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Chemical oxidation with hydrogen peroxide for domestic wastewater treatment

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Abstract

The recycling of domestic wastewater is an effective means of coping with the water shortage in Tunisia. After hydrogen peroxide oxidation, the refractory organic substances in wastewater were decomposed. COD, offensive odor and foaminess in the effluents were reduced with increasing dose. Hydrogen peroxide oxidizes both organic and inorganic pollutants which contribute to BOD and COD. The Oxidation of sulfides into sulfates by H_2O_2 may be applied directly to aqueous wastes containing these odorants. Inactivation efficiencies of bacteria in the secondary effluents by H_2O_2 oxidation was investigated. The number of total coliforms exponentially decreased with increasing dose and fell to low levels at the dose of 2.5 ml/L.

Keywords: Wastewater; Hydrogen peroxide; BOD/COD; Deodorization and disinfection

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1. Introduction

In Tunisia, some considerable investments have been set in motion to mobilize these resources in water to the advantage of cities, industry and agriculture. Other investments have also been put in place to collect and to treat the rejected wastewater. Situated in an arid to semi-arid climate where water is rare, Tunisia had adopted an integrated approach in the management of resources water including wastewater. Indeed, the water resources are in a decreasing trend during the next decades, whereas the wastewater is constantly increasing. These last potential resources in water represents a quite important quantity immediately available downstream the agglomerations independently of the seasons and rainy periods. These resources should be integrated in the natural cycle of the water use and to benefit from the fertilizing value of these waters. But this would not be valid and guaranteed after adapting the treatment to the use and to master the sanitary risks bound to the wastewater reuse [1]. Depending on specific needs of cleaned wastewater reuse, several levels of treatment are applied in Tunisia. The extensive techniques (lagoons, infiltration-percolation, and infiltration in soils) are well adapted to the climatic conditions of south regions in Tunisia [2]. In contrast, the intensive technologies (filtration and physico-chemical treatment) are well adapted to urban zones. The advanced processes for wastewater decontamination like chlorination, UV irradiation or ozonation are compact and guarantee a better quality of water produced [3,4] but they are more expensive.

Hydrogen peroxide has been used to reduce BOD, COD, offensive odor and foaminess in domestic or industrial wastewater for many years. While the cost to clean up these wastewater through the chemical oxidization is typically more expensive than through the physical or biologic means [5], hydrogen peroxide can be used as an autonomous treatment or as an improvement of existing physical or biologic treatment processes, according to the situation. Hydrogen peroxide can be used alone [6] or with a catalyst such as iron (Fe^{2+} or Fe^{3+}) [7], UV light [8], ozone (O_3) [9] catalytic autoxidation [10] and the alkali contribute to the reduction of the BOD/COD in the wastewater [11].

Due to effectiveness of hydrogen peroxide as a strong oxidative chemical in water treatment, the suitability of this AOP technique will been tested in this work for the disinfection and deodorization of domestic wastewater before agriculture reuse.

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Table 1
Characteristics of domestic wastewater diluted two times with potable urban water

Parameter	Amount
pH	7.41
COD (mg O_2/L)	322
BOD_5 (mg O_2/L)	40
Ca^{2+} (mg/L)	304
Mg^{2+} (mg/L)	57
K^+ (mg/L)	38
SO_4^{2-} (mg/L)	1031
Cl^- (mg/L)	568
HCO_3^- (mg/L)	378
Sulfides, S^{2-} (mg/L)	10

2. Experimental

2.1. Wastewater sampling

Fresh secondary wastewater samples were supplied from pumping station plant (STEP) in Gabes municipal (south of Tunisia). The Gabes municipal STEP receives wastewater from a combined sewer system serving approximately 30,000 person equivalents. The wastewater is domestic and contains no industrial inputs. The characteristics of this wastewater are monitored in Table 1. For our experiences effluent was diluted two times before used.

2.2. Experimental set-up

The reactor is constructed as a tank of 25 L equipped with a mixer of variable rotational speed (25–250 rpm). The reactor was aerated from the bottom of the reactor at the flow rate of 12 L/min. The reactor was equipped with a pH and redox potential control. Experiments were carried out at ambient temperature (25 °C).

2.3. Procedure

Sample of 25 L wastewater were batch-treated at different operating conditions. The treatment was done without any change in the solution pH value. The aerobic biological treatment involves identical microbial species to those naturally developed in the depuration station and provokes the oxidation of organic matter. The mixture was stirred at 100 rpm. In Fenton's reaction, Fe^{2+} was added in the form of $FeSO_4$, $7H_2O$ at the given concentration and hydrogen peroxide was added at the required amount from a 30% H_2O_2 extra pure stabilized solution.

Five different concentrations of H_2O_2 were tested (treatment with only H_2O_2): 0.25, 0.5, 1, 1.5 and 2.5 ml/L. Samples were collected during the reaction at 30, 60, 90 min, 2 and 3 h time intervals after H_2O_2 addition.

2.4. Analytical methods

The chemical oxygen demand (COD) was determined by using a bioblock (COD) analyzer based on the method of acidic oxidation by dichromate. The initial and treated wastewater solutions were also analyzed by measuring the 5-day biological oxygen demand (BOD_5) using the HACH BODTrak^{TM} method.

Sulfide concentrations in samples were measured by titrimetric procedure for acid-soluble and insoluble sulfides [12], wich is suitable for measuring sulfide concentrations in samples containing 0.2–50 mg/L of sulfide.

First, sulfide was precipitated in an zinc acetate scrubber as zinc sulfide. The sulfide is oxidized to sulfur by adding a known excess amount of iodine (0.1 N). The excess iodine was determined by titration with a standard solution of sodium thiosulfate until the blue iodine starch complex disappears. As the use of standard sulfide solutions is not possible because of oxidative degradation, quantification is based on sodium thiosulfate.

Sulfate ions were analyzed by gravimetric method after precipitation with saturated solution of barium chloride.

For the determination of the total fecal coliforms, 100 ml of wastewater was filtered through a 0.45 μm porosity membrane and incubated during 24 h at 35 °C in m-Endo medium. In these conditions, the biochemical reaction between the acetaldehyde (by-product of the fermentation), the basic fushine and sodium sulfite present in the culture medium permits the selective growth, the numeration and the presumptive identification of the total coliforms that appear in characteristic colonies with metallic green reflection.

3. Results and discussion

3.1. Influence of the addition of H_2O_2 on COD removal

Initially, the effect of the presence of Fe^{2+} ions on the COD removal shows that it does not have any effect on the COD removal. This means that Fe^{2+} ion does not have any effect either oxidizing or degrading of the organic matter. Besides, the consultation of the results obtained by the Fenton process (H_2O_2/Fe^{2+}) on the COD is efficient. The COD values remain relatively steady (322 mg O_2/L) during the first 30 min then decrease with time and reach the value of 66 mg O_2/L after 3 h of treatment. These results prove the degrading action of the Fenton process for the organic matter in the wastewater.

Based on these results, we achieved the purification of the domestic wastewater by the hydrogen peroxide only. Fig. 1 shows that the organic matter in this wastewater is easily oxidized. The activation by the hydrogen peroxide was largely sufficient. Otherwise it's well known that a significant fraction of the COD has mineral origin like sulfides, sulfites and thiosulfate. The use of hydrogen peroxide only is particularly efficient for COD removal in this case. The COD value decrease after 3 h of treatment to 44 mg O_2/L.

The pH values with time have the same regularities in the Fenton process and when used Fe^{2+} only (Fig. 2). The values decrease rapidly to nadir point at first, and then increase gradually. Therefore, the change of pH value in this case can be explained by the acidity of $FeSO_4$. Whereas in H_2O_2 and in biological processes, the values of pH increase gradually. This indicates that the degradation reaction occurs and leads to basic by-product like HCO_3^- (pH ≈ 8).

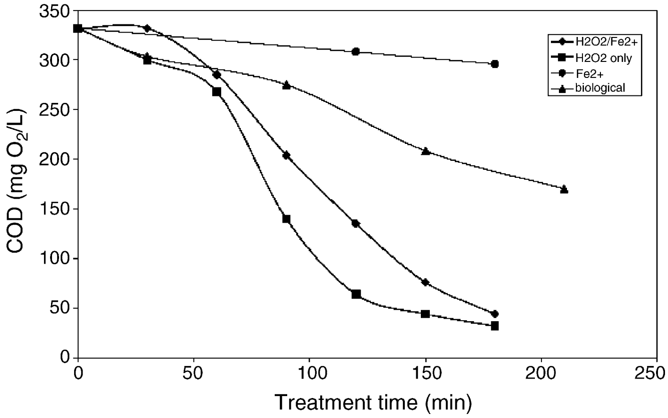

Fig. 1. COD removal from domestic wastewater at neutral pH under different conditions. (●) Fe^{2+} only (0.4 mM); (▲) biological process; (♦) H_2O_2 (1 ml/L) and Fe^{2+} (0.4 mM); (■) with H_2O_2 (1 ml/L) only.

In order to investigate the optimum amount of H_2O_2 for COD removal, a series of experiments was carried out at different hydrogen peroxide initial concentrations. In these experiments percentage of COD removal were measured throughout the reaction period of 2 h. In terms of contamination level reduction, an increase of hydrogen peroxide dose from 0.25 to 2.5 ml/L significantly improved the conversion of COD as shown in Fig. 3. The actual amount needed will be greater depending on the degree of COD removal needed. It can be concluded that the dose of 1.5 ml/L is the optimal dose to destroy the majority of product risks. Nevertheless, values of this reagent exceeding 1.5 ml/L did not improve the process performance.

3.2. *Biodegradability of domestic effluents after hydrogen peroxide oxidation*

The domestic wastewater was treated under operating conditions: (initial pH = 7.49 and 25 °C temperature reaction) using different amounts of H_2O_2. BOD_5/COD ratios of effluents obtained after each treatment were measured. The results are shown in Fig. 4. The initial BOD_5/COD ratio of the wastewater was 0.106, which indicated that it had poor biodegradability. The BOD_5/COD ratio of effluent treated with 2.5 ml/L of hydrogen peroxide (30%) increase to 0.47 indicating that the effluent was already biodegradable. Therefore, the biodegradability of domestic wastewater was improved greatly. Hydrogen peroxide can effectively improve the biodegradability because the intermediates, such as a short-chain carboxylic acid produced from ramified aliphatic chain in hydrogen peroxide oxidation are easily degraded by microorganisms [13]. The considerable increase of the BOD_5/COD ratio is also assigned to the transformation by the hydrogen peroxide of the mineral substances existing in the effluent such as sulfides, sulfites and thiosulfate into sulfates that not contribute in BOD_5/COD.

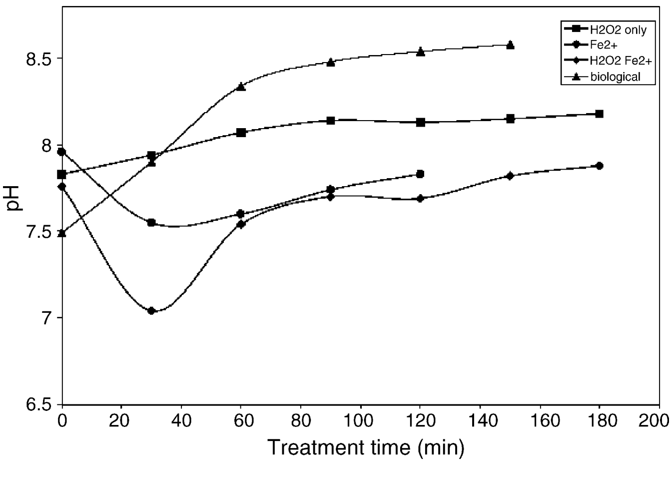

Fig. 2. pH value vs. time in domestic wastewater treatment under different conditions. (●) Fe^{2+} only (0.4mM); (▲) biological process; (♦) H_2O_2 (1 ml/L) and Fe^{2+} (0.4 mM); (■) with H_2O_2 (1 ml/L) only.

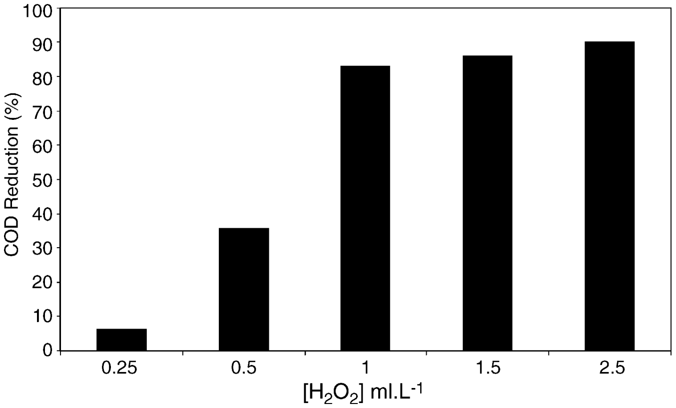

Fig. 3. Evolution of the percentage of COD removal during peroxidation for increasing amounts of H_2O_2 after 2 h time reaction.

3.3. *Influence of the addition of H_2O_2 on sulfides and sulfate concentrations*

It’s well known that reduced sulfur inorganic compounds like sulfides, sulfites, or thiosulfate contribute for a high fraction of the BOD/COD. Glaze et al., have shown that H_2O_2 is typically efficient for odor control [14]. According to the pH of wastewater, the oxidation of these compounds by hydrogen peroxide gives sulfate ions or colloidal sulfur, which does not contribute to BOD/COD [15]. In the absence of H_2O_2, we remark an increase in sulfides concentrations until 90 min of time treatment

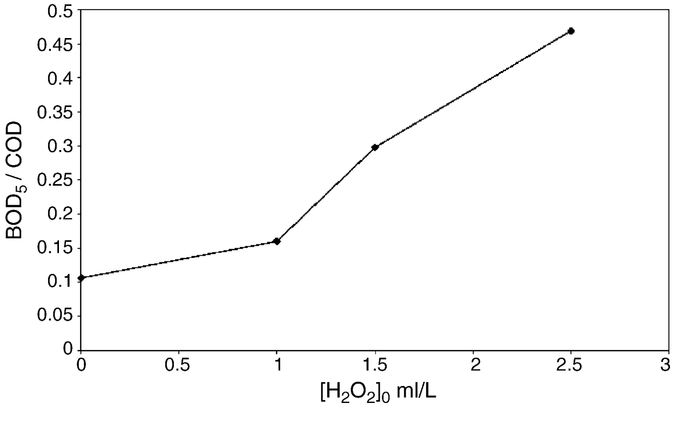

Fig. 4. The variety of BOD_5/COD during H_2O_2-peroxidation process.

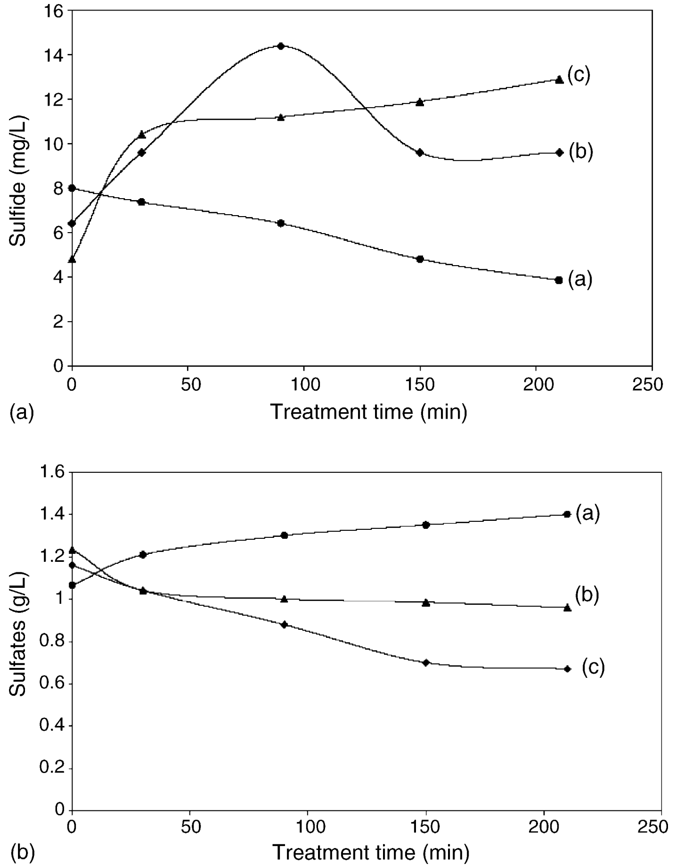

Fig. 5. (A) Sulfide reaction profile in domestic wastewater treatment under different conditions. (a) With H_2O_2 (1 ml/L) only; (b) H_2O_2 (1 ml/L) and Fe^{2+} (0.4 mM); (c) biological process. (B) Sulfate reaction profile in domestic wastewater treatment under different conditions. (a) With H_2O_2 (1 ml/L) only; (b) H_2O_2 (1 ml/L) and Fe^{2+} (0.4 mM); (c) biological process.

(Fig. 5a). In the same case the amounts of sulfates decrease from 1.5 to 1.025 g/L Fig. 5b. This can be explained first by the biological degradation of sulfured organic matters leading to sulfides and by the reduction of sulfates in sulfides this reaction proceeds accordingly the reaction 1 [16]:

$$SO_4{}^{2-} + 8e^- + 4H_2O \rightarrow S^{2-} + 8OH^- \quad (1)$$

By adding H_2O_2 we note an increasing in sulfates concentration and the diminution of sulfides in treated wastewater. From this we can conclude that sulfide and sulfates concentrations are inversely proportional. At a solution pH equal to 8.62, sulfides and sulfites are oxidized by hydrogen peroxide into sulfates according to the reactions below:

$$S^{2-} + 4H_2O_2 \rightarrow SO_4{}^{2-} + 4H_2O \quad (2)$$

$$SO_3{}^{2-} + H_2O_2 \rightarrow SO_4{}^{2-} + H_2O \quad (3)$$

$$HSO_3{}^- + H_2O_2 \rightarrow HSO_4{}^- + H_2O \quad (4)$$

Sulfate was the predominant product of sulfide oxidation [17] during this stage and a subsequent decline in pH was also observed in the Fig. 2. The use of Fe^{2+} in presence of H_2O_2 controls the odors while forming an insoluble precipitate FeS with the smelling agents (H_2S, HS^-, S^{2-},...) (Eq. (5)). During the Fenton reaction ferrous ions are converted to ferric ions. Fe(III) can remove sulfide by oxidizing it chemically to elemental sulfur while being reduced to Fe(II), which can subsequently produce FeS according to Eqs. (5) and (6) [18]. These complexes are decomposed during the analysis by iodine, which explains the increase of the sulfides quantity:

$$Fe^{2+} + HS^- \rightarrow FeS(s) + H^+ \quad (5)$$

$$2Fe^{3+} + HS^- \rightarrow 2Fe^{2+} + S^\circ + H^+ \quad (6)$$

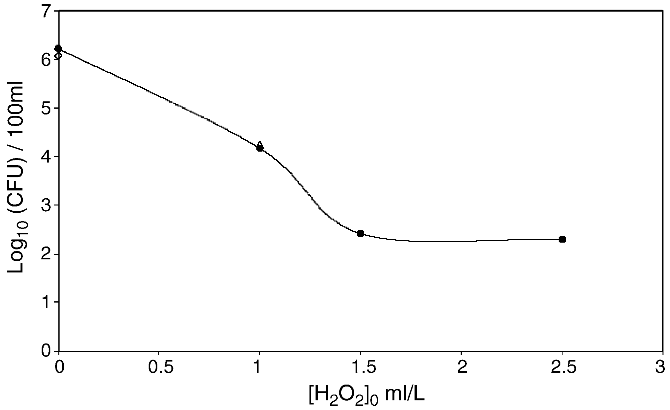

Fig. 6. Effect of initial H_2O_2 concentration on bacterial profile (CFU 100 ml^{-1}) after 2 h time reaction. (●) With H_2O_2 (1 ml/L) only; (◊) Fe^{2+} only (0.4 mM); (△) H_2O_2 (1 ml/L) and Fe^{2+} (0.4 mM).

Regarding these results we can conclude that the hydrogen peroxide activated the oxidization of the organic matter as well (Fig. 1) as reducing the sulfides content in the fairway oxidation level. The addition of Fe^{2+} does not have a significant effect on odor control in the presence of hydrogen peroxide. In this case Fe(III) produced by the auto-oxidation of ferrous ions leads to the formation of colloid sulfur.

3.4. Effectiveness of H_2O_2 for the reduction in total fecal coliforms

The reduction in colony forming units following the addition of increasing amount of H_2O_2 is displayed in Fig. 3. A relatively high rate of bacterial inactivation was observed, when the concentration of H_2O_2 is equal to 2.5 ml/L. The viable cell count decreased after 120 min to about 3 log order Fig. 6. When the wastewater is treated with hydrogen peroxide $[H_2O_2] = 1$ ml/L and Fe^{2+} (Fenton reagent), the reduction in viable count is equal to that observed with only H_2O_2 at the same concentration. From these results we can conclude that iron do not affect the destruction of bacteria. When wastewater was treated with Fe^{2+} only no reduction in viable counts was observed. The cell killing power of hydrogen peroxide is due to oxidation of intracellular constituents [19]. The active forms of oxidant are probably the hydroxyl radicals ($OH^\bullet$) and perhydroxyl ($HO_2{}^\bullet$) generated from the decomposition of H_2O_2. These species can have both lethal and sublethal effects on bacterial genome and other intracellular molecules resulting in physiological alterations, growth delay and oxidative disturbances of bacterial membranes resulting in growth inhibition [20,21]. Saito et al. [22] showed that potassium release from cells correlated with loss of % viability; this result explains the loss of membrane ionic controls are the cause of death. Hydrogen peroxide is very effective oxidant which can be used constructively and efficiently for disinfection of domestic wastewater for reuse.

4. Conclusion

Integration of aerobic biological treatment and chemical oxidation using hydrogen peroxide as oxidant allows the effective control of organic load, offensive odor and foaminess in domestic wastewater. The majority of organic compounds were found to be destroyed by hydrogen peroxide oxidation process, giving a 85% reduction of COD and BOD_5/COD ratio increase from 0.106 to 0.47. Control is achieved by adjusting the H_2O_2 concentration relative to COD load. The optimized dose determined in this study is equal to 1.5 ml of H_2O_2 per liter of wastewater with $300 < \mathrm{COD} < 400$ mg O_2/L. The oxidation of sulfides into sulfates by H_2O_2 is demonstrated by the decrease in total sulfides concentration and the increase of sulfates during the peroxidation reaction. Iron salt dose not have a significant effect on the treatment efficiency in the present study. The use of hydrogen peroxide oxidation has also demonstrated efficacy as treatment process for disinfection of domestic wastewater. With the optimal dose of 1.5 ml/L of H_2O_2, a substantial decrease in bacterial numbers was observed.

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