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Comparative study of Fenton's reagent performance in disinfection of raw wastewater and activated sludge effluent

Nabizadeh Ramin, Alimohammadi Mahmood, Aslani Hasan*, Mesdaghinia Alireza, Naddafi Kazem, Nemati Reza, Ghani Maryam

Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, P.O. Box 14155-6446, Tehran, Iran
Tel. +982188951582; Fax: +982188992666; email: Aslani.ha@gmail.com

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ABSTRACT

In this study, Fenton's reagent was investigated for its possible use in the disinfection of raw and secondary treated sanitary wastewater. Different doses of hydrogen peroxide, ferrous (Fe^{2+}) ions, and their combination were evaluated at three experimental phases of the disinfection of raw wastewater. Hydrogen peroxide and ferrous ions as single disinfectants showed no significant reduction in fecal coliforms. Fenton's reagent inactivated 4 and 3.16 log of fecal coliforms from raw wastewater and activated sludge effluent, respectively. However, at CT values up to 3750 mg min/l for raw wastewater and 11250 mg min/l for activated sludge effluent, no observable effects were noted. A dose of Fenton's reagent of 600 mg/l H_2O_2 plus 150 mg/l of Fe^{2+} ions led to a 3.16 log inactivation of fecal coliforms in the activated sludge effluent and discharge standards were achievable.

Keywords: Disinfection; Fe; Hydrogen peroxide; Fenton's reagent; Wastewater; Reuse

1. Introduction

Disinfection is one of the main processes carried out in wastewater treatment plants. Treated wastewater is considered a valuable available water resource for agricultural irrigation, but it is often reused without the proper application of disinfection methods [1,2]. Consequently, use of this wastewater has high risks due to the presence of excessive pathogenic microorganisms [1,3]. According to the World Health Organization, wastewaters which do not contain more than 1000 CFU (colony forming unit) 100 m/l of fecal coliforms (FC) and more than 1 helminth Egg/l can be safely used for irrigation purposes [3].

At different stages of the wastewater treatment system, destruction and inactivation of health-related microorganisms can be carried out through several mechanisms [3]. As none of the conventional wastewater treatment processes have proved to be sufficient to reduce these microbial agents, final disinfection seems to be an obligatory step, especially when final effluents are to be re-used [3,4].

Disinfection has proved crucial for ensuring public health in potable water treatment [5]. In spite of the advantages of chlorine in water and wastewater disinfection, concerns about health-related risks due to its disinfection by-products (DBPs) in addition to storage and handling safety problems have led to recent research into alternative disinfectants [2,4,6,7]. In the last few decades, oxidation compounds such as hydrogen peroxide (HP) have been introduced for wastewater disinfection. Hydrogen peroxide has disinfection capability and does not leave any unfavourable environmental effects [6,8]. Another possible technical method for the disinfection of raw or treated wastewater is the

*Corresponding author.

use of some synergistic agents such as silver (Ag) [1], copper (Cu) [1] and iron (Fe) in combination with HP. When HP is combined with ferrous iron such as Fe^{2+}, the oxidation system is called Fenton's reaction [4,9–11]. Fenton's reagent was discovered about one hundred years ago, however, the application of this reagent as an oxidizing agent for bacterial inactivation was not practiced until the late 1960s [7]. The disinfection potential of HP is due to the production of free radicals ($OH^{\bullet}$) in the absence of a catalyst, however, the rate of radical production is slow. Fenton's reagent, on the other hand, is an extremely strong producer of hydroxyl radicals. Its oxidation potential is 2.7 eV compared with 1.8 eV for HP [4,7,10–14]. The generation of $OH^{\bullet}$ radicals by Fenton's reagent involve the following reactions [4,7]:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^{\bullet}$$
$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + H^+ + HO_2^{\bullet}$$
$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + H^+ + O_2$$

As there is little information available on the disinfection potential of Fenton's reagent in raw wastewater, the main objective of the present study was to investigate the feasibility of Fenton's reagent for the disinfection of raw wastewater (RW) and activated sludge effluent (ASE). The results were compared with the effectiveness of HP alone and iron ions alone in the disinfection of similar test samples under similar conditions. It should be noted that the study of raw wastewater disinfection was essential in our study, since many treatment plants especially in developing countries try to by-pass the untreated influent in some occasions such as hydraulic over flow during rainy periods and failure of treatment processes, which cause microbial contamination in receiving water bodies.

2. Materials and methods

The materials used in the experimental set up involved iron sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, Allied-signal), hydrogen peroxide 30% solution (Merck no. 1.08597), sodium chloride (Merck no. 1.06404), sodium thiosulfate pentahydrate (Merck no. 1.06513) and A1-Medium (Merck no. 1.00415). The necessary stock solutions were made from the above materials and doubled distilled water. The glassware was washed and autoclaved at 121°C for 15 min before use.

2.1. Sampling and preparation of samples

Plastic containers each of 10 l volume were used for RW and ASE sampling. The samples were taken from a municipal wastewater treatment plant with an activated sludge process located in the north of Tehran city, Iran, and were immediately transported to the laboratory, where they were analyzed daily.

2.2. Procedure

The study was conducted in three phases as mentioned in Table 1 at an ambient temperature ranging from 21 to 26°C. The selected doses of the reacting substances are also shown in Table 1. Each experimental phase included 14 tests relating to different concentrations of each chemical. Doses of the reacting substances were increased gradually to determine the trend in disinfection activity. The research was carried out in model laboratory reactors of 1l volume. A series of 14 reactors were supplied with the RW and ASE at the same time and the chemical reagents at different concentrations were then added. In the third phase, Fenton's reagent was prepared at a constant weigh ratio of iron to HP of 1:4 and then supplied to the reactors. Samples were mixed thoroughly for one min and after 30 min contact time, disinfectant activity was stopped by adding a mole-to-mole ratio of sodium thiosulfate as a neutralizer. Comparison tests were carried out using only HP and Fe ions. The difference between the initial and final (after exposure to disinfectant) FC number was used to evaluate the disinfection efficacy.

To compare the efficacy of the disinfectant on RW and ASE, both alone and in synergy with Fe, was determined by calculating the $C_i t$ by multiplying the initial

Table 1
Experimental phases and applied doses of reacting substances

Dose	Phase 1 H_2O_2 (mg/l)	Phase 2 Fe^{+2} (mg/l)	Phase 3 Fenton reagent	
			Fe^{+2} (mg/l)	H_2O_2 (mg/l)
1	10	2.5	2.5	10
2	20	5	5	20
3	30	7.5	7.5	30
4	40	10	10	40
5	60	15	15	60
6	80	20	20	80
7	100	25	100	25
8	200	50	200	50
9	300	75	300	75
10	400	100	400	100
11	500	125	500	125
12	600	150	600	150
13	700	175	700	175
14	800	200	800	200

disinfectant concentration (C_i) in mg/l by the time (T) in minutes (min) that the applied disinfectant was in contact with the wastewater influent.

2.3. Microbiological analysis

Microbiological analyses of the RW and ASE were performed in triplicate; before and after the disinfection process according to the doses shown in Table 1. Fecal coliforms were analyzed by the direct (without enrichment) multiple fermentation tube procedure (Standard Methods, 9221E-2). The samples were inoculated and incubated on A1-Medium and their ability to produce gas was determined. For the enumeration of FC bacteria, the samples were incubated at 37°C for 3 h and the tubes were then transferred to a 44.5°C water bath for 19–21 h [15].

3. Results and discussion

The physico-chemical and microbiological properties of the RW and ASE samples used during the period of this research are shown in Table 2. It can be clearly seen that treating municipal wastewater with the activated sludge process reduced the COD, BOD, TSS and FC by 92.52, 92.22, 92.86 and 98.65%, respectively. From the standpoint of FC reduction and health-related risks, it is obvious that the activated sludge process alone cannot produce an effluent appropriate for re-use purposes.

The disinfection performance of the phase-1 reaction (H_2O_2 alone) on RW and ASE is shown in Fig. 1. Results obtained in this phase of the experiment showed that HP doses in the range of 10 to 800 mg/l and 30 min contact time corresponding to CT values of 300–24000 mg min/l, led to no significant (0.02–0.66) log inactivation of FC_s in RW. The results are in good agreement with the findings of Marcine Debowski and Miroslaw Krzemieniewski (2007), they applied HP as a single disinfectant for sewage sludge disinfection and after 24 h contact time the highest used dose of HP decreased coliforms bacteria by 1.1 log inactivation. An HP dose of 600 mg/l and 30 min contact time (CT = 18000) led to a 0.85 log inactivation of FC in ASE. In this case, the results also are similar to Velasquez et al. (2008). they used HP for the disinfection of advanced primary treatment effluent and found that the maximum fecal coliforms removal occur at a dose of 250 mg/l of HP and at an exposure time of 120 min (CT 30000), they stated that fecal contamination decreased by 2.2 log inactivation.

Table 2
Physico-chemical and microbiological characteristics of RW and ASE

Parameter	RW	ASE
COD (mg/l)	648 ± 112	48 ± 13
BOD (mg/l)	360 ± 76	28 ± 6
pH	7.48 ± 0.5	7.2 ± 0.25
TSS (mg/l)	420 ± 20	30 ± 4
FC (MPN/100 ml)	1.48E + 07	2.00E + 05

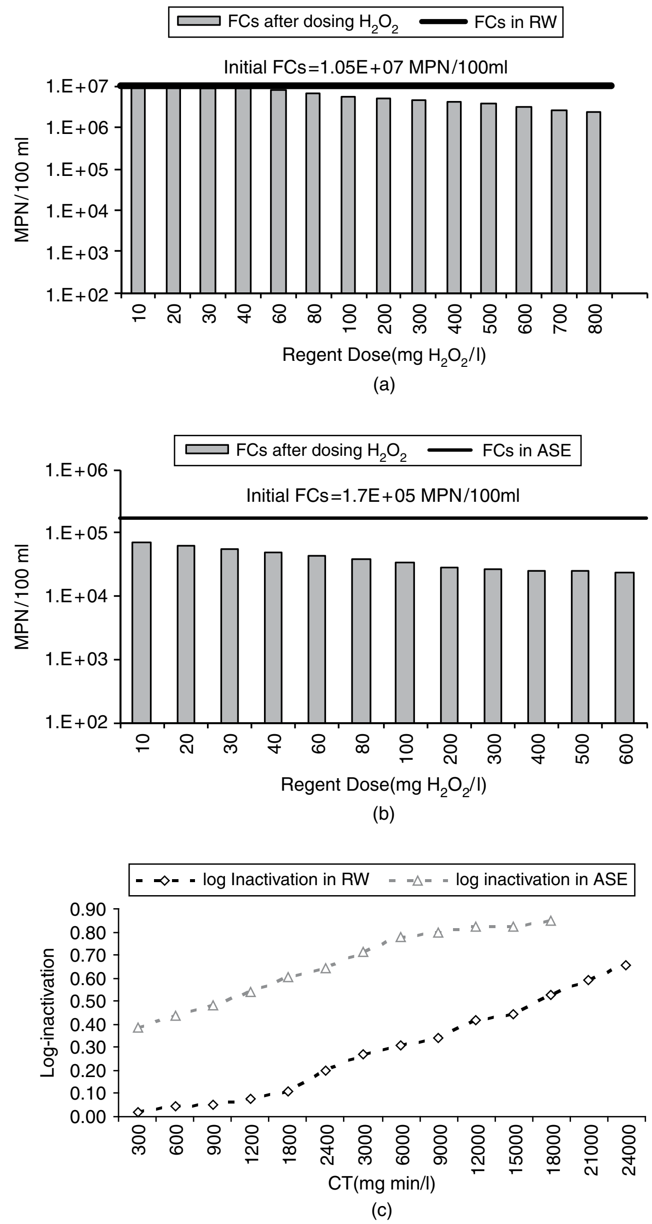


Fig. 1(a). Fecal coliforms reduction in phase 1 of the experiments (in the RW); (b) Fecal coliforms reduction in phase 1 of the experiments (in the ASE); (c) Log-inactivation vs. the CT factor for FC reduction, using HP for disinfecting of RW and ASE.

In addition, it can be inferred from Figs. 1(a) and 1(b) that at CT values of 24000 and 18000 mg min/l, the highest doses of HP applied to RW and ASE, respectively; the number of surviving FC were 2.31E+06 and 2.4E+04 MPN/100 ml, respectively. In addition, it can be inferred from Fig. 1(c) that the number of organisms has a notable effect on HP disinfection intensity. For RW, HP doses of less than 60 mg/l had no considerable disinfection effect [Fig. 1(a)], but in the case of ASE this value was 10 mg/l [Fig. 1(b)]. These figures clearly show that HP alone did not have a significant disinfection effect, and this is in accordance with the findings of other researchers [1,16–18].

The disinfection performance of phase 2 of the experiment (Fe alone) on RW and ASE is shown in Fig. 2(a) and 2(b), respectively. As seen in Fig. 2(a), the highest concentration of Fe (200 mg/l) did not have a significant effect on FC removal. The maximum removal efficacy achieved with Fe was 0.18 log inactivation. Fig. 2(b) shows the impact of Fe on FC numbers in ASE. It can be seen that even at a low number of FC (1.70E+05 MPN/100 ml) Fe did not have a meaningful disinfection effect. In this case, the FC content in ASE was reduced to 2.3E+04 MPN/100 ml, thus the reduction was a 0.87 log inactivation at a CT value of 4500 mg min/l.

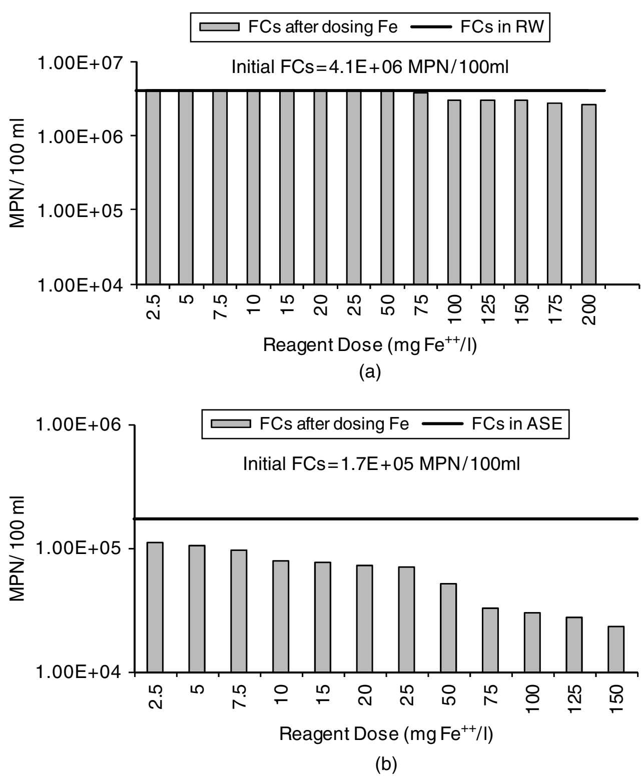


Fig. 2(a). Fecal coliforms reduction in phase 2 of the experiments (in the RW); (b) Fecal coliforms reduction in phase 2 of the experiments (in the ASE).

In phase 3 of the experiment, the disinfection performance of Fenton's reagent was evaluated. Figs. 3(a) and 3(b) demonstrate the results of this series of experiments. The results presented in these figures show that the efficiency of Fenton's reagent improved to a satisfactory level with increasing chemical concentrations. The

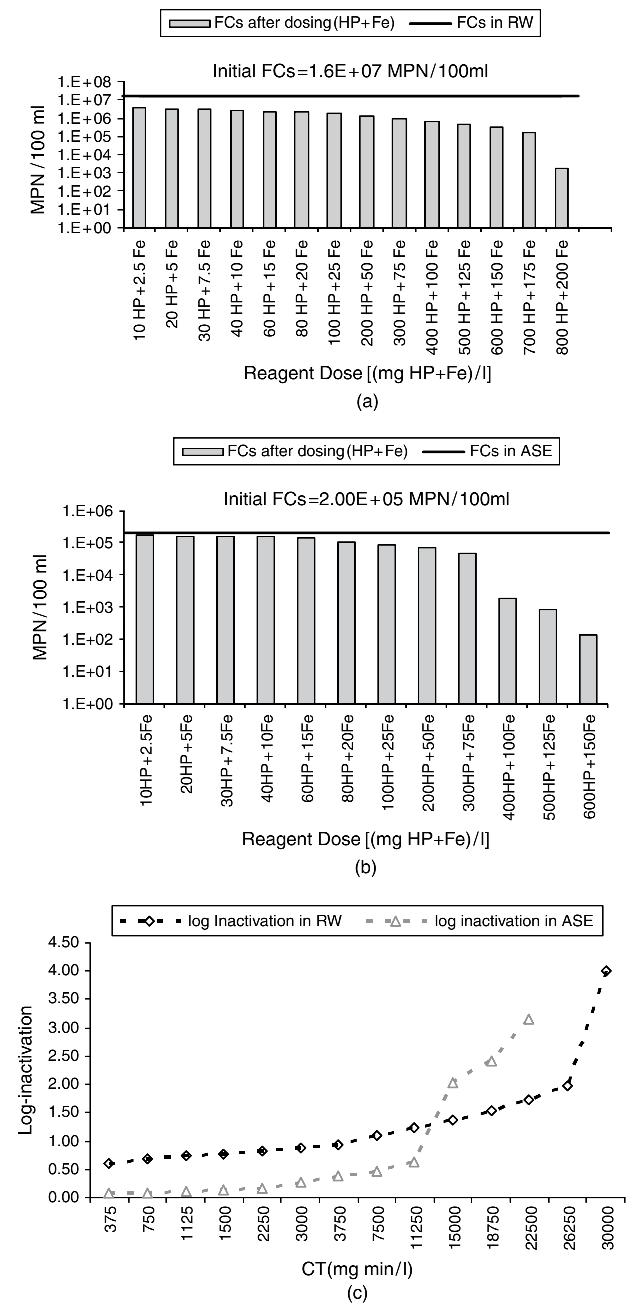
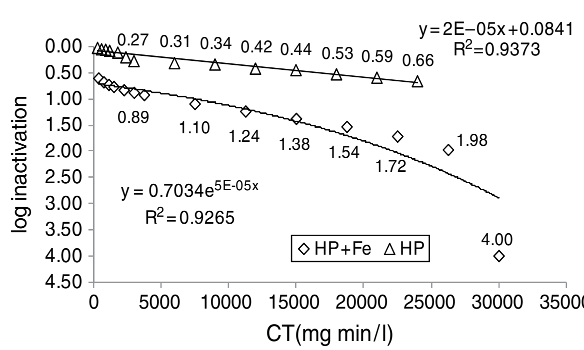


Fig. 3(a). Fecal coliforms reduction in phase 3 of the experiments (in the RW); (b) Fecal coliforms reduction in phase 3 of the experiments (in the ASE); (c) log-inactivation vs. the CT factor for FC reduction using Fenton's reagent for disinfecting of RW and ASE.

figures show that the addition of Fe^{2+} ions to HP had a significant synergistic effect on HP disinfection capacity. For example, the application of a combination of HP and Fe^{2+} ions (600 + 150 mg/l) to ASE, led to a 3.16 log inactivation of FC, while HP alone at the same dose led to a 0.85 log inactivation, and applying (700 + 175 mg/l and 800 + 200 mg/l) to RW, resulted in an approximate 2 and 4 log inactivation, respectively.

A comparative study of the impact of different CT values on the removal efficiency of FC from RW and ASE is shown in Fig. 3(c). The trend change at CT values lower than 11250 mg min/l was very slow for both RW and ASE, but in both cases and at CT values up to 11250 mg min/l, a gradient variation occurred rapidly. It can be seen that at CT values up to 3750 mg min/l for RW or 11250 mg min/l for ASE (log inactivation was less than 1log) no observable effect was noted. Importantly, the observed log inactivation at CT values up to 11250 mg min/l for RW was greater than that for ASE, but at higher CT values, the trend was reversed.

Fig. 4(a) shows HP and Fenton Reagent performance in RW disinfection. As shown, the trend of fecal coliforms log-reduction for HP as a single disinfectant is linear, but the trend of fecal coliforms log-reduction for Fenton reagent seems to be exponential. It is shown that at C_iT about 17000 Fenton reagent and HP can led to 1.38 and 0.44 log-reductions, respectively. Therefore,



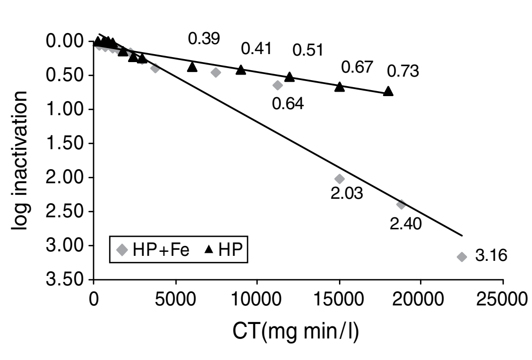


Fig. 4(a). Comparison of HP and Fenton's reagent performance in RW disinfection; (b) Comparison of HP and Fenton's reagent performance in ASE disinfection.

it is obvious that adding Fe^{2+} ions has notable synergistic effect on the disinfection performance of RW using HP.

Efficiency of HP and Fenton reagent in ASE disinfection are shown in Fig. 4(b). It is shown that at C_iT about 15000 Fenton reagent and HP can led to 2.03 and 0.67 log-reductions, respectively. It can be seen that both (HP and Fenton) removal trends are in linear form; since there is high concentration of organic and inorganic compounds in RW, free $OH^{\bullet}$ radicals as a main oxidant produced in Fenton systems would be consumed to oxidizing such compounds and FCs removal line changes exponentially [19].

The aim of this study was to evaluate and compare the disinfection efficiency of hydrogen peroxide, Fe^{2+} ions and Fenton's reagent on FC reduction in RW and ASE. During the past two decades, researchers have been interested in using AOPs for the destruction of pathogenic bacteria. The use of AOPs for disinfection can reduce COD, TOC, heavy metals and NOM concentrations in addition to economical benefits. However, the presence of such compounds negatively affects the disinfection potential of Fenton's reagent by consuming $OH^{\bullet}$ radicals [20]. In addition, Fenton's reagent has been used in other applications. Weiwei Ben et al. used Fenton's reagent for the removal of veterinary antibiotics from pretreated swine wastewater in a sequencing batch reactor, and Walter et al. used Fenton's reagent for trihalomethanes oxidation [21,7].

The results show that the application of HP alone had only mild or low disinfection ability on the RW, even at high doses such as 800 mg/l. In addition, the application of Fe^{2+} ions alone had no significant disinfection effect. The combination of these two agents and the generation of Fenton's reagent showed significant disinfection ability. However, in the case of RW disinfection, even at very high doses of Fenton's reagent (800 mg/l H_2O_2 plus 200 mg/l Fe^{2+} ions) a significant reduction of about 4 log inactivation in FC did not enable us to achieve the Iranian national wastewater discharge standards (<400 MPN/100 ml) for receiving waters and for agricultural re-use. Moreover, achieving the EPA standard (200 MPN/100 ml) for agricultural re-use was impossible. However, in the case of ASE, it can be seen that at a CT value of 22500 mg min/l (Fig. 3(b)) a 3.16 log inactivation of FC density was achievable. When this value was compared with that achieved when HP was applied alone at the same dose of 600 mg /l (0.65 log inactivation), this demonstrated that Fe^{2+} ions had a notable synergistic effect on HP disinfection performance. Moreover, by reducing the MPN to 160 per 100 ml with reagent doses of 600 mg/l H_2O_2 plus 150 mg/l Fe^{2+} ions, both national and EPA discharge standards were achievable in the disinfection of ASE. According to other researches, the main inactivation mechanisms for FC removal is the $OH^{\bullet}$ production that cause damage bacteria cell wall. All particles can be affected by free radicals. This reaction leads to the limitation of cell's biological and biochemical activity [10].

4. Conclusions

In certain areas, wastewater is sometimes the only available water source for agricultural irrigation. However, its use poses health-related risks due to high levels of pathogenic microorganisms, including fecal coliforms. Conventional treatment processes such as ASE can lower these levels, however, the treatment of raw wastewater to a healthy low-risk liquid without disinfection is impossible. Therefore, unconventional disinfection methods were studied in this research.

- The application of HP alone for disinfection of raw wastewater and activated sludge effluent is not practicable due to low observed efficiency.
- The use of Fenton's reagent allowed us to obtain notable results for activated sludge effluent disinfection and WHO guidelines (<1000 CFU/ml) for agricultural crop irrigation achievable, however, in the case of raw wastewater, the use of this process to achieve disinfection goals is not recommended.
- The efficiency of the methods used showed a direct relationship with increasing compound concentrations; however, at CT values ranging from 11250 to 30000 mg min/l, the removal rate was significant and the use of lower concentrations of Fenton's reagent for disinfection was unsuccessful.

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