

The Effect of H₂O₂ Interference in Chemical Oxygen Demand Removal During Advanced Oxidation Processes

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ABSTRACT

Hydrogen peroxide (H₂O₂) is one of the most oxidants in AOPs. By H₂O₂ dissociation, hydroxyl radical with a standard oxidation potential of 2.7 is produced. It is reported H₂O residual in AOPs has been led to interference in chemical oxygen demand (COD) test and it is able to hinder biological treatment of waste water. Because of high mixed organic load of solid waste leachate, this study investigated effect of H₂O₂ interference in COD removal from solid waste leachate.

In this study effect of parameters such as pH (3,5,7,12), H₂O₂ dose (0.01, 0.02, 0.03, 0.04 mol l⁻¹), and time reaction (10,20,30,40,50,60 min) evaluated on H₂O₂ interference in COD removal from solid waste leachate.

Optimum pH and concentration were 3 and 0.02 mol l⁻¹ respectively. With increasing reaction time, COD removal was increased. The false COD obtained between 0.49mg per 1mg of H₂O₂. The average of COD removal by H₂O₂ for 60 min was 6.57%. Also reaction rate of this process was 0.0029 min⁻¹.

The presence of H₂O₂ leads to overestimation of COD values after reaction time because it consumes the oxidation agent. The extent of H₂O₂ interference in COD analysis was proportional to the remaining H₂O₂ concentration at the moment of sampling.

Key Words: Hydrogen peroxide, Interference, COD, Leachate, Gonabad

INTRODUCTION

Many advanced oxidation processes are based on addition of hydrogen peroxide (H₂O₂) with the aim of producing hydroxyl radicals to oxidize organic contaminants in water and waste water [1-3]. H₂O₂ is one of the most oxidants in AOPs. By H₂O₂ dissociation, hydroxyl radical with standard oxidation potential (E_o) of 2.7 V is produced [1, 2]. Hydrogen peroxide is a multiuse oxidant applied in many treatment systems. It is one of the inexpensive oxidizers usually used in residual waters, with high oxidizing strength, available and water-soluble[3]. H₂O₂ can be used to remove cyanides, for removing chromium (VI), for oxidation of sulfur compounds, and elimination of some inorganic nitrogen compounds. Hydrogen peroxide can be applied directly or with a catalyst. In spite of its advantages, it is reported H₂O₂ residual in AOPs has been led to interference in chemical oxygen demand (COD) test and it is able to hinder biological treatment of waste water. In laboratory large scale, amount of H₂O₂ residual can be estimated 70 to 80% of its initial concentration and allocates to itself high mole concentration [3], thus this leading to overestimation of the COD measurements.

According to previous studies, amount of hydrogen peroxide interference is depending on the type of

pollutants. For example some researchers, for determination of H₂O₂ interference, have been suggested

$$\frac{8.5mgCOD}{mmolH_2O_2}, \frac{16mgCOD}{mmlH_2O_2} \text{ and } \frac{17-19.72mgCOD}{mmolH_2O_2} \text{ for pure water, synthetic waste}$$

water and livestock waste water, respectively [3].

The number of studies investigated H₂O₂ interference on waste water and solid waste leachate is very low [4-6] and mostly have not been referred to the H₂O₂ interference [7]. It seems to better know of H₂O₂ interference in COD test, solid waste leachate is a suitable option, because it is containing refractory organic and inorganic compounds. Solid waste leachate is a high strength wastewater with different organic and inorganic wastes, exhibiting acute and chronic toxicity [8, 9]. Leachate composite is depending on the nature of generated solid waste, soil characteristic, precipitation amount and leachate age [10]. The age of young leachate and mature leachate is ≤2 years and ≥5 years, respectively. With increasing leachate age, concentration of refractory compounds increases [11]. Therefore, purpose of this paper was studying interference effects of H₂O₂ on chemical oxygen demand removal during advanced oxidation processes.

MATERIALS AND METHODS

This paper was performed at Gonabad University of medical sciences in 2015. Required leachate for experiments prepared from self-service of Gonabad University of medical was collected in a plastic bottle and kept in temperature of 4^{0C} until the performance of experiments.

Leachate was diluted in 1/100 ratio. H₂O₂ with purity of 30% was purchased from Merck. Solutions were prepared with demonized water. In the first, some leachate characteristics according to table 1 were detected.

Table 1. The comparison of studied leachate characteristics with similar sample of other studies.

| Leachate Characteristics | | |
|---|----------------|--------------------|
| | Studied sample | Similar sample[12] |
| pH | 5.7 | 7.5 |
| Total hardness(mg/CaCO ₃) | 7000 | 950-11000 |
| Magnesium hardness (mg/lCaCO ₃) | 2600 | 200-6000 |
| Calcium hardness(mg/CaCO ₃) | 4400 | 750-7000 |
| Methyl orange alkalinity (mg/lCaCO ₃) | 7000 | 5185 |
| Phenol ftalyn alkalinity (mg/lCaCO ₃) | 0 | 0 |
| Total alkalinity | 7000 | 5185 |
| TKN(mg/l) | 806 | 50-5000 |
| Total COD(mg/l) | 61000 | 6000-60000 |

In this study effect of parameters such as pH (3,5,7,12), H₂O₂ dose (0.01, 0.02, 0.03, 0.04 mol l⁻¹) and time reaction (10,20,30,40,50,60 min) evaluated on H₂O₂ interference in COD removal during oxidation process [3].

After addition of H₂O₂ to leachate and reaction time intervals 10, 20, 30, 40, 50, 60 min, COD of samples was detected according to standard method [1]. In the end, obtained results were analyzed with Excel software.

Concentration of residual H₂O₂ was examined by the iodometric method. The existence of H₂O₂ increased the COD value since it acted as a reductant, especially in the chromate-based examination of COD [4].

The COD measured in the samples after reaction time was converted to prevent the interference of H₂O₂ on COD analysis (Eqs. (1,2) [4].

$$COD = COD_m - f[H_2O_2] \quad (1)$$

$$f = 0.4706[H_2O_2] - 4.06 \times 10^{-5}[H_2O_2] \quad (2)$$

Where COD, COD value before reaction (mg l⁻¹); COD_m, measured COD after reaction (mg l⁻¹); f, a constant; [H₂O₂]; concentration of residual H₂O₂ (mg l⁻¹).

RESULTS AND DISCUSSION

Effect of pH

pH has an important role in the mechanism of OH• production in AOPs. Fig. 1 depicts the effect of pH on COD removal. pH range was selected from 3 to 12 and H₂O₂ concentration was fixed at 0.02 mol l⁻¹. The minimum COD concentrations obtained before and after reaction at pH=3 were 36000 and 50000 mg l⁻¹ respectively. Also, at this pH, maximum COD removal was 20%. False COD concentrations (COD changes before and after reaction) at pH 3, 5, 7, 9 and 12 were 14000, 15680, 16800, 17920 and 20160 mg l⁻¹ respectively. Therefore, pH=3 was found at optimum pH. According to results of Shabiimam *et al.*, hydrogen peroxide alone at pH2 was able to remove of TOC and color from municipal landfill leachate with efficiency of 39% and 34% respectively [7]. Also, results of Pieczykolan confirm our results [4]. It seems that at pH higher than 7, H₂O₂ is unstable and decomposes to give O₂ and H₂O (Eq. (3)) and therefore lose oxidizing properties of H₂O₂ [13].

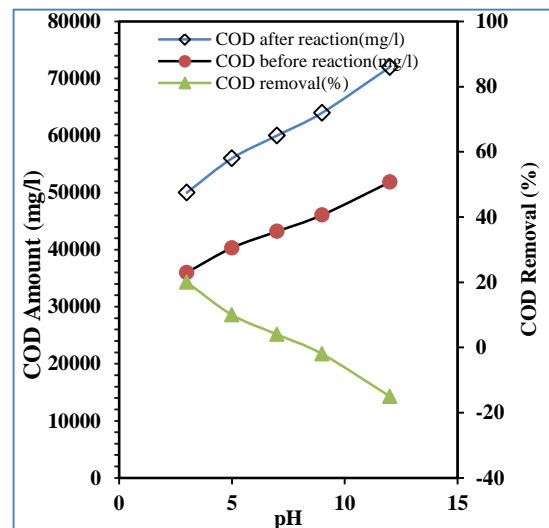
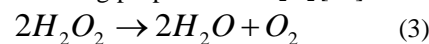


Fig. 1. Effect of pH on COD changes from solid waste leachate (pH= 3, 5, 7, 9, 12, initial COD = 36000 mg l⁻¹, H₂O₂ dose = 0.02 mol L⁻¹, reaction time = 30 min)

Effect of H₂O₂ concentration

In this step, pH was kept constant at 3. Dose of hydrogen peroxide was chosen 0.01, 0.02, 0.03 and 0.04 mol l⁻¹. Amount of COD removal of this concentration range was 7, 15, 3 and -15% respectively and false COD concentrations (COD changes before and after reaction) for these concentrations were 20765, 14415, 16233 and

18831 mg l^{-1} . Therefore, optimum dose of hydrogen peroxide was found as 0.02 mol l^{-1} . At higher doses, there was no further increase in COD removal, because with respect to Eq. (4), under high H₂O₂ concentration, scavenging of OH⁰ radicals is happened to produce HO₂^o radicals [14].



Also, according to previous studies, the residual amounts of H₂O₂ consume K₂Cr₂O₇, according to Eq.5, leading to an increase in COD amount [5, 13]. In this reaction, a green color appears. It is mostly owing to the Cr³⁺ ions formed by the reduction of potassium dichromate [15].

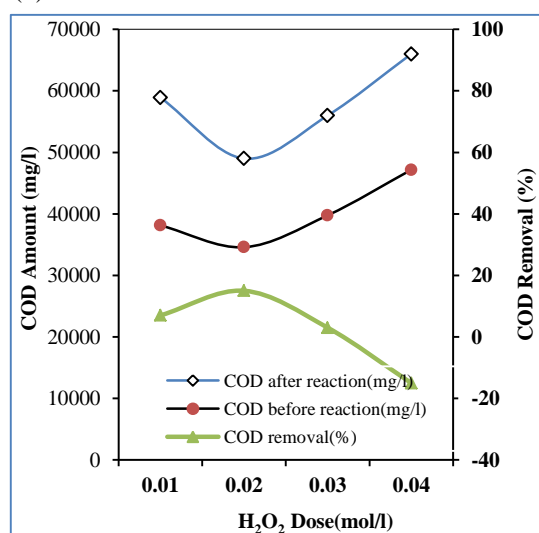
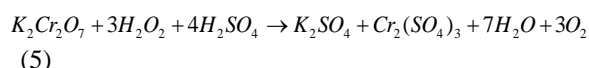


Fig. 2. Effect of H₂O₂ dose on COD changes from solid waste leachate (H₂O₂ dose= 0.01, 0.02, 0.03, 0.04 molL⁻¹, initial COD = 4100 mg L⁻¹, pH=3, reaction time = 30 min).

Effect of Reaction Time

Fig. 3 shows the effect of reaction time on COD removal by H₂O₂. In this part, times of 10, 20, 30, 40, 50 and 60 min was chosen and amount of COD removal for these times was 9, 10, 13, 15 and 18% respectively. During these reaction times, false COD concentrations were 31878, 10260, 6585, 6486, and 5793 mg l^{-1} . It is cleared with increasing reaction time, COD removal has been increased and amount of false COD has been decreased. In this field, Lee *et al.* results were agreement with our results. Based on their results, overestimation of COD during reaction time decreased [5].

Reaction Kinetics

Obtained results from reaction kinetics of COD removal from solid waste leachate demonstrated that COD removal follows first-order kinetics. In this study, K COD removal under H₂O₂ was 0.0029 min⁻¹ (Fig.4). Also previous study confirms our results. For example according to Asgari *et al.*

results, K related to pentachlorophenol removal under H₂O₂ only has been estimated 0.004 min⁻¹ [2].

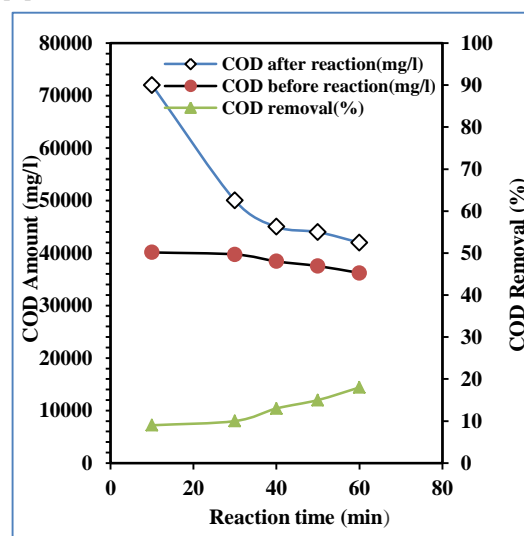


Fig. 3. Effect of reaction time on COD changes from solid waste leachate (reaction time= 10, 30, 40, 50, 60 min, initial COD = 44156 mg l^{-1} , H₂O₂ dose= 0.02 mol l^{-1} , reaction time = 30 min).

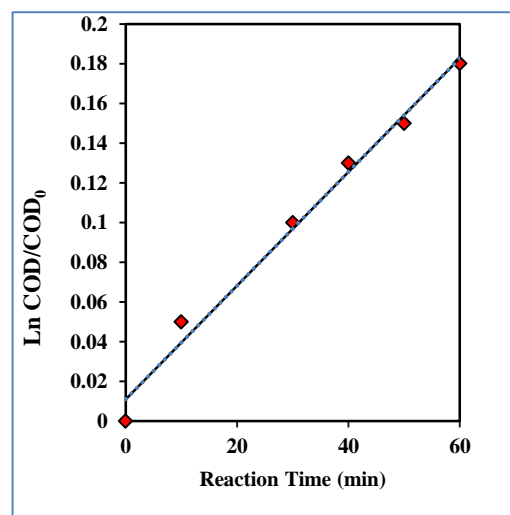


Fig. 4. Reaction rate of COD changes from solid waste leachate (reaction time= 10, 30, 40, 50, 60 min, initial COD=44156 mg l^{-1} , pH= 3, and H₂O₂ dose= 0.02 mol l^{-1}).

Error in Solid Waste Leachate COD Values Due to H₂O₂

To confirm the existence and range of H₂O₂ interference on the COD values, COD analysis was performed using different concentrations of H₂O₂. Results show that the existence of H₂O₂ always led to COD overestimation and its amount was proportional to the H₂O₂ concentration. In this study overestimation ratio in solid waste leachate (Δ COD) was 0.49 mg of COD per mg of H₂O₂. But according to the study by Lee *et al* Δ COD was estimated 0.52 mg of COD per mg of H₂O₂. It seems that H₂O₂ interference and existence of non-

organic in solid waste leachate are led to reduction of COD removal [5].

Also during this research average of COD after reaction, COD before the reaction, removed COD and false COD was 56206, 40650, 26707.57 and 13943 mg l⁻¹ respectively (Fig.5). This remove shows that amount of COD removal has been very low. With regard to reports of mixed waste chemicals existed in solid waste leachate, it seems, besides residual H₂O₂ other factors such as Chloride, Bromide, Iodate, 2 valances Ferric, sulfide and manganese are led to interference and errors in the COD test. In fact, these factors are resulted in false COD [6].

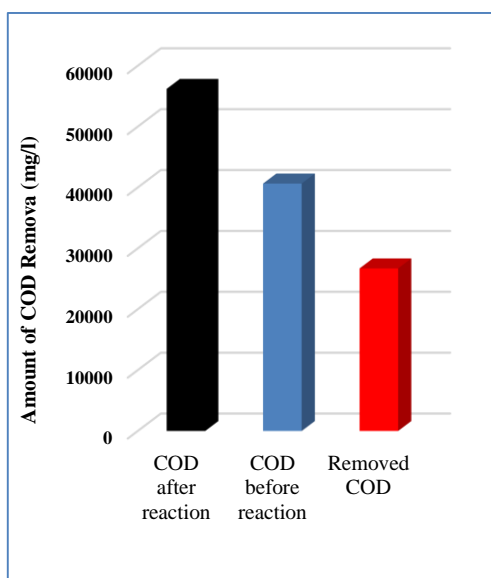


Fig. 4. Average COD changes from solid waste leachate (reaction time= 10, 30, 40, 50, 60 min, pH= 3, H₂O₂ dose= 0.02 mol l⁻¹).

CONCLUSION

This study investigated the effects of H₂O₂ interference during COD removal from solid waste leachate. The existence of H₂O₂ leads to overestimation of measured COD values because it consumes the oxidation agent. The ΔCOD detected between 0.49mg per 1mg of H₂O₂. The average of COD removal by H₂O₂ for 60 min was 6.57%. Also maximum COD removal was obtained at pH 3 and the reaction rate of this process was 0.0029 min⁻¹ and this shows that speed of COD removal by H₂O₂ is negligible. According to many using COD test in monitoring organic compounds of water and waste water, respect to an interventional effect of residual H₂O₂ and other oxidants during COD removal by AOPs based on H₂O₂ and other Oxidants is necessary.

ETHICAL ISSUES

Ethical issues such as plagiarism have not been observed.

CONFLICT OF INTERSTIS

Authors announce that is not any competing interest.

ATHORS' CONTRIBUTION

Chavoshani was director of this study, Rostami, Golzari and Gholinia conducted it.

FUNDING/ SUPPORTS

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