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# Biological Sludge Stabilization; Fenton and Ozonation Processes

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ABSTRACT

**Aims** In biological wastewater treatment processes, a large amount of sludge is produced. Stabilization of sludge is essential before disposal because of the risks to human health and environment. Therefore, selecting an appropriate process for stabilization this sludge may efficiently decrease risks. The aim of this study was to examine the compound efficiency of the advanced Fenton and ozonation oxidation processes in stabilization of biological sludge.
**Instrument & Methods** This experimental study was conducted on raw sludge taken from Kashan University of Medical Sciences' Wastewater Treatment Plant in Iran during 2014. Fenton and ozonation oxidation processes were used for sludge stabilization. H2O2 and Fe2+ concentration, along with their mutual interaction, were measured using repeated measures model. Then the effects of pH and time reaction on reduction efficiency of volatile solids (VS) were examined.
**Findings** The maximum removal efficiencies in Fenton process at pH=3 and in ozonation process in pH=7 were obtained 85.1% and 92.9%, respectively. By increasing the reaction time from 30 to 90min, VS reduction efficiency in Fenton and ozonation processes increased and then reduced after 60min. The maximum reduction efficiencies of VS were obtained at 3000mg/l H2O2 concentration, So that the optimum ratio of Fe2+/H2O2 for sludge stabilization was 1000/3000mg/l with the efficiency of 91.5%.
**Conclusion** Ozonation process efficiency in stabilizing biological wastewater sludge is higher than that of Fenton process.

**Keywords** Waste Water; Sewage; Fenton's Reagent; Ozonation

CITATION LINKS

[1] Semi full-scale thermophilic anaerobic digestion (TAnD) for advanced treatment of sewage sludge ... [2] Utilization of sewage sludge in EU application of old and new ... [3] Microbial monitoring of the influence of the stabilization degree of sludge ... [4] Sludge decomposition and ... [5] Evaluation of digestate stability from anaerobic process by thermogravimetric ... [6] Septage dewatering in vertical-flow constructed wetlands located in the ... [7] Photo-Fenton process for excess sludge ... [8] Aerobic sludge digestion in the presence of chemical oxidizing ... [9] Multivariate analysis of phenol mineralisation by combined hydrodynamic cavitation and heterogeneous advanced ... [10] Photodegradation of parathion in aqueous titanium dioxide and zero valent iron solutions in the presence of ... [11] Iron powder, graphite and activated carbon as catalysts for the oxidation of 4-chlorophenol with hydrogen peroxide in aqueous ... [12] Advanced oxidation processes for organic contaminant destruction based on the fenton reaction and related ... [13] A Fenton-like oxidation process using corrosion of iron metal sheet surfaces in the presence of hydrogen peroxide: A batch process study using model ... [14] A review of classic Fenton's peroxidation as an advanced oxidation ... [15] Influence of ultrasonication and Fenton oxidation pre-treatment on rheological characteristics of wastewater ... [16] Influence of ozone pre-treatment on sludge anaerobic digestion: Removal of pharmaceutical and personal care ... [17] Changes in biomass activity and characteristics of activated sludge exposed to low ozone dose. ... [18] Systematic analysis of biochemical performance and ... [19] Characterizing the fluorescent products of waste activated sludge in ... [20] Comparison between ozone and ultrasound disintegration on ... [21] Partial ozonation of activated sludge to reduce excess ... [22] Optimization of Fenton process for the treatment of ... [23] Review of the "Standard methods for ... [24] Effects of reaction conditions on the oxidation efficiency in ... [25] Physico-chemical pre-treatment and ... [26] Removal of steroid estrogens from waste activated sludge using Fenton ... [27] Treatment of coking wastewater by an ... [28] Removal of humic substances from ... [29] Effects of ultrasound assisted Fenton treatment on ... [30] New treatment of stabilized leachate by ... [31] The effect of operational parameters of the ... [32] Combination of ozonation and the Fenton processes for landfill ...

## Introduction

Sludge production in wastewater treatment plants has been significantly increased due to the obligation for wastewater treatment, stricter effluent limits and increasing in the population connected to the sewage network in the past few years [1]. Sewage sludge is classified as hazardous waste and should be stabilized *before disposing into environment* because of the *risks* for *human health and the environment* [2]. Stabilized sludge *has no damage* to the environment and does not create the unpleasant scenery [3]. *Total* sludge *stabilization* occurs when original solids have been converted to humic substances*, that have slow degradation and are odorless and* non-putrefaction [4].

There are different methods to estimate the level of sludge stabilization, e.g. color, smell, emission of hydrogen sulfide or combination of $CO_2$ and $CH_4$ in the gases produced in anaerobic condition. Currently, the most common reference method to evaluate sludge stabilization is the volatile solids (VS) content, the parameter for estimating the organic matter content of the sludge and linked to rotting potential [5]. The United States considered the value of 38% reduction of volatile solids as the indicator of sludge stabilization [6]. Recently, the possibility of using advanced oxidation processes (AOPs) has been extensively studied to reduce sludge quantity and degrade organic materials. The results of other studies indicated that AOPs have the highest potential in reducing the volume of excess sludge in wastewater treatment plant [7, 8].

Fenton process is the most significant among others studied in its economic consideration, feasible performance, and high oxidation capacity [9]. The main reaction of Fenton includes using hydrogen peroxide combined with ferrous salts (II) under acidic conditions to produce hydroxyl radicals ($Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^\bullet OH$), which makes the organic compound be oxidized in the solution [10-13]. In Fenton process, by selecting proper concentrations of reactive materials and their related conditions, all organic substances can be change into mineral salts [14]. Hence, this process is used in various studies for sludge treatment and removal [15].

Ozonation is also another AOP. Its capacity for the destruction of sludge cells has been widely studied [16-20]. In this process, biomass degradation can be described through two mechanisms; First, due to the destruction of suspended solids in sludge and second, mineralization occurs because soluble organic materials change into carbon dioxide due to oxidization. Therefore, since sludge ozonation has a highly oxidation capacity and no residual concentration and increasing of sludge salt, it has been widely considered [21].

It appears that, in the conducted researches on the ozonation process, excess and sludge destruction reduction in the activated sludge systems have not been studied [22]. Moreover, their effects on sludge reduction organic substances have not been assessed. In addition, it seems that no study has been conducted comparing the two processes. Therefore, the aim of this study was to examine the compound efficiency of the advanced Fenton and ozonation oxidation processes in stabilization of biological sludge.

## Instrument & Methods

This experimental study was conducted through a bench scale on raw sludge taken from Kashan University of Medical Sciences' Wastewater Treatment Plant (KUMS-WTP) in Iran during 2014. The samples, for preservation any change, were stored in a refrigerator at 4˚C, in the Faculty of Health.

In Fenton process, the effect of $Fe^{2+}$ and $H_2O_2$ concentration resulted in changing these two factors and stabilizing the other factors. Different ratios of $Fe^{2+}/H_2O_2$ with 1000, 2000, and 3000mg/l concentrations were analyzed in 3 variables including pH (3, 5 and 7), reaction time (30, 60 and 90min) and constant ozone dosage ($0.14gO_3$ g/TSS) on Fenton were studied. All the processes were performed at room temperature. Sulfuric acid and sodium hydroxide (2 normal) were added for pH regulation (TS-TECHNOLOGY pH 262; Iran). Fenton experiments were performed in 1000ml jars. A certain amount of $Fe^{2+}$ in the form of $FeSO_4(7H_2O)$ was added to the samples. $H_2O_2$ with 30% concentration was used and placed under the 200rpm stirrer.

The ozone produced by ARDA ozone generator at a rate of 10g/hr was inserted into ozone reactor. An air diffuser was installed at the bottom for the efficient spread of ozone, and a magnetic stirrer was also applied to complete mixing. Moreover, a gas flow meter was used to regulate ozone circulation.

In each process, all the experiments were repeated three times and their means were recorded as their rates. All the experiments were performed based on the standard methods for the examination of water and wastewater [23]. The equation for measuring the removal efficiency is VS(%)=C0-C/C0×100 ($C_0$=initial concentration; C=post concentration).

Data analysis was performed by SPSS 16 software using repeated measures model. Mean and standard deviation of the reduction percentage were first calculated based on numerous factors. Then, the effects of all the factors were measured based on VS through analytical variants and repeated measurements.

## Findings

The mean of the sludge sample pH was 7.72±0.39, and dry solids (DS) and VS were 8340.63±3155.95 and 5540.33±2331.15mg/l, respectively.

The maximum efficiency of VS in Fenton process was 85.1% at pH=3. Moreover, by increasing pH, the removal efficiency of this parameter was significantly reduced so that VS reduction efficiencies at pH=7 had the minimum removal (p=0.002). VS removal efficiency in the ozonation process was significantly raised by increasing pH (p=0.104). The maximum removal efficiencies in ozonation process at pH=7 were obtained 92.9% and then reduced slightly (Figure 1A). By increasing the reaction time from 30 to 90min, VS reduction efficiency in Fenton and ozonation processes increased and then reduced after 60min (Figure 1B).

As the optimum of sludge stabilization was seen at pH 3 by 60 minutes process, the optimum ratio of $Fe^{2+}/H_2O_2$ was measured in this condition (p=0.994). The optimum $Fe^{2+}$ concentration was 1000mg/l. Indeed, with increasing $Fe^{2+}$ concentration, the reduction efficiencies of VS in Fenton decrease. In Fenton process, the reduction efficiency of the VS increased when $H_2O_2$ concentration increased from 1000 to 3000mg/l. The maximum reduction efficiencies of VS were obtained at 3000mg/l $H_2O_2$ concentration, So that the optimum ratio of $Fe^{2+}/H_2O_2$ for sludge stabilization was 1000/3000mg/l with the efficiency of 91.5% (Figure 2).

Time variable alone had no significant effect on the sludge stabilzation (p=0.217), but the pH (p=0.04) and the kind of process (p=0.0001) had. The mixed effect of these factors was just significant in the case of pH and kind of process (p=0.37).

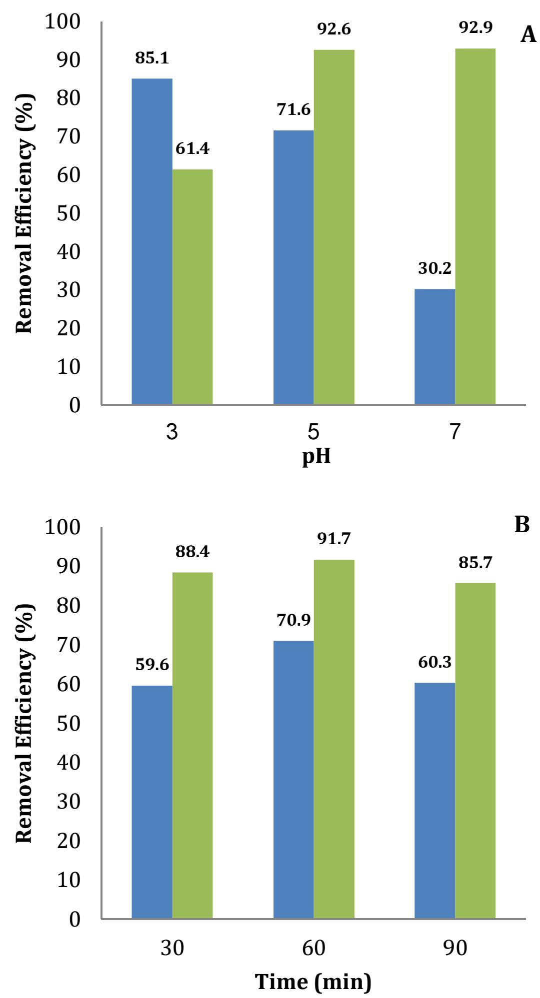


**Figure 1)** Removal efficiency of processes according to pH (A) and time (B)

## Discussion

The purpose of this study was to examine the compound efficiency of the advanced Fenton and ozonation oxidation processes in stabilization of biological sludge. Increasing in Fe2+ concentration was reduced removal efficiency of VS in Fenton process. Actually, by improving sludge mineralization, organic substances change into sludge phase. Then, by maintaining the oxidation and increasing oxidant, oxygenated organics change into minerals [25].

Kang & Hwang have suggested that highly increasing $Fe^{2+}$ concentration has preventive effects on production of hydroxyl radicals. Thus, it reduces the speed and removal efficiency of the pollutants due to turning off the hydroxyl radicals resulted from highly increasing $Fe^{2+}$ [24]. Actually, by improving sludge mineralization, organic substances change into sludge phase. Then, by maintaining the oxidation and increasing oxidant, oxygenated organics change into minerals [25]. Li & Zhang have suggested that in Fenton process, increasing the $H_2O_2$ dosage raises the removal efficiency of TSS and VSS in sludge [26] that is compatible with our results. In Chu *et al.*, increasing $H_2O_2$ concentration raises the destruction of organic substances of coke industrial wastewater in Fenton [27].

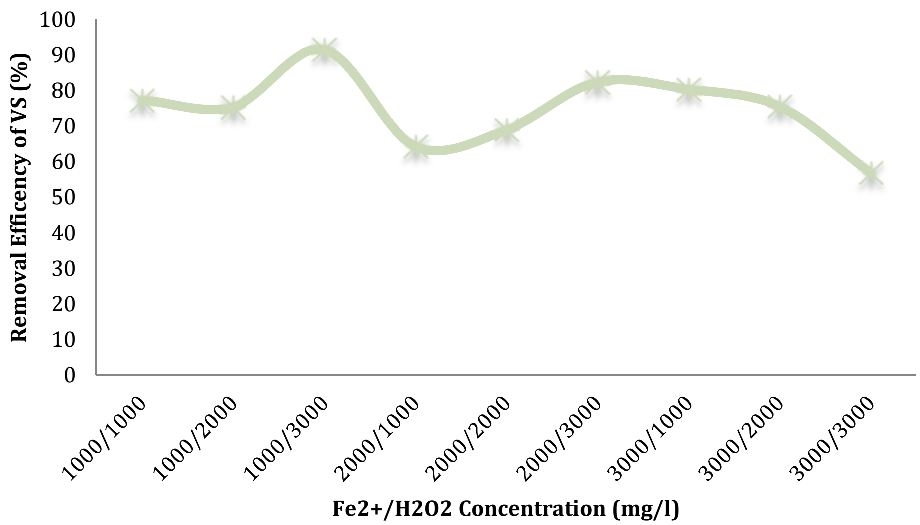


**Figure 2)** Removal efficiency of VS in different concentrations ratios of $Fe^{2+}/H_2O_2$ in Fenton process at pH 3 in 60 minutes

According to our results, In Fenton process, maximum efficiency obtained in pH=3 and pH higher than 3, $Fe^{2+}$ changes into $Fe^{3+}$. As a result, hydroxyl radical production is reduced [28]. For acidic pH, in contrast to alkaline pH, since $Fe^{2+}$ has a high concentration and hydrogen peroxide is degraded fast, more radicals are produced. In pH higher than 3, $Fe^{3+}$ is deposited as Fe $(OH)_3$, and hydrogen peroxide is degraded to oxygen and water. In addition to bivalent iron complex formation in alkaline pH and $Fe^{2+}$ concentration reduction in alkaline environment, reproduction of $Fe^{2+}$ through $H_2O_2$ and $Fe^{3+}$ reaction is prevented if compared with more acidic pH [12]. Thus, our results are consistent with Ning *et al.* who have suggested that treating industrial textile sludge through Fenton and ultrasonic process in acidic condition leads to good destruction of sludge [29].

Li & Zhang have shown that, by decreasing the level of sludge pH from 6.8 to 2.5 in Fenton process, TSS, VSS and TOC removal efficiencies increase [26] that is compatible with our results.

In ozonation process by increasing the level pH from 3 to 7, the removal efficiency of VS increased. Since pH has a significant effect on degrading ozone in aqueous solutions, formation of hydroxyl radical in ozonation process with a high pH level is accelerated. Consequently, indirect oxidation of hydroxyl radicals is more efficient than direct ozone molecules in acidic conditions. Therefore, ozonation with a high pH level is more efficient [30]. Amr & Aziz have also shown that maximum efficiency in the removal of the COD obtained at pH=7 in ozonation process [30].

Li & Zhang have reported that, by increasing the reaction time in Fenton process, sludge dissolution increased within 5 to 120min. TSS, VSS and TOC removal efficiencies led to decreased reaction in 60min, but it then increased significantly. Therefore, the reaction time is generally influenced by hydroxil radical formation and its reaction with organic compounds [26]. Manterola *et al*. have reported no change in dissolving organic compounds in the sludge ozonation process with increasing reaction time from 10 to 58min. They have shown that there is a fast reaction between sludge solution compounds and ozone [31]. Goi *et al*. have removed 72% of COD from landfill leachate through mixing Fenton and ozonation processes after passing 240min [32].

There was no limitation on implementation of our study. We suggest that similar study would be carrying on microbial quality of wastewater sludge for pathogens removal.

## Conclusion

Ozonation process efficiency in stabilizing biological wastewater sludge is higher than that of Fenton process.

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**Ethical Permission:** This study was done with written permission of Ethics Committee of Deputy of Research in Kashan University of Medical Science.

**Conflict of Interests:** We certify that there is no conflict of interest in this manuscript.

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