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Oxidation behavior of aqueous contaminants in the presence of hydrogen peroxide and filter media

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Abstract

Hydrogen peroxide has been used as an oxidant to degrade contaminants in solutions and soils. A poor understanding of the numerous variables that are involved makes it difficult to determine dominant contaminant removal mechanisms. Our primary objective was to examine the relationship between contaminant (quinoline and nitrobenzene) degradation rate and the rate of hydrogen peroxide decomposition on filter media. Both batch and continuous flow column experiments were conducted. In general, the rate of contaminant degradation was proportional to the rate of hydrogen peroxide decomposition, but the mass of contaminant removed depended on the amount of hydrogen peroxide decomposed, filter medium concentration, and filter medium characteristics. For increasing filter medium concentration and equivalent loss of hydrogen peroxide, the mass of contaminant degraded was found to decrease. In addition, acid–hydroxylamine treatment of the selected filter medium, to examine the role of reducible metal oxide coatings, resulted in greater contaminant removals than the parent material despite a slower hydrogen peroxide decomposition rate. The observed hydrogen peroxide decomposition and contaminant oxidation results are consistent with a reaction scheme whose central elements include: (1) a rate limiting filter medium surface catalyzed reaction initiating hydrogen peroxide decomposition with the formation of a reactive intermediate, (2) a competing reaction of the intermediate with the filter medium surface, and (3) reaction of the same intermediate with the aqueous organic contaminant. Loss of quinoline and nitrobenzene is most likely a solution phase reaction because sorption of these compounds was small over the pH range 7–8 and oxidation efficiency did not increase with increasing filter medium concentration, which would be expected if the reactions were occurring on the surface. Finally, enhanced oxidation of quinoline and nitrobenzene on the treated material is explained by more efficient use of the reactive intermediates for contaminant oxidation due to a reduction in the number of scavenging sites associated with reducible metal oxide coatings.

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1. Introduction

Oxidation processes are potentially one important class of treatment technology that may lead to the destruction of aqueous contaminants and yield harmless products. Advanced oxidation processes are broadly defined as those involving reactions of organics with reactive species such as hydroxyl radical, super oxide, hydrated electrons, and singlet oxygen. Ozone with ultraviolet light and ozone with hydrogen peroxide have been successfully used for the treatment of synthetic organics and chemicals resistant to biological degradation [1–5]. However, these processes suffer from being more expensive than traditional water treatment processes and are subject to radical traps that can severely reduce their efficiency [6].

The reaction of hydrogen peroxide with ferrous iron, commonly referred to as Fenton's reagent, has been shown to produce the hydroxyl radical. Hydroxyl radical is one of the most powerful oxidizing species known, capable of reacting with a wide range and number of organic compounds [7]. Recent work on the use of hydrogen peroxide and Fenton's reagent to degrade hazardous organics indicates that surface reactions on soils and oxides may play an important role in the oxidation of organic contaminants, although the role of different surfaces has not been characterized [8–10]. Enhanced oxidation in the presence of surfaces may occur because hydroxyl radicals or other reactive species are produced in close proximity to adsorbed contaminant. An oxidation process based on the use of filter media to initiate reactions of hydrogen peroxide might be effective and potentially result in the transformation of organic contaminants to harmless products. Water treatment facilities with iron and manganese oxide coated filter media could potentially implement this process to treat drinking water with little plant modification. The purpose of this research was to investigate the relationship between the rate of hydrogen peroxide decomposition and contaminant degradation rate in the presence of the filter media.

2. Experimental

2.1. Chemicals

The water used for all the experiments and solution preparation was deionized by a Barnstead ULTRO pure water system. All chemicals used were at least reagent grade. Certified A.C.S. 30% hydrogen peroxide solution was obtained from the Fisher Chemical Company (Pittsburgh, PA). Quinoline and nitrobenzene were obtained from the Fisher Chemical Company (Pittsburgh, PA) with stock solutions prepared by dilution with deionized water to a desired concentration.

2.2. Analytical methods

The pH was measured with a Beckman Model 72 meter after appropriate calibration. Analysis of hydrogen peroxide was made by iodometric titration with phenylarsine oxide solutions [11]. Analysis of quinoline was performed using high

pressure liquid chromatography (HPLC) with a reverse phase Synchropak C-18 column (25 cm × 4.6 mm ID). The detector was a Spectra 100 UV detector. The UV detector was set at 250 nm and the mobile phase consisted of 40% Fisherbrand HPLC grade acetonitrile and 60% deionized water with 15 m*M* phosphate at a flow rate of 0.9 ml/min. Analysis of nitrobenzene was performed using gas chromatography (Hewlett-Packard 5890 A, with a flame ionization detector and a Vocol capillary column from Supelco with 17.5 mm ID and 60 m in length). The GC oven temperature was 185 °C for the entire length of the run. The detector temperature was 250 °C. The filter medium was acid digested using EPA Method 3050 A in preparation for iron and manganese analysis by atomic absorption spectrophotometry with a graphite furnace.

2.3. Filter media

Aquifer material used for filter media (AMFM) with an effective size of 0.49 mm was obtained from Northern Gravel Company (Muscatine, IA). In addition, an acid rinsed filter medium (ARFM) was prepared using AMFM that was soaked (1.25 g medium/1 ml solution) in a 2 *M* HCl–hydroxylamine (20 g/l hydroxylamine) solution for 3 days (the solution was removed at the end of each day and replaced with fresh HCl–hydroxylamine). This was done to dissolve oxide coatings. Important filter medium characteristics are shown in Table 1. The possible contamination of the media by bacteria was controlled by gamma irradiation (5×10^6 rads for 24 h) and then stored in sterilized (autoclaved) bottles. The size of the media particles ranged from 0.84 mm to 0.18 mm.

2.4. Apparatus

The experiments for this research were performed in both mixed batch reactors and a fixed bed reactor. The batch reactors consisted of 30 ml glass vials and 250 ml stoppered Erlenmeyer flasks, gently mixed using a heavy duty wrist action shaker. All batch reactors were prepared for use by filling with dry media and then sealing them to prevent media contamination.

The fixed bed reactor used for this research was a 30 cm long glass column with a 1.0 cm inner diameter (empty volume of 23.56 cm^3) obtained from Kontes (Vineland, NJ). The medium was loaded into the column by first filling the column with water

Table 1
Characteristics of the two filter media used

Characteristic	AMFM	ARFM
Organic carbon[a]	0.1%	0.1%
Iron (mg/kg)	2330	2300
Manganese (mg/kg)	240	50
pH	7.4	7.0

[a] Analysis performed by Minnesota Valley Testing Laboratories (Nevada, IA).

and then slowly adding the medium and gently tapping the column until it was full. Solutions were introduced into the column by a Harvard Apparatus Pump Model 22.

2.5. Kinetic studies

All experiments were performed at 20 °C. Hydrogen peroxide was varied from 10–100 m*M* (340–3400 mg/l). Quinoline was varied from 0.01–0.10 m*M* (1.3–13 mg/l), and nitrobenzene was varied from 0.01–0.10 m*M* (1.2–12 mg/l). The pH range for decomposition and oxidation experiments was 7–8. For batch oxidation experiments, the contaminant was put into the reactor for one hour and then the start of experiments was marked by the addition of hydrogen peroxide. For fixed bed experiments, the contaminant alone was fed until breakthrough, at which time hydrogen peroxide was mixed with the contaminant and then the mixture was introduced into the column.

2.6. Experimental controls

Volatilization of quinoline and nitrobenzene was negligible in our studies. Direct reaction of hydrogen peroxide with quinoline and nitrobenzene was also small, with less than 3% degradation over the course of the experiment. Direct reaction of quinoline and nitrobenzene with the filter media in the absence of hydrogen peroxide was not observed. No evidence of external mass transfer limitations was observed in the column experiments for flow rates ranging from 0.2–2.0 ml/min (i.e. the observed hydrogen peroxide decomposition rate was inversely proportional to the flow rate over this range). Finally, control experiments were done to show that quinoline and nitrobenzene degradation resulted from the heterogeneous reaction of hydrogen peroxide and the filter media, and not soluble species dissolved from the filter media. This was examined by taking water in contact with the filter media for two hours, separating the solution from the filter media, and then respiking the solution with hydrogen peroxide. Quinoline and nitrobenzene were not degraded in filtered solutions (0.2 μm) spiked with 800 mg/l hydrogen peroxide, indicating that soluble species originating from the filter media are inactive with respect to quinoline and nitrobenzene degradation.

3. Results and discussion

3.1. Decomposition of hydrogen peroxide

The decomposition rate of hydrogen peroxide followed a first order relationship in both batch and fixed bed experiments for both media types according to the integrated rate expression,

$$\mathrm{Ln}\,\frac{[H_2O_2]}{[H_2O_2]_0} = -k_{obs}t, \tag{1}$$

where $[H_2O_2]_0$ and $[H_2O_2]$ are the initial and final hydrogen peroxide concentration, t is time or hydraulic residence time, and k_{obs} is an observed first order rate constant. The effect of pH on the observed hydrogen peroxide decomposition rate on the selected media is shown in Fig. 1. The effect of the initial hydrogen peroxide concentration on the observed hydrogen peroxide decomposition rate on the selected media is shown in Fig. 2. These figures show the observed hydrogen peroxide decomposition rate to be relatively consistent for variable initial hydrogen peroxide concentrations over the pH range 7–8.

A comparison of the observed decomposition rates for the selected filter media under similar experimental conditions is shown in Fig. 3. Treatment by acid–hydroxylamine, reduced the catalytic activity to approximately 10% of that measured for AMFM. Looking at the metal analysis in Table 1, the acid–hydroxylamine treatment was ineffective at reducing the total iron concentration, but did effectively reduce the manganese concentration by 80%. Manganese oxides have been shown to be effective catalysts for the decomposition of hydrogen peroxide [12]. Based on the measured hydrogen peroxide decomposition rates and metal concentrations, the hydrogen peroxide decomposition rate on the selected filter media is predominantly a function of the manganese concentration.

The observed peroxide decomposition constant, k_{obs}, was also shown in both batch and column experiments to be proportional to the concentration of filter medium

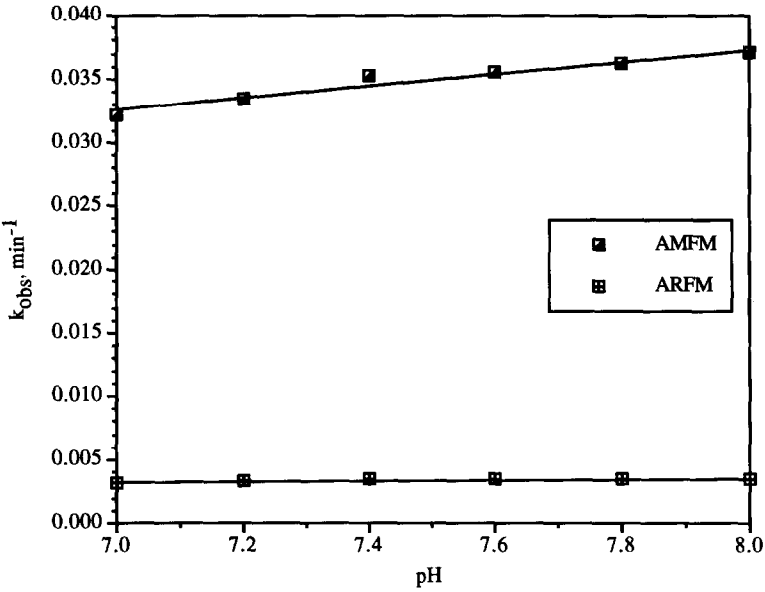

Fig. 1. Hydrogen peroxide decomposition in the presence of AMFM and ARFM filter media as a function of pH. Initial hydrogen peroxide concentration of 22.1 mM (751 mg/l) and batch reactors with 40 g of medium in 100 ml solution.

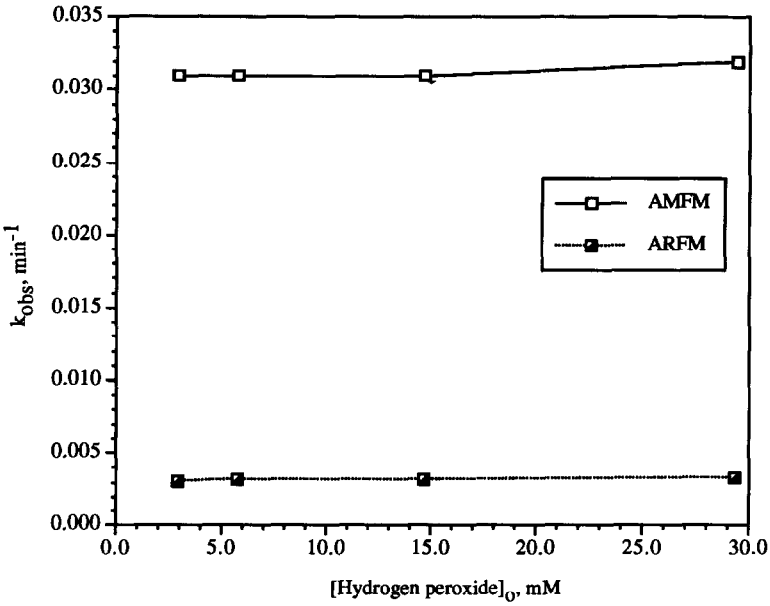

Fig. 2. Hydrogen peroxide decomposition in the presence of AMFM and ARFM filter media as a function of initial hydrogen peroxide concentration. Batch reactors with 40 g of medium in 100 ml solution.

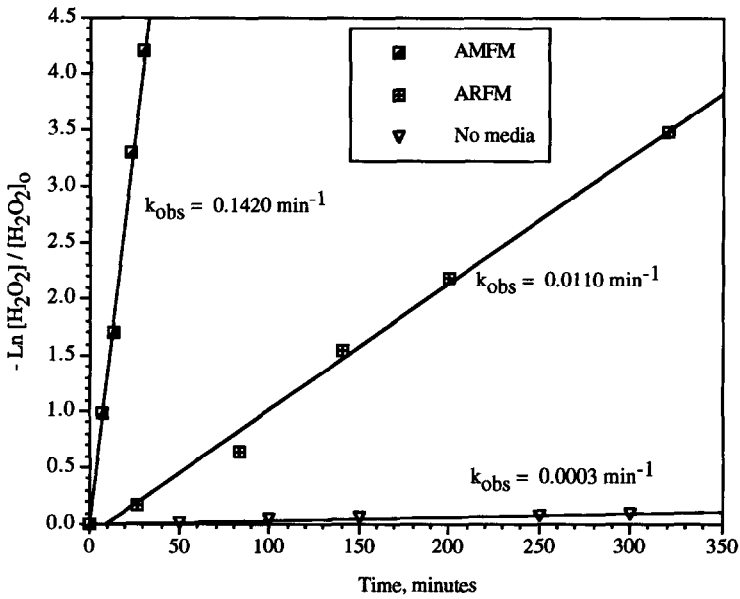

Fig. 3. Hydrogen peroxide decomposition in the presence of AMFM and ARFM filter media. Initial hydrogen peroxide concentration of 22.1 m*M* (751 mg/l), batch reactor with 5 g of medium in 4 ml solution, and pH = 7.7.

present in solution. This relationship can be described by the equation

$$k_{norm} = \frac{k_{obs}}{[M]}, \tag{2}$$

where k_{norm} is the hydrogen peroxide decomposition rate constant normalized to the filter medium concentration in solution $[M]$ (units of g/ml), and k_{obs} is the observed decomposition rate constant. A plot of k_{obs} values measured for corresponding filter medium concentrations for both AMFM and ARFM are shown in Fig. 4. Linear regression calculation of the slopes gives an overall normalized hydrogen peroxide decomposition rate for each filter medium. The normalized hydrogen peroxide decomposition rate for AMFM was found to be 0.0882 (min^{-1}) $(g/ml)^{-1}$ and 0.0086 (min^{-1}) $(g/ml)^{-1}$ for ARFM. Our measured rates on AMFM are similar to those reported on aquifer material by Barcelona and Holm [14].

3.2. Filter medium surface catalyzed oxidation of quinoline and nitrobenzene

We initially hypothesized that contaminant oxidation could occur by reaction with a reactive intermediate produced from filter medium surface catalyzed hydrogen peroxide decomposition. It follows then that the rate of contaminant oxidation would

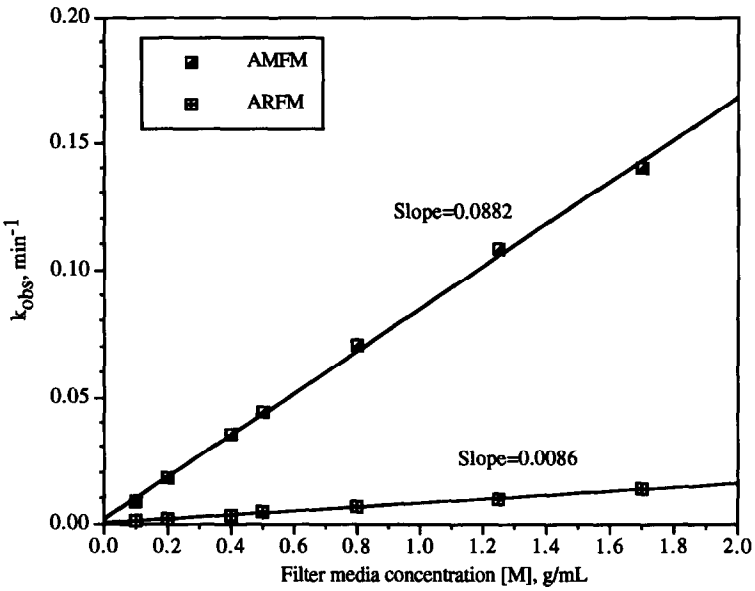

Fig. 4. Hydrogen peroxide decomposition in the presence of AMFM and ARFM filter media as a function of the filter medium concentration. Initial hydrogen peroxide concentration = 27.9 mM (950 mg/l) and pH = 7–8.

be proportional to the rate of hydrogen peroxide decomposition:

$$\frac{d[\text{contaminant}]}{dt} = k\frac{d[H_2O_2]}{dt} \tag{3}$$

where k is a proportionality constant. Relationship (3) also implies that the amount of contaminant oxidized would be proportional to the amount of hydrogen peroxide decomposed:

$$\Delta[\text{contaminant}] = k\Delta[H_2O_2]. \tag{4}$$

The amount of quinoline oxidized in the presence of AMFM could be described by relationship (4) at a fixed M value and for different initial concentrations of hydrogen peroxide (Fig. 5). However, relationship (4) did not hold for variable M values, as the efficiency of quinoline degradation (proportionality constant k) decreased with increasing M as shown in Fig. 6. Column oxidation experiments ($M = 4.25$) also followed this trend with minimal quinoline degradation (data not shown).

Batch oxidation experiments involving quinoline with ARFM found the efficiency of oxidation to be greater on ARFM than AMFM. For example, removals increased from 14% to 48%, shown in Fig. 7 and Fig. 8 for approximately equivalent loss of hydrogen peroxide and similar experimental conditions. These results also show that while the rate of quinoline degradation was proportional to the rate of hydrogen peroxide decomposition for both AMFM and ARFM, ARFM ultimately degraded more quinoline than AMFM despite a slower rate of oxidation.

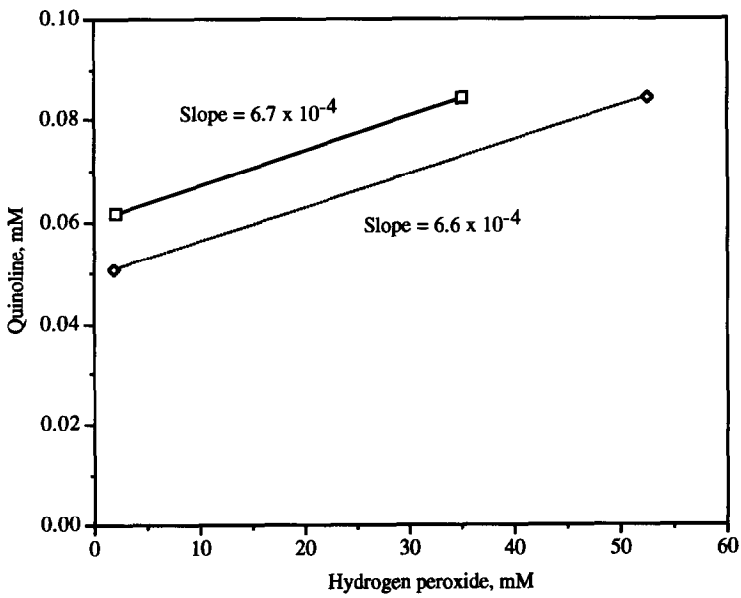

Fig. 5. Hydrogen peroxide decomposition and quinoline loss in the presence of AMFM filter media for two different initial hydrogen peroxide concentrations and $M = 1.25$.

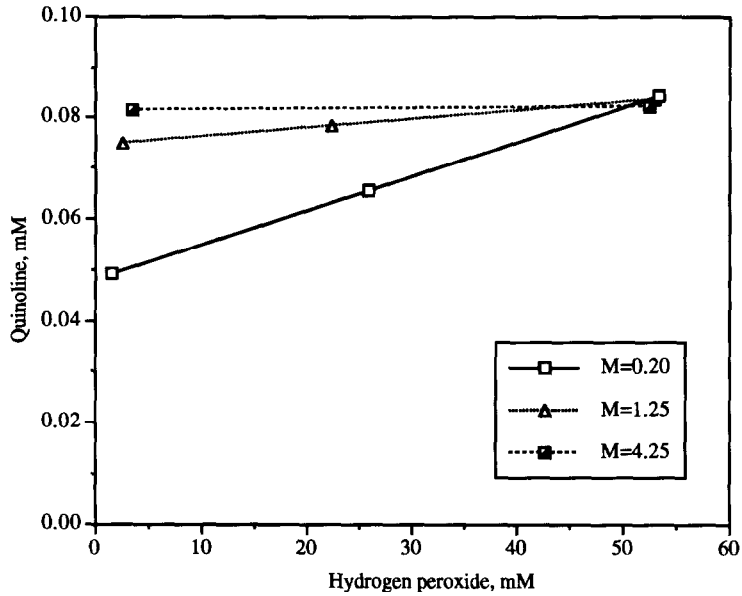

Fig. 6. Hydrogen peroxide decomposition and quinoline loss in the presence of AMFM filter media at different M values.

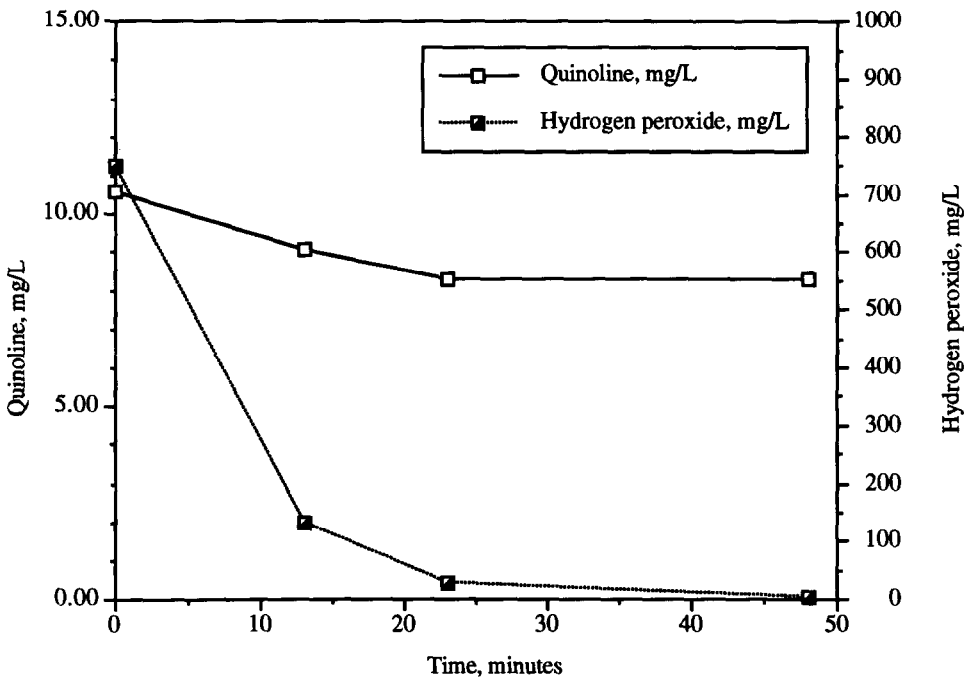

Fig. 7. Hydrogen peroxide decomposition and quinoline loss in the presence of AMFM filter media. $[\text{Quinoline}]_0 = 10.6$ mg/l, $[H_2O_2]_0 = 750$ mg/l, $M = 1.25$ g/ml, and pH = 7.7.

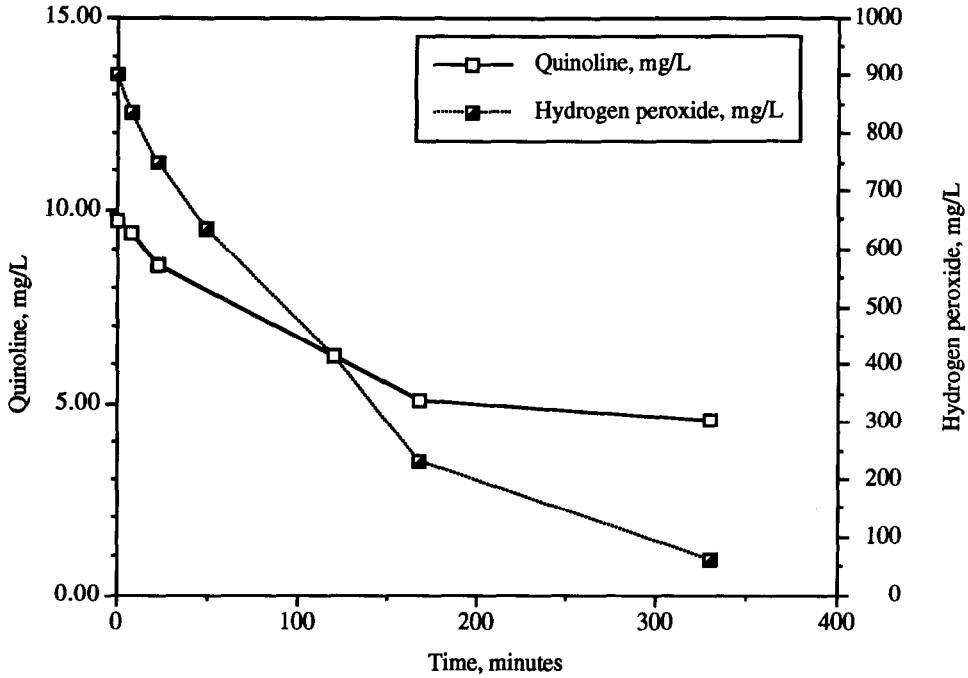

Fig. 8. Hydrogen peroxide decomposition and quinoline loss in the presence of ARFM filter media. $[\text{Quinoline}]_0 = 9.7$ mg/l, $[H_2O_2]_0 = 900$ mg/l, $M = 1.25$ g/ml, and pH = 7.7.

Batch oxidation experiments involving nitrobenzene were run to examine the effects of the filter medium concentration and filter medium type on a different contaminant. Similar to quinoline, the loss of nitrobenzene was related to both the loss of hydrogen peroxide and the filter medium concentration. For example, on the AMFM filter medium, after a loss of 1600 mg/l of hydrogen peroxide, only 3.3% of the nitrobenzene reacted with $M = 0.5$ g/ml. At $M = 0.2$ g/ml, the loss of nitrobenzene increased to 10.6% for similar hydrogen peroxide decomposition. The oxidation behavior of nitrobenzene on the treated filter medium was also similar to that observed with quinoline. For example, with ARFM and $M = 0.2$ g/ml, decomposition of 1600 mg/l of hydrogen peroxide gave 68.4% nitrobenzene loss.

The observed hydrogen peroxide decomposition and contaminant oxidation results are consistent with a reaction scheme whose central elements include: (1) a rate limiting filter medium surface catalyzed reaction initiating hydrogen peroxide decomposition with the formation of a reactive intermediate, (2) a competing reaction of the intermediate with the filter medium surface, and (3) reaction of the same intermediate with the aqueous organic contaminant. Quinoline and nitrobenzene loss is most likely a solution phase reaction because sorption of these compounds was small over the pH range 7–8 and oxidation efficiency did not increase with increasing M value, which would be expected if the reactions were occurring on the filter medium surface.

4. Conclusions

Our primary objective was to examine the relationship between quinoline and nitrobenzene degradation rate and the rate of hydrogen peroxide decomposition. Both batch and continuous flow column experiments were conducted. In general, the rate of contaminant degradation was proportional to the rate of hydrogen peroxide decomposition, but the mass of contaminant removed depended on the amount of hydrogen peroxide decomposed, filter medium to water ratio, and filter medium characteristics. For decreasing filter medium concentrations and equivalent loss of hydrogen peroxide, the mass of contaminant degraded was found to increase. In addition, acid–hydroxylamine treatment was found to increase the extent of contaminant oxidation in comparison to the parent filter medium for comparable loss of hydrogen peroxide, explained by more efficient use of the reactive intermediates for contaminant oxidation due to a reduction in the number of scavenging sites associated with reducible metal oxide coatings. To further understand what is determining the extent of the reaction, future work must address specific metal oxide coatings and their role in both reactive intermediate formation and scavenging.

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