Characterization of iron oxide nanocatalyst in mineralization processes

Altai Bach *, Adva Zach-Maor, Raphael Semiat

Grand Water Research Institute – Rabin Desalination Laboratory, Wolfson Faculty of Chemical Engineering, Technion – Israel Institute of Technology, Technion City, Haifa 32000, Israel

1. Introduction

Iron oxide plays an important role in wastewater treatment. The high versatility and structural chemistry variability of iron oxide is a result of the existence of two oxidation stable states for iron, ferrous ions (Fe²⁺) and ferric ions (Fe³⁺) in a wide range of pH and the result of the existence of two oxidation states for iron, ferrous (Fe⁰) and ferric ions (Fe³⁺) in a wide range of pH and the condensation phenomena [9-11,23].

Ferric iron introduces hexacoordinated complexes within water. The polarization of the water molecules depends upon the oxidation states of the cations (ferrous or ferric ions) and their size. It was reported [10], that hydroxylated complexes (an addition of hydroxyl group into the iron oxide molecule) are generated from bivalent and trivalent iron in different pH spectrums. In acidic pH between 0 and 5, ferric hydroxo complexes are formed.

The acidic solution is formed due to the proton that migrates from the coordinated water molecules (Eq. (3)) to the Fe³⁺ ion and then to the free water molecule [7].

The second mechanism is oxilation, which represents the condensation phenomena of the iron species. The condensation process of any hydroxylated complex can be performed through two main mechanisms.

The first mechanism is olation, which releases a coordinated water molecule and forms hydroxyl group bridges between the ferric ions. The second mechanism is oxilation, which represents the condensation of oxohydroxo species – complexes which do not contain coordinated water molecules.

The condensation mechanism depends on the nature of the cations’ coordination sphere. Therefore, ferric hydroxo complexes have a pronounced tendency to condense via the olation mechanism.

Complete hydrolysis occurs in time when all six water ligands are deprotonated in order to form iron oxides, i.e.

$$[\text{Fe(H}_2\text{O)}_6]^{3+} + \text{H}_2\text{O} \rightarrow [\text{Fe(OH)}_2\text{O}_5\text{H}]^{2+} + \text{H}_3\text{O}^+ \quad (3)$$

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The generation of complexes’ clusters and particles in the solution is due to the condensation phenomena of the iron species. The condensation process of any hydroxylated complex can be performed through two main mechanisms.

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1.1. Advanced oxidation process (AOP)

AOP is an oxidation technique by which a large quantity of hydroxyl radicals (•OH) are generated and various organic pollutants are oxidized [27]. These radicals enable very rapid reactions with most organic contaminants mainly due to their high oxidation potential (2.8 V) and non-selective nature. Since hydroxyl radical half-life is only microseconds, they must be generated incessantly in situ through chemical reactions. Environmental applications of the Fenton process include the use of hydrogen peroxide, with the substitution of different catalysts such as ferric iron and naturally occurring iron oxides [2].

The mechanism of the Fenton reagent has been reported extensively [15,17,18,26].

1.2. H₂O₂/iron oxide system

Dissolution of iron oxide, such as FeOOH, occurs via protonation [7]. The general reaction between iron oxide and the protons is presented in Eq. (5):

$$\text{FeO(OH)} + n\text{H}^+ \rightarrow \left[\text{Fe(OH)}_{(3-n)}\right]_{\text{aq}}^{n+} + (n-1)\text{H}_2\text{O}$$

For \(n = 3\), the reaction will be:

$$\text{FeO(OH)} + 3\text{H}^+ \rightarrow \text{Fe}^{3+} + 2\text{H}_2\text{O}$$

The nano-iron oxide particle (such as FeOOH) oxidation mechanism includes dissolution, a step that requires proton, which binds to the iron oxide surface and releases ferric ion into the bulk solution. The dissolution of iron oxide increases with a decrease in pH solution. The high affinity of protons to structural O₂⁻ helps release the iron atom from the surface to the bulk solution. The detachment of ferric ion to the solution initiates a chain of reactions, called Fenton-like reagents, as shown in Fig. 1.

The objective of this work was to investigate the ability to reuse iron oxide nanoparticles in the H₂O₂/iron oxide system for the mineralization process based on Fenton-like reagents (Fig. 1). The stability of iron oxide nanoparticles in de-ionized water with dissolved organic solution was studied as a function of pH solution and was correlated with the particles’ average size. The optimal pH value for the mineralization process was determined. The organic model compounds selected for the current study were phenol and ethylene glycol.

2. Experimental

2.1. Materials

Iron (3)-chloride hexa-hydrate, FeCl₃·6H₂O and hydrogen peroxide, 30%, were purchased from Merck, Germany; phenol, analytical grade (Fluka) and chemically pure ethylene glycol were purchased from Bio Lab Ltd., Israel. All chemicals were analytical grade and were used as received.

Ethylene glycol is used in large quantities as a car cooling fluid or as an airplane and runway deicer. Deicer large quantities of ethylene glycol have created environmental hazards leading to the serious pollution of drinking water [1,16,21,22].

Several types of industrial waste contain phenols. They are very harmful and highly toxic towards microorganisms [6,8]. 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.

2.2. Experimental Setup

Batch experiments were carried out in a 250 mL beaker stirred by magnetic stirrers, with 100 mL of organic model compounds in de-ionized (DI) water at the desired concentration and room temperature. Hydrogen peroxide and iron oxide were added simultaneously at the beginning of each experiment. pH was adjusted using HCl (1 N) or NaOH (5 N). At pre-determined time intervals, samples were taken from the beaker for analysis.

2.3. Analysis

Multi N/C 2100/2100 analyzer (Analytik Jena, Germany) was used to determine total organic carbon (TOC). pH solution was measured with a Consort C931 pH meter. Imaging was done with Transmission Electron Microscopy (TEM) using a FEI Tecnai T12 G2 TEM, with low electron dose at an acceleration voltage of 120 kV. Characterization of the dispersion was made using Cryogenic Transmission Electron Microscopy (cryo-TEM). Samples were prepared in a controlled-environment vitrification system (CEVS) [12,25].

Total iron concentration was measured by the HACH DR2010 Portable Data logging spectrophotometer using method 8008 with FerroVer Iron Reagent Powder Pillows.

NanoZS-3600 (Malvern Instruments Ltd., UK) was used to determine average particle size, size distribution and zeta potential of the FeOOH particles.

The preparation procedure of FeOOH nanoparticles is explained in detail elsewhere [4].

3. Results and discussion

3.1. Iron nanoparticle characterization

In order to characterize the particles in their natural environment, a cryogenic microscope was used. Cryo-TEM sample preparation involves the fast-freezing of thin liquid films of solution and therefore does not produce drying artifacts. Fig. 2 illustrates cryo-TEM images and the electron diffraction pattern of the synthesized iron nanoparticle.

From these microphotographs, mostly the particles having a rod-like morphology with average lengths of 50 ± 10 nm are observed. The rod-like crystals were identified as either α-FeOOH or β-FeOOH from the electron diffraction patterns.

As expected, beside the immediate hydrolysis that takes place to a strong acid and a weak base, slow hydrolysis also occurs that could
take days and even months for its termination. These results are in good agreement with Wagner et al. [23] and Jean-Pierre et al. [11].

The slow hydrolysis was monitored not only with an increase in conductivity and a decrease in pH, but also with color changes in the nanoparticle solution, from yellowish to red. Particle size analysis indicates differences in particle size only during the first few hours, after which it remained stable and did not change over a lengthy period of time. Fig. 3 illustrates the continuous size distribution of FeOOH nanoparticles. The horizontal axis shows size distribution in nm, while the vertical axis shows the partial volume fraction as calculated from light intensity distribution.

All of the above samples were taken from the same freshly made 200 mg/l as ferric iron solution and were monitored with time. The first measurements were taken each hour between the fourth and sixth hour and the last measurement was taken after one month. According to Fig. 3, after 4 h, the sample contains mainly small particles (around 15 nm) and a much less amount of larger particles (around 50 nm). An hour later the distribution changes and displays an almost even distribution between the small and large particles. However, after 6 h it seems like the small particles disappears and a mono modal peak appears, indicating the existence of one population of particles around 50 nm. That size distribution seems to be constant as for it didn’t change over long periods of time (even after one month). The same behavior repeated itself with different Iron oxide nanoparticles samples after different aging periods. The high solubility of smaller particles may lead to their transformation into larger ones via solution, a process called Ostwald Ripening [20]. This thermodynamically-driven spontaneous process occurs because larger particles are more energetically favored than smaller particles. Large particles, which possess greater volume to surface area ratio, represent a lower energy state (and have a lower surface energy). As the system tries to lower its overall energy, molecules on the surface of a small (energetically unfavorable) particle will tend to diffuse through solution and adhere to the surface of larger particles. Therefore, the smaller particles continue to shrink, while larger particles continue to grow until equilibrium is reached.

3.2. Solution stability

The correlation between pH solution, and the stability and average size of iron oxide particles was studied. It is important to find out the conditions where the particles are stable as nano-particles and where they aggregate to form larger particles.

Fig. 4a and b shows the zeta potential versus the pH of samples of de-ionized water and water containing an organic model compound (ethylene glycol or phenol), respectively. The two compounds were chosen to represent common industrial water pollutants. The concentration of the iron oxide particles was 200 mg/L as iron in both solutions and the organic compounds concentration was 200 ppm as TOC. Solutions with zeta potential higher than 30mV or

![Fig. 2. TEM images of FeOOH samples synthesized with distilled water and the corresponding electron diffraction pattern. The iron oxide nanoparticles were at a concentration of 200 mg/L as Fe.](image1)

![Fig. 3. Size distribution over time of freshly prepared iron nanoparticle solution generated by dynamic light scattering. Red- After 4 Hours, Green- After 5 Hours, Blue- After 6 Hours, Black- After 1 Month. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image2)

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lower than $-30 \text{ mV}$ are normally considered stable. Between these two values the solution is considered to be unstable. The stability and instability of the solutions were examined by raising the pH from 2 to 8.7 and reducing it back to 2.

The de-ionized water zeta potential results (Fig. 4a) indicate that between a pH of 2 and 4.7, the solution could be regarded as stable. The pH range at which the solution is stable decreases when organic model compounds are introduced into the solution (Fig. 4b). Results are identical for the two organic compounds that were checked. Here, the stability ranges between pH 2 and 3.2. Both solutions become unstable at the point the particles would most likely aggregate. Both samples display almost complete overlap when decreasing or increasing solution pH.

When comparing average particle size shifts with increasing pH (Fig. 5a and b), it is clear that the result of average size in both solutions corresponds to the results in Fig. 4a and b. Above a pH of 4.5 (Fig. 5a) and 3.2 (Fig. 5b), the solutions become unstable and the average particle size increases dramatically from around 50 nm and 100 nm to a few tens of microns respectively.

Both solutions show clearly the reversible effect by displaying that there is no hysteresis when raising or lowering the solution pH.

The iron oxide particles’ surface is positively charged when pH is kept in the stability range. When base is added to either solution, it is attracted to the surface of the suspended particles, therefore, the particles do not repel each other and have the tendency to aggregate. These aggregates are growing with pH increase (Fig. 5a, b) and finally sediment due to gravity. Under these conditions, both solutions become unstable (Fig. 4a, b). However, the formation of those aggregates could be overturned; hence, adding an acid causes a reverse affect. First the aggregates become separated and thus the suspended particles have a greater positive charge which induces a rejection between them.

The average size of iron oxide nanoparticles in the organic model solution was greater compared to the size in de-ionized water (for the

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**Fig. 4.** a. Zeta potential as a function of pH in de-ionized water solution. $[\text{Fe}]_{\text{Total}} = 50 \text{ mg/L}$. b. Zeta potential as a function of pH in organic model compounds solution. $[\text{Fe}]_{\text{Total}} = 50 \text{ mg/L}$. [TOC]$= 200 \text{ mg/L}$.

**Fig. 5.** a. Average size versus pH in de-ionized water solution. $[\text{Fe}]_{\text{Total}} = 50 \text{ mg/L}$. b. Average size versus pH in organic model compounds solution. $[\text{Fe}]_{\text{Total}} = 50 \text{ mg/L}$. [TOC]$= 200 \text{ mg/L}$.

**Fig. 6.** Ethylene glycol and phenol mineralization versus pH. $[\text{H}_2\text{O}_2]/[\text{Fe}]_{\text{Total}} = 16$, [TOC]$= 200 \text{ mg/L}$, t = 120 min, $[\text{H}_2\text{O}_2]_0 = 8250 \text{ mg/L}$.

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same pH (Fig. 5a, b). It has been proven previously [5] that iron oxide has the ability to absorb organic matter, therefore it is suggested that the difference between average particle sizes for both solutions is probably due to the adsorption of dissolved organic matter onto the iron oxide nanoparticles.

3.3. Iron oxide nanoparticles as a catalyst

Some soluble iron ions exist in aqueous solution due to the dissolution of iron oxide, as explained earlier. The complexes mentioned, along with the detachment of ferric ion (due to the dissolution process) from the solution, initiate a chain reaction, called the Fenton-like process.

The catalytic behavior of the \( \text{H}_2\text{O}_2/\text{iron oxide} \) system was investigated versus pH in two organic model solutions: ethylene glycol and phenol.

The experiments were performed at pH values ranging from 1 to 7. The weight ratio between hydrogen peroxide and total iron was 16. The percentage removal of total organic compound (TOC) as a function of the solution pH for both organic compounds is shown in Fig. 6.

Generally, the results show that the Fenton-like reaction in the presence of the \( \text{H}_2\text{O}_2/\text{iron oxide} \) system efficiently mineralizes the organic model solutions. The behavior of both organic models as a function of pH is similar.

The highest mineralization was achieved for both organic models between pH 2.5 and 3. In the optimal pH, nearly 95% and 85% of the ethylene glycol and phenol solutions respectively were mineralized.

Phenol and ethylene glycol mineralization was not observed at pH above 7 and below 1 within the reaction time applied (120 min). These results are suitable with previous studies that have shown that Fenton’s process is most effective at an acidic pH between 2 and 4, with an optimum pH of approximately 3 [19,24]. Lucking et al. (1998) [13] in his study demonstrated that the oxidation properties of \( \text{H}_2\text{O}_2 \) and hydroxyl radicals depend on the solution’s pH. At a solution pH of 0 the redox potential for \( \text{H}_2\text{O}_2 \) and hydroxyl radicals are 1.77 V and 2.8 V respectively. At a solution pH of 14 the redox potential for \( \text{H}_2\text{O}_2 \) and hydroxyl radicals is 0.88 V and 2 V respectively. As a result of this fact, acidic conditions are applied for oxidative treatment of wastewaters with \( \text{H}_2\text{O}_2 \).

Regarding nano-catalyst aging, it was observed but not shown here that even after two years, the iron oxide nano-catalyst in solution can mineralize organic pollutants with the same efficiency as after they are produced.

3.4. Iron oxide nanocatalyst recovery

A series of experiments was conducted in order to investigate the catalytic behavior of the virgin and recovered iron oxide nanoparticles in successive catalytic runs. The results are summarized in Fig. 7a and b. The weight ratio between the hydrogen peroxide and the total iron was 16 and the pH values ranged from 2.5 to 3. Seven mineralization cycles are demonstrated both of ethylene glycol (Fig. 7a) and phenol (Fig. 7b).

In both samples, aqua solution was separated from iron oxide particles after the mineralization process. Removal of the Iron oxide nanocatalyst was performed by means of precipitation via adjusting solution pH level to 4.0–4.5 (according to previous results, see Fig. 4b). After its recovery, the spent iron oxide nanocatalyst was used once again for a second catalytic run. No iron nanocatalyst residues were found in the treated solutions after their recovery. The glass with the spent iron particles was filled with fresh solution of the organic model. The fresh solution pH was then adjusted to 2.75–3.0 (according to previous results, see Fig. 6) by adding HCl, after which solutions were mixed for 3 h at room temperature in order to obtain optimal acidity required for catalytic mineralization of the organic matters. This procedure was repeatedly performed for a total of six catalytic runs. Results are showing that at least seven stages of catalytic mineralization–recovery cycles can be made without a reduction in the catalytic properties of the iron oxide nanocatalyst. All seven cycles showed that nearly 95% and 85% for ethylene glycol and phenol solutions were mineralized respectively. Higher mineralization may be achieved at modified conditions.

The use of the reported technique for cleaning water from organic matter requires catalyst recovery which is possible through sedimentation or filtration. The consumption cost of hydrogen peroxide, acid and base needed for the process should be compared with other water cleaning techniques in order to provide the best economical solution to a problem. Obviously, the reported technique may be used in order to clean relatively small streams of industrial or maybe secondary treated wastewater.

4. Conclusions

The disadvantage of a classic Fenton process derives from the fact that when a homogeneous catalyst is added as an iron salt, it cannot be retained in the process, thus causing additional water pollution. In our study, the use of a nanocatalyst was investigated. Based on characterization and batch experiments with the organic model solutions, it was suggested that the iron oxide nanoparticle could enable us to both separate it from the final solution and reuse it in at

![Fig. 7. a. Ethylene glycol mineralization with time as a function of recovery rate of FeOOH particles. \([\text{H}_2\text{O}_2]/[\text{Fe}]_{\text{total}} = 16, [\text{TOC}]_0 = 200 \text{ mg/L, } [\text{H}_2\text{O}_2]_0 = 8250 \text{ mg/L.}\) b. Phenol mineralization with time as a function of recovery rate of FeOOH particles. \([\text{H}_2\text{O}_2]/[\text{Fe}]_{\text{total}} = 16, [\text{TOC}]_0 = 200 \text{ mg/L, } [\text{H}_2\text{O}_2]_0 = 8250 \text{ mg/L.}\)]
least six more successive catalytic runs. Further investigations are needed to study these results with real water treatment, which consist of various inorganic and organic constituents that may affect the efficiency of reused nanoparticles.

The optimal pH value for mineralization of nearly 95% and 85% of the ethylene glycol and phenol solutions, respectively, was found to be 2.8.

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