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Original article

Effect of Ozonation and Hydrogen Peroxide on Reducing the Volume and Chemical Oxygen Demand of Waste Water Treatment Plants Sludge

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A B S T R A C T

Background: Ozonation decays solids and accelerates their consolidation due to strong oxidation capability; hence, decreasing the problems and expenses of equipment and operating the sludge digestion and disposal. In this study, we aimed to investigate the effect of separate and combined effects of ozone and hydrogen peroxide in reducing contamination volume.
Methods: Sludge ozonation was conducted with concentrations of 0.0557 to 0.5573mg O3/mgTSS5573 from 5 to 50 min. Total suspended solids (TSS), volatile solids (VS), chemical oxygen demand (COD) parameters, soluble COD, and the sludge settleability were investigated before and after the process.
Results: The results demonstrated that after 50 min of ozonation and injection of mgO3/mg TSS 0.3901 ozone, sludge volume reduction reached 42%. Furthermore, after 50 minutes of ozonation, TSS and VS with a 43% and 48% reduction, reached to 4261mg/l and 3193mg/l, respectively. Total COD after 35 min of ozonation decreased 39% from 12524mg/l to 7639mg/l. Also injection of 6ml of hydrogen peroxide (30%) leading to a reduction in TSS and VS by 64 and 65%, respectively, and injection of 4ml of it, resulting in a 58% reduction in COD and 75% in the volume of sedimented sludge. The effect of the combination of ozone and hydrogen peroxide resulted in the reduction of only 10% of sedimented sludge volume and also reduced removal of COD by 42%.
Conclusion: According to the results, ozone and hydrogen peroxide injection to sludge, decrease sludge volume, improve in sedimentation and reduce the pollution load at the level of standards.
Keywords: Hydrogen Peroxide, Sewage, Waste Water
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A R T I C L E I N F O

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Introduction

The activated sludge process is extensively used in biological treatment throughout the world. This method produces considerable amounts of surplus waste sludge, which contains large volumes of suspended and volatile solids and more than 95% water. Compared to other processes such as fixed film, activated sludge treatment method has a better performance, but the final disposal of the sludge entails substantial costs due to large amounts of solids contained as well as environmental constraints, such that the cost of treatment and disposal of surplus sludge resulting from sewage treatment claims 50% to 60% share of the total operation costs (1-3). Thus, it is important to identify and develop new techniques to minimize the resulting sludge from sewage treatment plants and use processes that produce less sludge. The organic carbon contained in sewage is partly consumed in vital activities of microorganisms, and partly in reproduction and ultimately the production of biomass and sludge. Thus, reducing the sludge production depends on the large proportion of organic carbon in sewage consumed in vital activities of microorganisms and a small percentage used in reproduction (4-6). In such situation various techniques have been used including thermal degradation (7-10), chemical degradation using acids and alkaline (11), using combined thermal-chemical degradation (12, 13), physical and mechanical disintegration by grinding or ultrasound wave energy (14, 15), alternate freezing and thawing of sludge (1), biological hydrolysis using enzymes (16), simultaneous use of ultrasound energy and alkaline (17), using advanced oxidation processes such as ozone, hydrogen peroxide (13, 17-21) or their combinations, which are known as stealth destruction and growth techniques. Activated sludge is mainly composed of microorganisms, which consist of cells, membrane, and cytoplasm. These membranes prevent successful dehydration of sludge. To increase the sludge digestion efficiency, solids contained in sludge should be degraded and turned into biodegradable matter. Disintegration of a cell leads to the release of intracellular nutrients into the wastewater medium and increases the wastewater organic load. The released organic matter from cell disintegration reenters the metabolic cycle of other microorganisms, and its carbon content is partly consumed in the vital activities of other microorganisms, resulting in the reduction of sludge volume (4, 22).

Because of their ability to degrade microorganisms' cell membrane, ozone and hydrogen peroxide have a major role in increasing biodegradation, and thus reducing the volume of sludge produced. Thus, in the present study, the separate and combined effects of ozone and hydrogen peroxide in reducing contamination volume and load of the disposed activated sludge were investigated.

Methods

Source and characteristics of sludge

To examine the stabilization of the disposed activated sludge and also the efficiency of Ozonation in reducing volume and load of contamination, the activated sludge from hospital wastewater treatment with an extensive activated sludge and aeration system was used. Samples were taken instantaneously from returning activated sludge to aeration reservoir inlet, and sludge properties including total suspended solids (TSS), volatile solids (VS), chemical oxygen demand (COD), solution COD, and sludge settling ability were measured based on the principles presented in the manual of wastewater testing standards (23).

Sludge Ozonation

Following initial sludge analysis, tests were performed on sludge degradation by ozonation. For each test, 100ml of initial sludge sample was taken from the main sample container and poured into a 250 ml cylinder in preparation for ozonation process. The required ozone was produced by an ozone generator (ARDA, MHP1H) with production adjusted at $5gO_3$/h, using pure oxygen. The entire ozone production device, connections and test cylinder were placed under a hood in laboratory conditions, so that ozone degradation and gas escape can take place properly and according to safety recommendations. The ozone injection tube was inserted into the cylinder in such a way to cover all contents. Ozonation of similar samples was performed for 5, 10, 20, 30, 35, 40, 45, and 50 minutes.

Hydrogen peroxide injection

100ml of sludge was taken from the fully mixed contents in the main container and added to relevant vessels. Then, 1, 2, 3, 4, 5, and 6ml of hydrogen peroxide 30% was injected for every 100ml. The reduction in sludge volume and contamination load was assessed by proxone process (Ozone+Hydrogen peroxide).

Analysis

After completion of ozonation and hydrogen peroxide injection, TSS, VS, total COD and solution COD, and sludge settling ability were measured again. The volume of settled sludge at 30, 60, 90, and 120 minutes after ozonation was recorded. Twenty-four hours after completion of ozone and hydrogen peroxide injections, the final volume of settled sludge for all samples was recorded. To assess changes and stabilization process of sludge, changes in TSS, VS, total COD and solution COD, and sludge settling ability before and after ozonation and hydrogen peroxide injection were analyzed taking into account the time and amount of injection. All tests were repeated three times and mean results were reported. The results were analyzed in Excel.

Results

Properties of raw sludge

According to some researchers, with properly working system, the sludge produced in extensive aeration processes has the right quality and ability to be disposed directly into the environment, but others believe that these sludges should be stabilized before disposal (24). The results from initial tests on raw sludge are presented in table 1.

Table 1. Characteristics of Initial Raw Sludge

Parameter	Unit	Amount	Parameter	Unit	Amount
TCOD	Mg/l	12524	TS	g/l	8/6
SCOD	Mg/l	1600	TSS	g/l	7.476
pH	-	7.3	VS	g/l	6.140
Volume	Ml/100ml	35	VSS	g/l	5.230

Given that complete dehydration of activated sludge was not possible, initial sludge volume was determined after 100cc of sludge sample settled into 35cc of condensed sludge and supernatant of clear water for 24 hours. Thus, sludge volume in the initial sample was estimated at 35%. Values of TS and VS were determined 8.16 and 6.14 respectively, with VS to TS ratio of 0.75, indicating that the sludge sample taken had not stabilized.

Sludge properties following ozonation and hydrogen peroxide injection

After determining the initial sludge volume and analysis, ozonation process was performed according to ozone injection time and amount. Table 2 presents duration and amounts of injected ozone into sludge sample. After each stage, TSS, VS, total COD and solution COD, and sludge settling ability were assessed again.

Table 2. Duration and Amounts of Ozone Injected into Sludge Samples

Ozonation Duration (min)	Ozonation amount mgO_3/mg TSS	Ozonation Duration (min)	Ozonation amount mgO_3/mg TS
5	0.0557	35	0.3901
10	0.1114	40	0.4458
20	0.2229	45	0.5016
30	0.3344	50	0.5573

Figure 1 shows changes in sludge TSS due to increased ozonation dosage. It can be seen that the amount of suspended solids in sludge is further reduced with increasing ozonation dosage, suchthat TSS reduction efficiency for ozonation durations of 0.0557 to 0.5573 mgO_3/mg TSS increases from 15% to 43%. Also, to assess the effect of hydrogen peroxide on TSS reduction, different amounts of hydrogen peroxide (1ml to 6ml) were injected into 100ml sludge samples. Figure 1 shows that TSS decreases with increasing doses of hydrogen peroxide, such that TSS reduces by 64%with injectionof 6ml of hydrogen peroxide per 100ml.

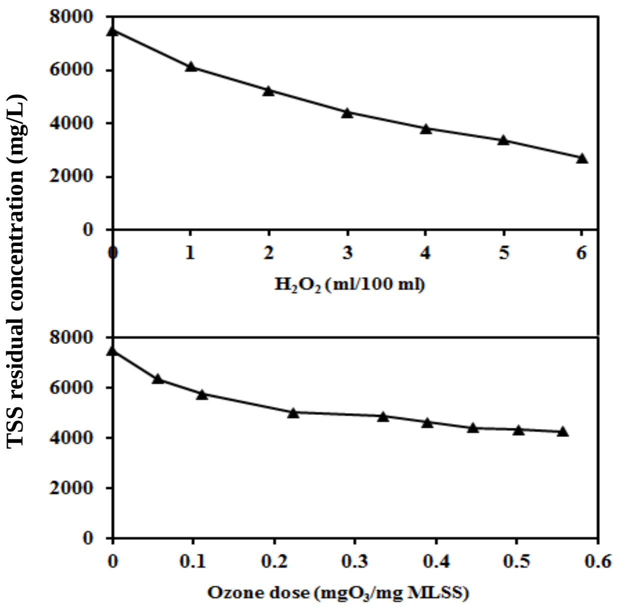

Figure 1. Trend of TSS Changes With Changes in Ozonation and Hydrogen Peroxide Doses.

The amount of VS in sludge is one of the indicators of sludge stability, and reduction in VS is used as a criterion in assessing the effect of a process on sludge stabilization and reduction in absorption of carriers. EPA has declared VS reduction rate of 38% for reducing absorption of carriers (25). Figure 2 shows changes in sludge VS due to increased dosage of ozonation and hydrogen peroxide. It can be seen that the mass of VS further reduces with increasing ozonation dose, such that sludge VS decreases from 16% to 46% following an increase in ozonation dose from 0.0557 to 0.5573 mgO_3/mg TSS. According to figure 2, 35 minutes of ozonation (0.3901 mgO_3/mg TSS) reduces sludge VS by 40%, which is acceptable. Moreover, the percentage of reduction in VS increases with increasing dose of hydrogen peroxide.

Figure 3 shows the reducing trend of COD following ozonation and hydrogen peroxide injection processes at different doses. Accordingly, the highest reduction in COD occurs at ozonation dose of 0.3901 mgO_3/mg TSS, and then COD increases with increasing ozonation time and dosage. Also, the highest COD reduction in oxidation with hydrogen peroxide was observed at the injection dose of 4ml in 100ml of sludge, which led to a 58% reduction in COD.

Figure 4 shows the reducing trend of settled sludge volume after ozonation for different periods compared to the initial volume of settled sludge. According to the amount of settled sludge recorded 24 hours after ozonation process at different doses from 0.0557 to 0.5573 mgO_3/mg TSS, the amount of sludge settled reduced from 6% to 46%. Following hydrogen peroxide injection, turbulence was observed in the movement of sludge particles, which resulted in reduced sludge settlement speed, and due to the continued movement of matters, volume of settled sludge was measured 24 hours after hydrogen peroxide injection. Among different amounts of hydrogen peroxide injected, the 4 ml hydrogen peroxide injection produced the best efficiency in sludge volume and contamination load reduction, as the lowest volume of settled sludge was observed with injection of 4ml of hydrogen peroxide 30%, which led to a 75% reduction in the volume of settled sludge.

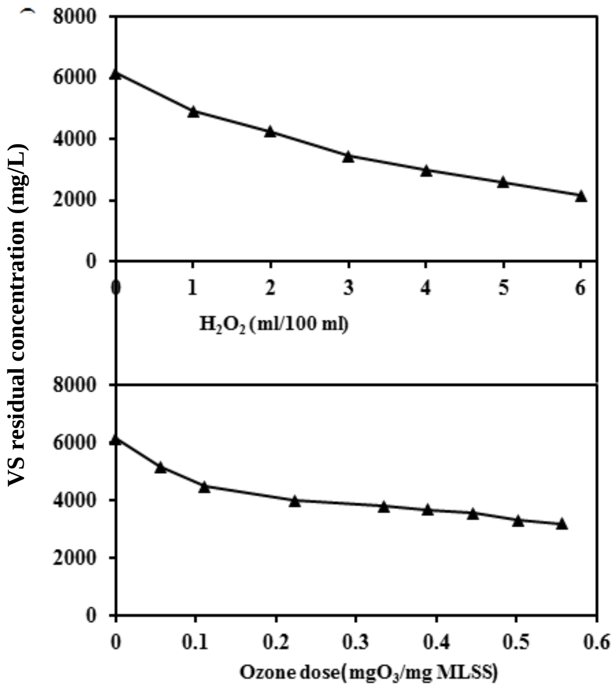

Figure 2. Trend of VS Changes With Changes in Ozonation and Hydrogen Peroxide Doses.

In addition to ozonation and hydrogen peroxide injection processes, the effect of combined ozone and hydrogen peroxide in reducing volume and load of sludge contamination was investigated, which led to only 10% reduction in sludge volume and 42% reduction in COD elimination.

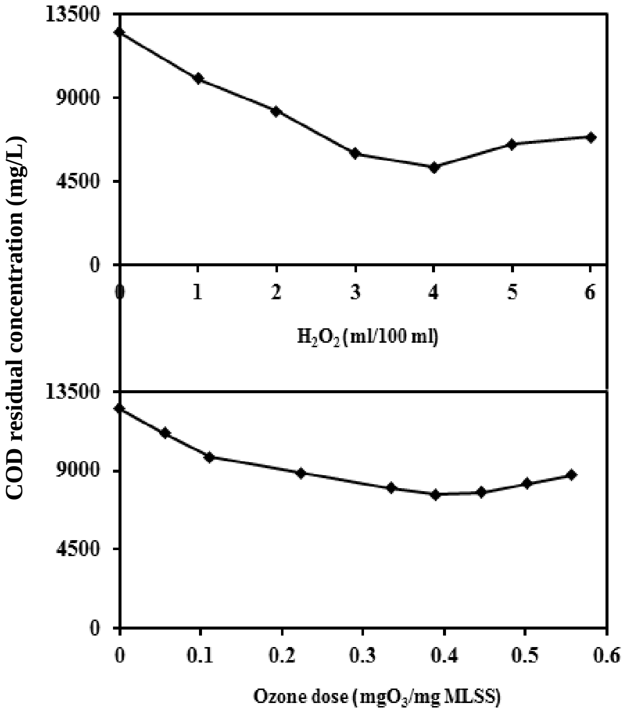

Figure 3. Trend of COD Changes With Changes in Ozonation and Hydrogen Peroxide Doses.

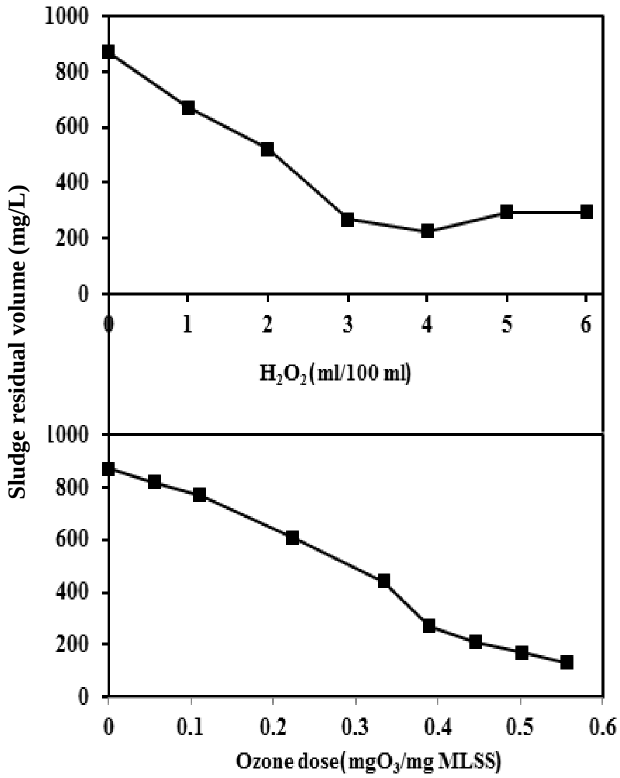

Figure 4. Trend of Sludge Volume Reduction With Changes in Ozonation and Hydrogen Peroxide Doses

Discussion

According to the present study results, biomass degradation due to sludge ozonation process occurs through two main mechanisms. First, suspended solids in sludge degrade and disintegrate, then organic mattersoxidize into carbon dioxide and finallymineralization occurs. Thus, because of its high oxidation property, ozone dissolves organic matter in activated sludge, and this has a direct relationship with the dose of ozone injected (26).

Regarding TSS changes, because of the increased cell wall permeability, ozone destroys and lyses bacteria and releases their organic matter into the sludge liquid (27), and in fact, TSS is partly turned into TDS, and sludge mass reduces. Moreover, hydrogen peroxide is able to convert particulates into soluble compounds. Generally, organic compounds in flocks and cells are dissolved during oxidation and released into liquid, and thus reduce TSS and increase sCOD/TCOD ratio (28).

Regarding VS changes, ozonation process has reduced sludge VS down to an acceptable level. The percentage reduction in VS increases with increasing hydrogen peroxide dosage.

Regarding changes in COD, ozonation actually increases sCOD due to cell lysis and release of intracellular organic matter. The degree of cell lysis depends on ozonation concentration and duration. Tests performed by Ement (2001) showed that ozonation does not increase sCOD in filtered solution, but it does so in unfiltered solution (29, 30). Oxidation with hydrogen peroxide led to a significant reduction in COD.

Regarding changes in the state of sludge settlement, the most important reason for the improved sludge settlement can be considered reduction in bonded water and reduction in the mass of stranded microorganisms due to ozonation process, since the amount of bonded water has a key effect in the sludge dehydration and volume reduction. The reduction in bonded water following ozonation process is due to increased hydrophobic property and release of trapped waters in cells and flocks (31). After ozonation process, sludge settlement speed significantly increases compared to initial sludge sample, but reduces after a while. According to studies conducted by Park and Deleris (2002), sludge ozonation improves the speed of settlement and reduces SVI. Also, hydrogen peroxide injection reduces the volume of settled sludge to an acceptable level (31, 32).

In accordance with previous study, combination of ozonation and hydrogen peroxide injection processes was also effective in reducing sludge volume and contamination load, and led to reduced volume of settled sludge and reduced COD (3, 33).

Conclusion

Ozonation process reduces biomass production coefficient, and thus reduces production of surplus sludge, with subsequent acceptable reduction in volatile and suspended solids in sludge, and reduces volume of settled sludge, and this leads to reduced size of sludge facilities, treatment and disposal costs. Injection of 4ml of hydrogen peroxide also significantly affected reduction in sludge volume and contamination load. The proxon process had negligible effect compared to ozonation and hydrogen peroxide injection. Notably, the increase in COD at outlet occurs if ozonation is continued, and this is because of the cell destruction and release of intracellular organic matter and also reduced microbial activity due to partial loss of microorganisms responsible for degradation of organic matter, which reduces the efficiency of COD elimination.

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Ethical consideration

This study has been reviewed and approved by Institutional review board of Iran University of Medical Sciences, Tehran, Iran.

Conflict of interests

The authors declared no potential conflict of interest.

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