeyens, 2003).

The mechanism for producing free hydroxyl radicals in Fenton (Fe^{+2}/H_2O_2) and Fenton-like processes (Fe^{+3}/H_2O_2) is very complex and thought to occur in the following stages (Walling, 1975; Lin and Gurol, 1998; De Heredia et al., 2001; Safarzadeh-Amiri et al., 1996; Neyens and Baeyens, 2003):

$$Fe^{+3} + H_2O_2 \rightarrow Fe - OOH^{+2} + H^{+} \quad (1)$$

$$Fe - OOH^{+2} \rightarrow Fe^{+2} + HO_2^{\bullet} \quad (2)$$

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

$$Fe^{+2} + OH^{\bullet} \rightarrow Fe^{+3} + OH^{-} \quad (4)$$

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \quad (5)$$

$$2Fe^{+2} + H_2O_2 + 2H^{+} \rightarrow 2Fe^{+3} + 2H_2O \quad (6)$$

The first three equations are responsible for the continuous production of the active radical (Walling, 1975; Lin and Gurol, 1998), the next two for the decay of this radical, and the final one for reducing the peroxide concentration.

Inorganic anions (HCO_3, $PO_4/HPO_4/H_2PO_4$, Cl, SO_4, Ca, Na, Mg, etc.) often present in wastewater also play a significant role in the reaction rate of the Fenton process (Beltran et al., 1998; Hernandez et al., 2002; Andreozzi et al., 1999; De Laat et al., 2004; Maciel et al., 2004). De Laat et al. (2004) investigated the effects of chloride, perchlorate, sulfate and nitrate ions on the decomposition rates of H_2O_2 and the oxidation of organic compounds by $Fe(2)/H_2O_2$ and $Fe(3)/H_2O_2$. They showed that the efficiency of the $Fe(3)/H_2O_2$ oxidation process can be reduced in the presence of chloride and sulfate ions. These inhibitory effects were attributed to a decrease in the rate of generation of hydroxyl radicals and the formation of $Cl_2^{\bullet-}$ and $SO_4^{\bullet}$ radicals that are less reactive than the $OH^{\bullet}$ radical. Some inorganic ions, such as HCO_3 and PO_4, can also reduce the efficiency of the oxidation process through the formation of radicals less reactive than $OH^{\bullet}$, $HCO_3^{\bullet}$ and PO_4 (Andreozzi et al., 1999; Hernandez et al., 2002).

Lu et al. (1997) investigated the effects of inorganic ions on the oxidation of dichlorvos (dimethyl 2,2-dichloroethenyl phosphate) insecticide with Fenton's reagent. Anions suppress the decomposition of dichlorvos in the following sequence: $H_2PO_4^{-} \gg Cl^{-} > NO_3^{-} \approx ClO_4^{-}$. The main reason for the suppression of phosphate ions is that these ions produced a complex reaction together with ferrous and ferric ions, causing loss of catalytic activity.

Photochemical degradation and mineralization of phenol and the effect of the presence of radical scavengers (PO_4, SO_4 and Cl ions) were investigated by Bali et al. (2003). The highest negative effect was observed with solution containing PO_4 ions. Thus, the determination of the limiting concentrations of radical scavengers making the oxidation process inefficient and the study of the influence of different oxidation process parameters on the radical scavenger-limiting concentrations are very important for the application of Advanced Oxidation Processes for water treatment. Following water treatment by AOPs, the post-treatment must eliminate the Fenton reagents as colloidal particles. The separation of colloidal precipitates requires the use of additional processes such as coagulation, sedimentation and filtration.

Nano-particles of inorganic materials such as metal oxides and semiconductors have generated considerable attention due to their novel properties (Iwasaki et al., 2000; Kamat and Meisel, 2002). A number of reports have shown that iron-oxide has special photochemical and catalytic properties (Stramel and Thomas, 1986). However, only a few studies have been made of the catalytic activity of colloidal iron-oxide nano-particles. Zelmanov and Semiat (2008) investigated the catalytic properties of iron-based nano-particles for the degradation of some organic pollutants in wastewater using the Fenton-like reaction in the presence of hydrogen peroxide at room temperature without the need for UV or visible radiation sources. A strong effect of nano-catalyst and hydrogen peroxide concentration on reaction rate was shown. The kinetic reaction was found and the reaction rate coefficient was calculated. A novel approach for the recovery of spent activated carbon using an advanced oxidation process with iron-oxide-based nano-catalysts was proposed and investigated by Bach et al. (2008). It was shown that there are several advantages in using catalytic oxidation recovery of activated carbon with iron-oxide-based nano-catalysts: low temperature reactivity of catalytic recovery without heating; and a relatively large number of adsorption–recovery cycles, without a reduction in the adsorptive properties of the virgin activated carbon or without a decrease in performance from the first adsorption–recovery cycle of the new modified adsorptive properties of the activated carbon. Results show a high efficiency of catalytic recovery of spent activated carbon using iron-oxide-based nano-catalysts. A 97–99% efficiency of spent activated carbon catalytic regeneration was achieved under selected conditions after 15–20 min of reaction. The nano-catalyst may be immobilized on inert surfaces, foams or nano-fibers (Yeber et al., 2000) and thus avoid the post-treatment elimination of the Fenton reagents following water purification by AOPs.

The objective of this research work was to investigate the catalytic behavior of iron(3)-oxide-based nano-catalysts by phenol oxidation and mineralization in wastewater containing possible radical scavengers, such as HCO_3, $PO_4/HPO_4/H_2PO_4$, Cl, SO_4, Ca, Na and Mg ions. In addition, the effects of the concentrations of the iron(3)-oxide-based nano-catalyst, hydrogen peroxide and inorganic ions (HCO_3, $PO_4/HPO_4/H_2PO_4$, Cl, SO_4, Ca, Na and Mg ions) and the influence of pH on the oxidation kinetics of organic pollutants are reported.