

## The Effect of H<sub>2</sub>O<sub>2</sub> Interference in Chemical Oxygen Demand Removal During Advanced Oxidation Processes

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### ABSTRACT

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is one of the most oxidants in AOPs. By H<sub>2</sub>O<sub>2</sub> dissociation, hydroxyl radical with a standard oxidation potential of 2.7 is produced. It is reported H<sub>2</sub>O 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 H<sub>2</sub>O<sub>2</sub> interference in COD removal from solid waste leachate.

In this study effect of parameters such as pH (3,5,7,12), H<sub>2</sub>O<sub>2</sub> dose (0.01, 0.02, 0.03, 0.04 mol l<sup>-1</sup>), and time reaction (10,20,30,40,50,60 min) evaluated on H<sub>2</sub>O<sub>2</sub> interference in COD removal from solid waste leachate.

Optimum pH and concentration were 3 and 0.02 mol l<sup>-1</sup> respectively. With increasing reaction time, COD removal was increased. The false COD obtained between 0.49mg per 1mg of H<sub>2</sub>O<sub>2</sub>. The average of COD removal by H<sub>2</sub>O<sub>2</sub> for 60 min was 6.57%. Also reaction rate of this process was 0.0029 min<sup>-1</sup>.

The presence of H<sub>2</sub>O<sub>2</sub> leads to overestimation of COD values after reaction time because it consumes the oxidation agent. The extent of H<sub>2</sub>O<sub>2</sub> interference in COD analysis was proportional to the remaining H<sub>2</sub>O<sub>2</sub> 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 (H<sub>2</sub>O<sub>2</sub>) with the aim of producing hydroxyl radicals to oxidize organic contaminants in water and waste water [1-3]. H<sub>2</sub>O<sub>2</sub> is one of the most oxidants in AOPs. By H<sub>2</sub>O<sub>2</sub> dissociation, hydroxyl radical with standard oxidation potential (E<sub>o</sub>) 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]. H<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> interference on waste water and solid waste leachate is very low [4-6] and mostly have not been referred to the H<sub>2</sub>O<sub>2</sub> interference [7]. It seems to better know of H<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> 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<sup>0C</sup> until the performance of experiments.

Leachate was diluted in 1/100 ratio. H<sub>2</sub>O<sub>2</sub> 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 <sub>3</sub> )	7000	950-11000
Magnesium hardness (mg/lCaCO <sub>3</sub> )	2600	200-6000
Calcium hardness(mg/CaCO <sub>3</sub> )	4400	750-7000
Methyl orange alkalinity (mg/lCaCO <sub>3</sub> )	7000	5185
Phenol ftalyn alkalinity (mg/lCaCO <sub>3</sub> )	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), H<sub>2</sub>O<sub>2</sub> dose (0.01, 0.02, 0.03, 0.04 mol l<sup>-1</sup>) and time reaction (10,20,30,40,50,60 min) evaluated on H<sub>2</sub>O<sub>2</sub> interference in COD removal during oxidation process [3].

After addition of H<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> was examined by the iodometric method. The existence of H<sub>2</sub>O<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> on COD analysis (Eqs. (1,2) [4].

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

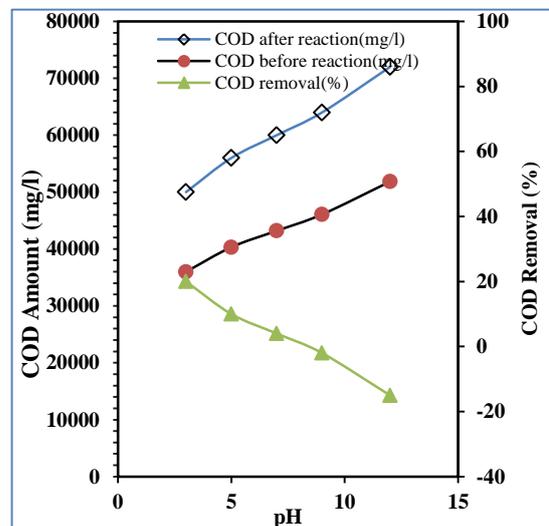
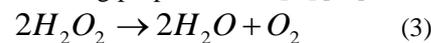
$$f = 0.4706[H_2O_2] - 4.06 \times 10^{-5}[H_2O_2] \quad (2)$$

Where COD, COD value before reaction (mg l<sup>-1</sup>); COD<sub>m</sub>, measured COD after reaction (mg l<sup>-1</sup>); f, a constant; [H<sub>2</sub>O<sub>2</sub>]; concentration of residual H<sub>2</sub>O<sub>2</sub> (mg l<sup>-1</sup>).

## 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 H<sub>2</sub>O<sub>2</sub> concentration was fixed at 0.02 mol l<sup>-1</sup>. The minimum COD concentrations obtained before and after reaction at pH=3 were 36000 and 50000 mg l<sup>-1</sup> 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<sup>-1</sup> 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, H<sub>2</sub>O<sub>2</sub> is unstable and decomposes to give O<sub>2</sub> and H<sub>2</sub>O (Eq. (3)) and therefore lose oxidizing properties of H<sub>2</sub>O<sub>2</sub> [13].

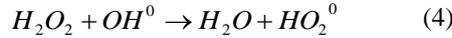


**Fig. 1.** Effect of pH on COD changes from solid waste leachate (pH= 3, 5, 7, 9, 12, initial COD = 36000 mg l<sup>-1</sup>, H<sub>2</sub>O<sub>2</sub> dose = 0.02 mol l<sup>-1</sup>, reaction time = 30 min)

### Effect of H<sub>2</sub>O<sub>2</sub> 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<sup>-1</sup>. 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<sup>l</sup><sup>-1</sup>. Therefore, optimum dose of hydrogen peroxide was found as 0.02mol<sup>l</sup><sup>-1</sup>. At higher doses, there was no further increase in COD removal, because with respect to Eq. (4), under high H<sub>2</sub>O<sub>2</sub> concentration, scavenging of OH<sup>0</sup> radicals is happened to produce HO<sub>2</sub><sup>o</sup> radicals [14].



Also, according to previous studies, the residual amounts of H<sub>2</sub>O<sub>2</sub> consume K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, 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 Cr<sup>3+</sup> ions formed by the reduction of potassium dichromate [15].

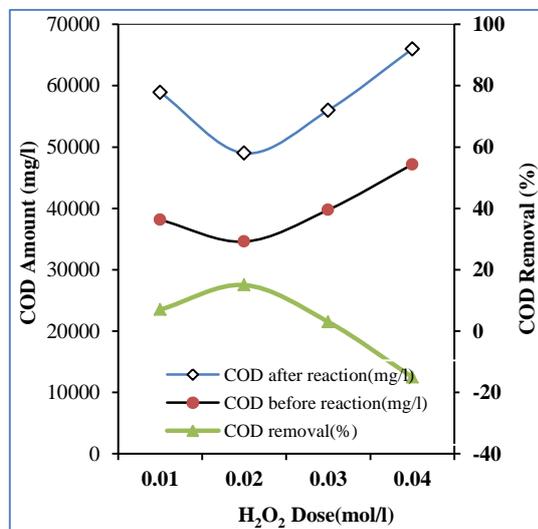
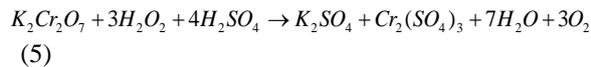


Fig. 2. Effect of H<sub>2</sub>O<sub>2</sub> dose on COD changes from solid waste leachate (H<sub>2</sub>O<sub>2</sub> dose= 0.01, 0.02, 0.03, 0.04 molL<sup>-1</sup>, initial COD = 4100 mg L<sup>-1</sup>, pH=3, reaction time = 30 min).

#### Effect of Reaction Time

Fig. 3 shows the effect of reaction time on COD removal by H<sub>2</sub>O<sub>2</sub>. 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 5793mg<sup>l</sup><sup>-1</sup>. 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 H<sub>2</sub>O<sub>2</sub> was 0.0029min<sup>-1</sup> (Fig.4). Also previous study confirms our results. For example according to Asgari *et al.*

results, K related to pentachlorophenol removal under H<sub>2</sub>O<sub>2</sub> only has been estimated 0.004 min<sup>-1</sup> [2].

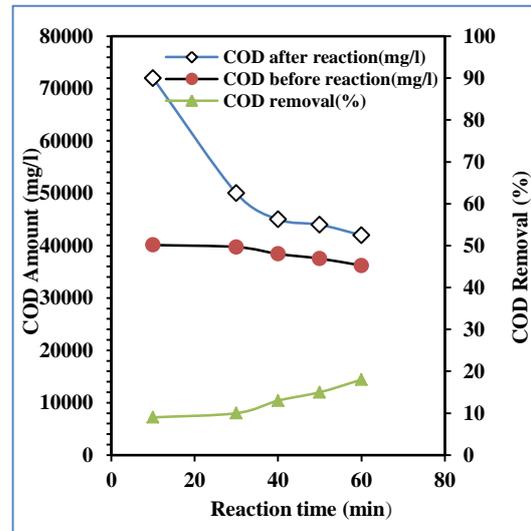


Fig. 3. Effect of reaction time on COD changes from solid waste leachate (reaction time= 10, 30, 40, 50, 60 min, initial COD = 44156 mg<sup>l</sup><sup>-1</sup>, H<sub>2</sub>O<sub>2</sub> dose= 0.02 mol<sup>l</sup><sup>-1</sup>, reaction time = 30 min).

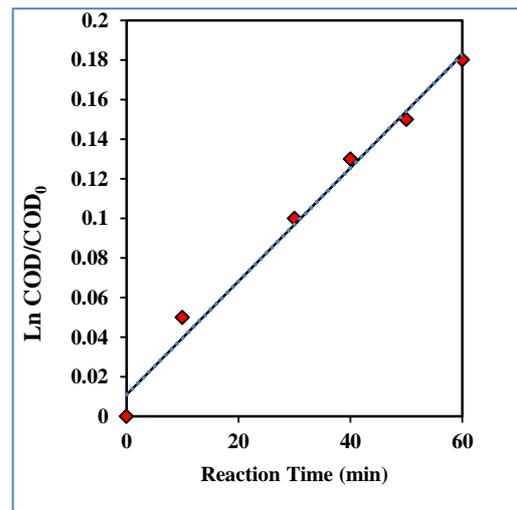


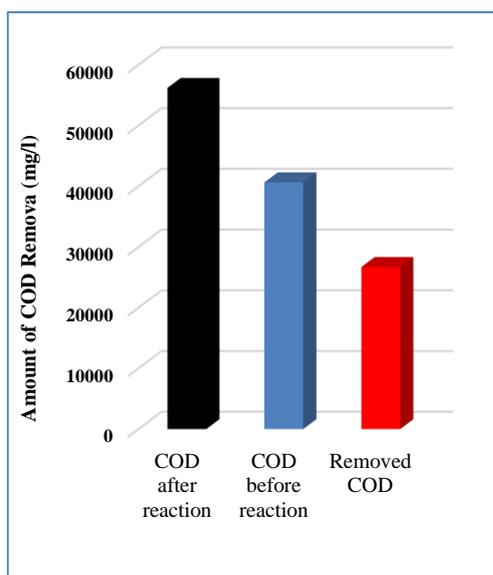
Fig. 4. Reaction rate of COD changes from solid waste leachate (reaction time= 10, 30, 40, 50, 60 min, initial COD=44156 mg<sup>l</sup><sup>-1</sup>, pH= 3, and H<sub>2</sub>O<sub>2</sub> dose= 0.02 mol<sup>l</sup><sup>-1</sup>).

#### Error in Solid Waste Leachate COD Values Due to H<sub>2</sub>O<sub>2</sub>

To confirm the existence and range of H<sub>2</sub>O<sub>2</sub> interference on the COD values, COD analysis was performed using different concentrations of H<sub>2</sub>O<sub>2</sub>. Results show that the existence of H<sub>2</sub>O<sub>2</sub> always led to COD overestimation and its amount was proportional to the H<sub>2</sub>O<sub>2</sub> concentration. In this study overestimation ratio in solid waste leachate (ΔCOD) was 0.49 mg of COD per mg of H<sub>2</sub>O<sub>2</sub>.But according to the study by Lee et al ΔCOD was estimated 0.52mg of COD per mg of H<sub>2</sub>O<sub>2</sub>. It seems that H<sub>2</sub>O<sub>2</sub> 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<sup>-1</sup> 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 H<sub>2</sub>O<sub>2</sub> 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, H<sub>2</sub>O<sub>2</sub> dose= 0.02 mol l<sup>-1</sup>).

## CONCLUSION

This study investigated the effects of H<sub>2</sub>O<sub>2</sub> interference during COD removal from solid waste leachate. The existence of H<sub>2</sub>O<sub>2</sub> leads to overestimation of measured COD values because it consumes the oxidation agent. The ΔCOD detected between 0.49mg per 1mg of H<sub>2</sub>O<sub>2</sub>. The average of COD removal by H<sub>2</sub>O<sub>2</sub> 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<sup>-1</sup> and this shows that speed of COD removal by H<sub>2</sub>O<sub>2</sub> is negligible. According to many using COD test in monitoring organic compounds of water and waste water, respect to an interventional effect of residual H<sub>2</sub>O<sub>2</sub> and other oxidants during COD removal by AOPs based on H<sub>2</sub>O<sub>2</sub> 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.

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