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

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ABSTRACT

The influence of inorganic ions (HCO₃, PO₄/HPO₄/H₂PO₄, Cl, SO₄, 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 HCO₃, PO₄/HPO₄/ H₂PO₄, 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, SO₄, Ca, Na and Mg ions had no significant effect on the kinetics of phenol oxidation.

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1. Introduction

Drinking water, groundwater, domestic and industrial wastewater contain inorganic ions (HCO₃, PO₄/HPO₄/H₂PO₄, Cl, SO₄, 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 (Catalaky et al., 2003; Bali et al., 2003).

Organic and biological pollutants 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.
This radical is generated by the decomposition of hydrogen peroxide with ferrous iron (Fe^{2+}) (Wallin, 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 bond 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 CO₂, H₂O and mineral acids (Oliveros et al., 1997; Neyens and Baeyens, 2003). Fenton and Fenton-like systems (Fe^{2+}/H₂O₂) are often used for industrial water treatment (Fenton, 1894; Neyens and Baeyens, 2003).

The mechanism for producing free hydroxyl radicals in Fenton (Fe^{2+}/H₂O₂) and Fenton-like processes (Fe^{3+}/H₂O₂) is very complex and thought to occur in the following stages (Wallin, 1975; Lin and Gurol, 1998; De Heredia et al., 2001; Safarzadeh-Amiri et al., 1996; Neyens and Baeyens, 2003):

\[
\begin{align*}
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe} - \text{OOH}^{2-} + \text{H}^+ \\
\text{Fe} - \text{OOH}^{2-} & \rightarrow \text{Fe}^{2+} + \text{HO}_2 \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^+ + \text{OH}^- \\
\text{Fe}^{2+} + \text{OH}^- & \rightarrow \text{Fe}^{3+} + \text{OH}^- \\
\text{H}_2\text{O}_2 + \text{OH}^- & \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \\
2\text{Fe}^{2+} + \text{H}_2\text{O}_2 + 2\text{H}^+ & \rightarrow 2\text{Fe}^{3+} + 2\text{H}_2\text{O}
\end{align*}
\]

The first three equations are responsible for the continuous production of the active radical (Wallin, 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 (HCO₃, PO₄/HPO₄/H₂PO₄, Cl, SO₄, 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 H₂O₂ and the oxidation of organic compounds by Fe(2)/H₂O₂ and Fe(3)/H₂O₂. They showed that the efficiency of the Fe(3)/H₂O₂ 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 Cl₂ and SO₄ radicals that are less reactive than the OH' radical. Some inorganic ions, such as HCO₃ and PO₄, can also reduce the efficiency of the oxidation process through the formation of radicals less reactive than OH', HCO₃ and PO₄ (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-dichloroethyl phosphorate) insecticide with Fenton's reagent. Anions suppress the decomposition of dichlorvos in the following sequence: H₂PO₄ ≥ Cl > NO₃ ≈ ClO₄. 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 effects of the presence of radical scavengers (PO₄, SO₄ and Cl ions) were investigated by Bali et al. (2003). The highest negative effect was observed with solution containing PO₄ 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 HCO₃, PO₄/HPO₄/H₂PO₄, Cl, SO₄, 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 (HCO₃, PO₄/HPO₄/H₂PO₄, Cl, SO₄, Ca, Na and Mg ions) and the influence of pH on the oxidation kinetics of organic pollutants are reported.
Phenol was chosen as a problematic organic contaminant for this study. Several types of industrial wastes contain phenols; they are very harmful and highly toxic towards microorganisms. Many phenol compounds are used as solvents or reagents in industrial processes and are therefore very common contaminants in industrial wastewater and contaminated drinking water sources (Cheng et al., 1995).

2. Experimental

2.1. Materials

Iron(3)-chloride hexa-hydrate, FeCl₃·6H₂O (analytical grade; Merck, KGaA, Germany), 30% hydrogen peroxide (analytical grade; PA, Panreac Quimica SA), phenol (analytical grade; Fluka), sodium bicarbonate (chemically pure; Frutarom Ltd., Israel), potassium dihydrogeno-phosphate (analytical grade; Sigma–Aldrich, GmbH), sodium sulfate deca-hydrate (extra pure; Merck, KGaA, Germany), sodium nitrate (chemically pure; Frutarom Ltd., Israel), calcium chloride 2-hydrate (analytical grade), and magnesium chloride hexa-hydrate (extra pure; Merck, KGaA, Germany) were used as received.

2.2. Analysis and equipment

A morphology study was performed using Philips CM120 Transmission Electron Microscopy (TEM). A Malvern Nano ZetaSizer model ZEN3600 was used to measure the size distribution of the nano-sized particles. The pH was determined using a Consort P-931 electrochemical analyzer. Phenol content analyses were carried out in a data logging Hach DR/2010 spectrophotometer using the phenols 4-aminoantipyrine method. The detection limit (DL) for the method is 0.003 ppm phenol. Total iron and iron ferrous concentrations were determined in a data logging Hach DR/2010 spectrophotometer by using FerroVer and phenanthroline methods consequently.

2.3. Preparation of nano-particle catalysts

The starting material used for preparing the iron(3)-oxide-based nano-particles was iron(3) chloride hexa-hydrate, FeCl₃·6H₂O (analytical grade; Merck). Hydrolysis was used to prepare a 10% sol with iron nano-catalysts with initial acidity (pH = 0.8):

\[
\text{FeCl}_3 \cdot 6\text{H}_2\text{O} \rightarrow \text{Fe}(3) - \text{oxide} - \text{basednano} - \text{particles} + \text{HCl}
\]  

(7)

A series of iron hydroxide nano-catalysts was then prepared by diluting the initial solution. Fig. 1 shows an example of a TEM image of a cluster of rod-like nano-particles. The corresponding electron diffraction pattern (Fig. 1B) reveals that the Fe(3)-oxide-based nano-particles are nano-particles of FeOOH, as calculated by the Bragg equation lattice constants (characteristic inter-planar distances) of 3.3, 2.48 and 1.75. Fig. 1C shows the particle size distribution of the same nano-particles.

3. Phenol destruction model

The phenol destruction with FeOOH nano-catalysts in the presence of phosphorous or HCO₃ ions in solution may be simulated as follows:

\[
\frac{C}{C_0} = 1, \text{ for } t < \tau
\]

\[
\frac{C}{C_0} = \exp \left[ -\left( \frac{t - \tau}{\alpha + \beta(t - \tau)} \right) \right], \text{ for } t > \tau
\]  

(8)
where $\tau$ is the lag time period (min), $\alpha$ (min) and $\beta$ (dimensionless) are two constants.

The derivation of $C/C_0$ over time $t$ can be formulated as follows (Zelmanov and Semiat, 2008):

$$\frac{d(C/C_0)}{dt} = -\frac{\alpha}{(\alpha + \beta(t - \tau))^2} \left(\frac{C}{C_0}\right)$$

(9)

When $(t - \tau)$ is small $(t - \tau \ll \alpha/\beta)$, Eq. (9) can be rewritten as:

$$\frac{d(C/C_0)}{dt} = -\frac{1}{\alpha} \frac{C}{C_0}$$

(10)

Eq. (10) represents the first-order reaction kinetics, where $\alpha$ is the reciprocal of the first-order reaction rate coefficient $k$.

For a long time period $(t \rightarrow \infty)$, Eq. (9) can be rewritten as:

$$\frac{C_{t \rightarrow \infty}}{C_0} = \exp(-1/\beta)$$

(11)

or

$$1/\beta = -\ln(C_{t \rightarrow \infty}/C_0)$$

(12)

$\beta$ is therefore inversely proportional to the logarithm of the maximum phenol destruction capacity.

Eq. (8) can be rewritten in the following form:

$$-(t - \tau)/\ln(C/C_0) = \alpha + \beta(t - \tau)$$

(8a)

4. Results and discussion

The results of the experiments are presented in Figs. 2–8. All figures show change in phenol concentration with time. $\text{Fe}^{2+}$ measured concentrations are also shown in most of the figures. The results are shown on semi-logarithmic scale in order to demonstrate the low phenol concentration level obtained in the experiments. In all these figures, the dots represent the experimental data and the solid lines the model calculations.

4.1. Effect of phosphorous ions on phenol oxidation rate

A series of experiments was conducted to investigate the effect of phosphorous ion ($\text{PO}_4/\text{HPO}_4/\text{H}_2\text{PO}_4$) concentration on phenol oxidation rate under otherwise constant conditions. All of the experiments were carried out at room temperature, at room lighting with no other light source, and in some cases in a darkened vessel with no light in the reaction (the latter did not differ from regular light) and at an initial phenol solution concentration of 1100 ppm. The concentrations of FeOOH nano-catalysts varied from 80 to 200 ppm, of hydrogen peroxide from 0.48 to 0.96%, and of phosphorous ions from 0 to 75 ppm. The results are presented in Figs. 2–4. Fig. 2 shows the marked effect of phosphorous ion concentration on overall phenol oxidation rates. Increasing the phosphorous ion...
concentration from 0 to 75 ppm for a nano-catalyst concentration of 80 ppm and an initial 0.48% hydrogen peroxide concentration caused an increase in lag time period before the oxidation reaction started, followed by a decrease in phenol oxidation reaction rate. Therefore, when no phosphorous ions dissolved in water, the phenol concentration drops from 1100 ppm to 0.35 ppm in 5 min. However, when the phosphorous ion concentration exceeded 75 ppm, the other extreme condition here, the phenol concentration remained unchanged throughout the experiment. For intermediate phosphorous ion concentrations of 10–50 ppm, up to a 3-min lag time period was observed before the reaction started, followed by a lower reaction yield. This decrease in phenol oxidation reaction rate can be attributed to the complexation reactions of Fe$^{3+}$ by PO$_4$/HPO$_4$/H$_2$PO$_4$ ions (Stein and Weiss, 1951). The ferric complexes cannot react efficiently with hydrogen peroxide (Lu et al., 1997) therefore a decrease in Fe$^{3+}$ concentration leads to a decrease in Fe$^{2+}$ concentration, as shown in Fig. 2. A decrease in Fe$^{2+}$ concentration, under otherwise constant conditions, leads to a decrease in rate of generation of active free radicals and consequently a decrease in rate of phenol oxidation, as shown in Fig. 2. Thus, for a phosphorous ion concentration of 10 ppm, Fe$^{2+}$ concentration increased from 0 to 20 ppm after 0.5 min of reaction. Increasing the Fe$^{2+}$ concentration to this level initiated the start of phenol oxidation.

Fig. 5 – Effect of HCO$_3$ ions on the phenol oxidation rate in the Fenton-like process. Concentration of hydrogen peroxide: 0.48%. Concentration of nano-catalyst, ppm: 80. Concentration of HCO$_3$ ion, ppm: ○ – 0, ▲ – 100, ▼ – 125, and ■ – 150. Solid line represents changing phenol concentration, ppm. Dashed line represents changing Fe$^{1+2}$ concentration, ppm.

Fig. 6 – Effect of HCO$_3$ ions on the kinetics of phenol oxidation in the Fenton-like process. Concentration of HCO$_3$ ion: 150 ppm. Concentration of hydrogen peroxide: 0.48%. Concentration of nano-catalyst, ppm: ▲ – 80, ○ – 100, ■ – 120, and ▼ – 200. Solid line represents changing phenol concentration, ppm. Dashed line represents changing Fe$^{1+2}$ concentration, ppm.

Fig. 7 – Effect of the presence of HCO$_3$ ions on the phenol oxidation rate in the Fenton-like process. Concentration of nano-catalyst: 80 ppm. Concentration of HCO$_3$ ion: 150 ppm. Concentration of hydrogen peroxide, %: ■ – 0.48, ▲ – 0.72, ▼ – 0.96, ○ – 1.2. Solid line represents changing phenol concentration, ppm. Dashed line represents changing Fe$^{1+2}$ concentration, ppm.

The influence of FeOOH nano-catalyst concentrations on the rate of phenol oxidation and the reduction of Fe\(^{3+}\) to Fe\(^{2+}\) is shown in Fig. 3 for a phosphorous ion concentration of 75 ppm and a hydrogen peroxide concentration of 0.48%. For a concentration of the nano-catalysts less than 80 ppm, no reduction of Fe\(^{3+}\) to Fe\(^{2+}\) or phenol oxidation was observed. An increase in the concentration of the Fe\(^{3+}\) nano-catalyst from 80 to 100 ppm led to an increase in the Fe\(^{2+}\) concentration from 0 to 1.2 ppm after 10 min and to 23 ppm after 17 min (Fig. 3). Increasing the Fe\(^{2+}\) concentration to a level of 20–23 ppm initiated the intensive generation of active free hydroxyl and phosphorous radicals, and consequently led to the initiation of the phenol oxidation reaction after 17 min, the lag time length. A further increase in the Fe\(^{2+}\) nano-catalyst concentration caused a decrease in the lag time period and an increase in the phenol oxidation rate, as shown in Fig. 3.

Similarly, the direct effect of initial hydrogen peroxide concentration on the reduction of Fe\(^{3+}\) to Fe\(^{2+}\) and phenol oxidation rate for a phosphorous ion concentration of 75 ppm and a Fe\(^{3+}\) nano-catalyst concentration of 100 ppm is shown in Fig. 4. An examination of these results shows that hydrogen peroxide concentration has a significant influence on the reduction of Fe\(^{3+}\) to Fe\(^{2+}\) and on phenol oxidation rate. An increase in initial hydrogen peroxide concentration leads to a decrease in lag time period. Thus, increasing the initial hydrogen peroxide concentration from 0.48 to 0.96% causes a reduction in lag time from 17 to 3 min. For an initial hydrogen peroxide concentration of 0.48%, the Fe\(^{2+}\) concentration increased from 0 to 1.2 ppm after 5 min and to 23 ppm after 17 min (Fig. 4). Increasing the Fe\(^{2+}\) concentration to a level of 20–23 ppm initiated the intensive generation of active free hydroxyl and phosphorous radicals and hence led to the start of the phenol degradation reaction after 17 min of lag time. Increasing the initial concentration of H\(_2\)O\(_2\) to 0.96% caused the Fe\(^{2+}\) concentration to increase from 0 to 8 ppm in 3 min and to 9–10 ppm after 10 min. Increasing the Fe\(^{2+}\) concentration to 8 ppm for an initial 0.96% hydrogen peroxide concentration initiated the intensive generation of active free hydroxyl and phosphorous radicals, and consequently led to the start of phenol degradation after 3 min. It should be noted that the phenol oxidation reaction for an initial 0.96% H\(_2\)O\(_2\) concentration started at a Fe\(^{2+}\) concentration of about 8 ppm compared to its initiation at a Fe\(^{2+}\) concentration of 20–23 ppm for an initial 0.48% H\(_2\)O\(_2\) concentration. The start of phenol oxidation requires a certain concentration of free active radicals. Increasing the initial concentration of H\(_2\)O\(_2\) increases the radical’s generation rate and hence its concentration (see reactions (1)–(3)). Therefore, the same concentration of radicals may be achieved with different concentrations of Fe\(^{2+}\) and H\(_2\)O\(_2\).

4.2. Effect of HCO\(_3^-\) ions on phenol oxidation rate

Figs. 5–8 present the experiments conducted in order to learn the effect of HCO\(_3^-\) ion concentration on dissolved phenol oxidation. In these experiments, the initial phenol solution concentration was 1100 ppm, the concentration of FeOOH nano-catalyst varied from 80 to 200 ppm, the hydrogen peroxide concentration from 0.48 to 1.2%, the HCO\(_3^-\) ion concentration from 0 to 375 ppm, and the pH values from 1.7 to 4.16. As demonstrated above with the phosphorous ions, HCO\(_3^-\) ion concentration had a significant influence on phenol degradation rate and lag time period. The effect of HCO\(_3^-\) ion concentration on phenol oxidation rate and lag time duration of the reaction, under otherwise constant conditions, is shown in Fig. 5. For a nano-catalyst concentration of 80 ppm and an initial 0.48% hydrogen peroxide concentration, increasing the HCO\(_3^-\) ion concentration from 0 to 150 ppm, led to a decrease in oxidation reaction rate and an increase in lag time period. Thus, for a nano-catalyst concentration of 80 ppm, the phenol concentration dropped from 1100 to 0.35 ppm after 5 min without HCO\(_3^-\) ions, and to 135 ppm after 5 min with a 100 ppm HCO\(_3^-\) ion concentration. For an HCO\(_3^-\) ion concentration of 150 ppm, no phenol oxidation reaction was observed. By increasing the HCO\(_3^-\) ion concentration, the reaction’s lag time period was increased, as shown in Fig. 5.

Again, this decrease in phenol oxidation rate can be attributed to the complexation reactions of Fe\(^{3+}\). The ferric complexes cannot react efficiently with hydrogen peroxide, therefore a decrease in Fe\(^{3+}\) concentration leads to a decrease in Fe\(^{2+}\) concentration, as shown in Fig. 5. A decrease in Fe\(^{2+}\) concentration, under otherwise constant conditions, leads to a decrease in rate of generation of active free radicals and, for this reason, a decrease in phenol oxidation rate (Fig. 5).

Fig. 6 shows the effect of nano-catalyst concentration on phenol oxidation rate and on the reduction of Fe\(^{3+}\) to Fe\(^{2+}\). For a HCO\(_3^-\) ion concentration of 150 ppm, an initial 0.48% hydrogen peroxide concentration, and a nano-catalyst concentration less than 80 ppm, no reduction in Fe\(^{3+}\) to Fe\(^{2+}\) or phenol degradation was observed. A change in nano-catalyst concentration from 80 to 200 ppm leads to an increase in oxidation reaction rate and a decrease in reaction lag time.

The strong effect of the initial hydrogen peroxide concentration on the phenol oxidation rate and on the reduction of Fe\(^{3+}\) to Fe\(^{2+}\) in the presence of HCO\(_3^-\) ions is illustrated in Fig. 7. For a HCO\(_3^-\) ion concentration of 150 ppm, a nano-catalyst concentration of 80 ppm and a hydrogen peroxide concentration less than 0.48%, no reduction in Fe\(^{3+}\) to Fe\(^{2+}\) or phenol degradation was observed. Increasing the initial hydrogen peroxide concentration from 0.72 to 1.2% leads to a decrease in phenol concentration from 1100 to 110 ppm after 20 min of reaction with a 0.72% hydrogen peroxide concentration, and to 1.2 ppm after 20 min reaction with a 0.96% hydrogen peroxide concentration, as shown in Fig. 7. An increase in the initial hydrogen peroxide concentration from 0.72 to 1.2% causes the reaction lag time to decrease by about 50%, from 17 to 8 min. As for the phosphorous ions, this may be easily explained by the kinetics reduction of Fe\(^{3+}\) to Fe\(^{2+}\), as shown in Fig. 7. As demonstrated above with the phosphorous ions, the phenol oxidation reaction for an initial 0.96% H\(_2\)O\(_2\) concentration starts at a Fe\(^{2+}\) concentration of about 9 ppm compared to its initiation at a Fe\(^{2+}\) concentration of 11–12 ppm for an initial 0.72% H\(_2\)O\(_2\) concentration. As explained above, the start of phenol oxidation requires a certain concentration of free active radicals. Increasing the initial H\(_2\)O\(_2\) concentration increases the rate of generation of radicals and consequently concentration reactions (1)–(3).

The direct effect of pH level in the presence of HCO\(_3^-\) ions on phenol oxidation rate and lag time period is shown in Fig. 8. As follows from these lines, a change in pH has a strong effect on
the kinetics oxidation of phenol and its achieved concentration. As established above, these changes in phenol oxidation reaction rate and lag time duration of the reaction can be attributed to the change in Fe\(^{3+}\) concentration with a varying pH (Fig. 8), and, for this reason, a change in the generation rate of active free hydroxyl radicals – \((\cdot OH)\) and HCO\(_3\) radicals. Therefore, for pH values less than pH = 2 and over 4.15, no phenol oxidation reaction was observed. Increasing the pH value from 2 to 3.3 caused an increase in Fe\(^{3+}\) concentrations from 0 to 20 ppm in 3 min and initiated the start of phenol oxidation. Increasing the Fe\(^{3+}\) concentration, under otherwise constant conditions, resulted in a sharp phenol oxidation as the concentration reached 0.5 ppm for pH = 3.3. A further increase in pH led to a rapid increase in achieved phenol concentration to 0.22 ppm at pH = 3.5. For pH values 3.5 and 3.3, lag time periods of 8 and 2 min, respectively, were observed for phenol oxidation. For low and high pH values (pH < 2 and pH > 4.15), no reduction in Fe\(^{3+}\) to Fe\(^{2+}\) or phenol oxidation was observed (see Fig. 8). Thus, a maximum yield in the destruction of phenol can be explained by the kinetics reduction of Fe\(^{3+}\) to Fe\(^{2+}\).

4.3. Model applicability

Fig. 9 demonstrates sample results presented as quantity \(- (t - \tau)/\ln(C/C_0)\) versus reaction time \(t - \tau\). From the linear lines shown, the constants \(a\) and \(b\) may be calculated (Chan and Chu, 2003) for different initial concentrations of hydrogen peroxide and nano-catalyst. The linearity of the curves in Fig. 9 demonstrates the validity of the model adapted for phenol destruction in solution using the chosen catalyst.

4.4. Effect of SO\(_4\), Cl, Ca, Na and Mg ions on phenol oxidation rate

A series of experiments were conducted to investigate the influence of the concentrations of Cl, SO\(_4\), Ca, Na and Mg ions on phenol degradation rate. In all of these experiments, the initial phenol solution concentration was 1100 ppm, the FeOOH nano-catalyst concentration was 80 ppm, and the hydrogen peroxide concentration was 0.48%. The initial pH values ranged from 2.85 to 3.0. The inorganic ion concentration varied from 0 to 1000 ppm. The results showed no influence of this ion concentration. The sample results given in Fig. 10 show no significant influence of Cl ion concentration on overall phenol oxidation rates.

4.5. Discussion

The lines in Fig. 11 show a significant influence of PO\(_4\)\(^3-\) and HCO\(_3\) ions concentrations on phenol destruction rate and lag time period before the reaction started. The delay in the reaction is related to the interaction with the two anions. We can speculate that different reasons for this phenomenon exist. The phosphate is known to react with the iron-oxide and hence reduces its active concentration in the solution and its ability to start the set of reactions shown in Eqs. (1)-(6).
The influence of the acidic environment of the catalyst causes CO₂ to leave the solution, which may also affect the reaction conditions. Increased concentration of the catalyst may solve this problem. Further experiments are required in order to fully understand the reasons. Other anions and cations checked in the experiments did not have such an influence.

The main target in this work was to find a practical solution for the removal of phenol from water solutions. While this work concentrated on the destruction of phenol, some by-products of this reaction may also be harmful. An important question is how to proceed from this point onwards. Complete destruction is possible, yet is expensive for high concentrations due to the high cost of the peroxide. Partial destruction of organic matter may be used as pre-treatment before biological treatment.

It is important to note that the treatment of large streams of water with nano-catalysts is problematic due to the possible loss of catalysts to the water. While iron-oxide is not known to cause any health problems, very little is known about its behavior as small crystals in the water. Another issue is the concentration of the peroxide, which cannot be used in excess due to its high cost. A simple solution for this is the use of an adsorbent to remove the organic contaminants from the water. Cold catalytic regeneration of the adsorbent may be used, as demonstrated in Bach et al. (2008). The understanding gained from the phosphate reaction with the catalysts, as reported here, led into a technique for the removal of phosphates from solution (Zelmanov and Semiat, submitted for publication).

5. Conclusions

This study provides information about Advanced Oxidation Process kinetics oxidation of organic pollutants using iron(3)-oxide-based nano-catalysts in water containing inorganic ions (HCO₃⁻, PO₄⁻/HPO₄⁻/H₂PO₄⁻, Ca, Na and Mg ions). The main conclusions are as follows:

- The effect of the concentrations of radical scavengers HCO₃⁻, PO₄⁻/HPO₄⁻/H₂PO₄⁻ on phenol oxidation rate and lag time period was demonstrated.
- A significant effect of FeOOH nano-catalyst concentration and hydrogen peroxide concentration in the presence of phosphate ions on phenol oxidation rate and lag time period was demonstrated.
- A significant effect of nano-catalyst concentration and hydrogen peroxide concentration in the presence of HCO₃⁻ ion on phenol oxidation rate and lag time period was demonstrated.
- No significant influence of Cl, SO₄²⁻, Ca, Na and Mg ions on the kinetics of phenol oxidation was observed.

The results may lead to a better understanding and hence improved techniques for the removal of organic contaminants from solutions.

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