

Aerobic Sludge Digestion in the Presence of Chemical Oxidizing Agents Part I. Hydrogen Peroxide

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Abstract

The process of sludge digestion using hydrogen peroxide as the only oxidizing agent was carried out. It was pointed out that the application of H₂O₂ to the digestion process is possible provided that aerobic conditions of the process are strictly controlled in the course of the process. Since H₂O₂ should be added frequently into the digestion chamber it is highly recommended to supply the digestion chamber with the aeration system. It was shown that H₂O₂ may also be used to upgrade putrescible sludge, what is especially important in the break-down events and when long-term storage is needed.

Keywords: aerobic digestion, excess sludge, chemical oxidation, H₂O₂

Introduction

The excess sludges formed in biological wastewater treatment plants are a source of many serious troubles due to their large volume, tendency to putrescibility and bacteriological hazard. Moreover, during wastewater treatment processes, some harmful chemicals and pathogens can be concentrated in sewage sludge. Therefore the sludge should be processed and treated before its utilization or usage. Following are reasons for sludge processing:

- decreasing of putrescibility, i.e. sludge stabilization
- neutralization of pathogenic microorganisms
- mass and volume reduction-dewatering, drying and/or incineration.

The most widely spread methods of sludge stabilization are biological processes consisting of degradation of organic matter included in excess sludges, by microorganisms in anaerobic or aerobic conditions. The definition of stabilization is that the sludge is biologically stable and non-odorous, but no uniform parameter has been found to determine a univocal degree of stabilization and

digestion time. Sludge stabilization should lead to its mineralization. Nowadays, there are tendencies to define stabilization as a process leading to reduce organic matter content by at least 38% in the separated stabilization unit [1].

The advantage of aerobic digestion is the fact that low content of organic pollutions is observed in the supernatant phase, and the supernatants liquids which turn back to the treatment system do not have any influence on the wastewater treatment process [2]. The final result of the aerobic digestion process should be obtaining mineralized, well-settling, easily thickening and dewatering sludge. However, due to low capital costs and high energy-consumption, intensive efforts have been made to accelerate and improve the efficiency of aerobic digestion.

Much importance in industrial wastewater treatment has been recently attached to application of strong chemical oxidants, as ozone and its derivatives or hydrogen peroxide solutions, also including reagents based on H₂O₂, e.g. Fenton's reagent (H₂O₂ + Fe²⁺) [3-10]. Hydrogen peroxide is a powerful oxidant that has been used

to degrade contaminants either directly or in conjunction with a catalyst or an activator. In these catalytic systems, decomposition of hydrogen peroxide initiated by reaction with UV light, ozone or iron ions, leads to the formation of very reactive free radicals, especially the hydroxyl radicals (OH^*). These radicals are second only to fluorine among common oxidants and are capable of reacting with a wide variety of organic compounds [11, 12, 13].

Application of H_2O_2 has several advantages. In process of its decomposition oxygen and water are formed, i.e. ecologically neutral substances. Hydrogen peroxide oxidizes sulphides and many other hazardous substances included in industrial wastewater. Application of H_2O_2 enables removal of iron and chromium ions from wastewater formed in metal processing industry. It has recently found application in paper (in combination with ozone) [14, 15] and textile (as a Fenton's reagent) [16, 17] wastewater treatment processes. It is also used as the addition oxygen source for activated sludge systems.

Application of strong chemical oxidants, such as H_2O_2 or a Fenton's reagent, may also take place in intensification of the aerobic digestion of sludges, especially from biological industrial wastewater treatment plants. Due to the oxidants, usage process duration (i.e. oxidation of organic sludge matter) and its energy-consumption may be highly decreased. It is most likely that sludge disinfection takes place simultaneously. On the other hand it seems to be of importance to answer a question whether these methods may improve sludge tendencies to thickening and dewatering.

This paper presents the results of experiments concerning application of hydrogen peroxide, as the only source of oxygen, in aerobic digestion of excess sludge.

Materials and Methods

Experimental Procedure

Experiments were carried out in four reactors R-0 to R-3 of a 10 dm^3 volume each. The sludges in three reactors (R-1 to R-3) were magnetically stirred without aeration, while the fourth reactor R-0 (a reference one) was only aerated with compressed air introduced in the bot-

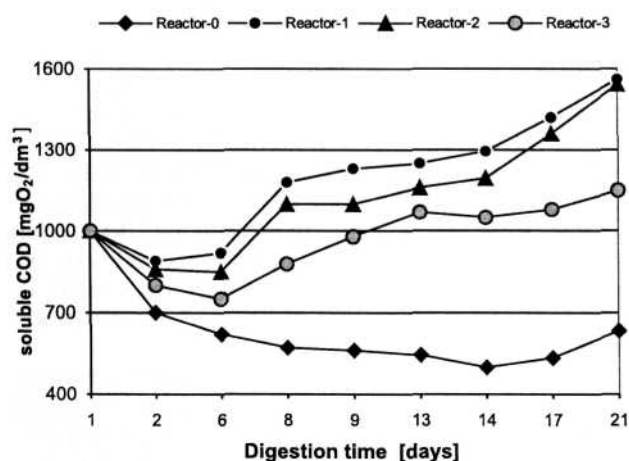


Fig. 1. COD changes for supernatants during aerobic digestion in the presence of H_2O_2 .

torn of the reactor. Excess sludge was obtained from full-scale activated sludge plant treating industrial wastewater from chemical works located in the district of Opole (southern Poland).

The excess sludge was thickened to obtain initial total solids concentration 8.0 g dm^{-3} (dry mass per liter) and was brought to laboratory batch reactors (R-0 to R-3). Various doses of 30% H_2O_2 were then added to the reactors R-1, R-2 and R-3. H_2O_2 was added daily during the whole experiment. The reference reactor R-0 was aerated (without adding H_2O_2), as in the standard aerobic digestion. The air flow intensity was adjusted with the aid of a precalibrated rotameter to maintain the content of dissolved oxygen concentration (DO) in the reactor at the range of $2.0\text{-}2.5 \text{ mg dm}^{-3}$. Evaporation losses were made up each day with distilled water prior to sampling. The aerobic digestion was continued for 21 days.

Analytical Methods

The measurements of soluble chemical oxygen demand (COD), total and volatile suspended solids (TSS, VSS), dissolved oxygen (DO), sludge volume index (SVI) and settleability, capillary suction time (CST) as well as pH and oxidation-reduction potential (ORP) were performed to monitor the progress of aerobic digestion process. The changes of sludge hydration and putrescibility of supernatant (in the presence of methylene blue), were also analysed. All above analytical procedures were measured in accordance with Standard Methods [18]. Diluted (1:1 with tap water) SVI determinations were performed in unstirred 1 litre graduated cylinder.

Concentration of residual H_2O_2 was analyzed using the iodometric method. The residual H_2O_2 increases the COD value since it acts as a reductant, especially in the chromate-based analysis of COD. Thus, when the residual H_2O_2 was determined in the supernatant, COD was calculated according to the following formula [19]:

$$\text{COD (mg dm}^{-3}\text{)} = \text{COD}_m - d \cdot f$$

where:

COD_m - measured COD (mg dm^{-3})

d - H_2O_2 concentration in the sample (mg dm^{-3})

f - correction factor - 0.25 (it is valid for $20\text{-}1000 \text{ mg H}_2\text{O}_2 \text{ dm}^{-3}$).

Results and Discussion

The experiments were performed for 21 days. The time-table of H_2O_2 dosage is presented below:

experimental day	reactor 1	reactor 2	reactor 3
1-5	1.0 g dm^{-3}	2.0 g dm^{-3}	3.0 g dm^{-3}
6	3.0 g dm^{-3}	5.0 g dm^{-3}	8.0 g dm^{-3}
7	5.0 g dm^{-3}	5.0 g dm^{-3}	5.0 g dm^{-3}
8	10.0 g dm^{-3}	10.0 g dm^{-3}	10.0 g dm^{-3}
9-14	15.0 g dm^{-3}	15.0 g dm^{-3}	15.0 g dm^{-3}
15-21	5.0 g dm^{-3}	10.0 g dm^{-3}	15.0 g dm^{-3}

The examined sludge was obtained from chemical works biological treatment plant. Because of the high content of substances resistant to biodegradation (such as formaldehyde, *n*-butanal, acrolein, *o*-xylene, phthalates, phthalic acid, fumaric acid, maleic acid, benzoic acid), in wastewater conveying to treatment plant as well as the high concentration of organic mass in the sludge (92.5% of VSS), the application of a strong chemical oxidant, i.e. hydrogen peroxide, to intensify the aerobic digestion, was thought to be highly recommended.

Examinations on VSS and Hydration Changes

Hydrogen peroxide addition was followed by various efficiency of VSS decay. The results are shown below:

reactor	VSS decay (%)
R-0	28.2
R-1	28.6
R-2	34.3
R-3	40.0

It should be pointed out that in the all reactors clear decay of VSS was observed at H_2O_2 dose of $10 + 15 \text{ g dm}^{-3}$ ($2.7 + 3.6 \text{ gH}_2\text{O}_2 \text{ g}^{-1}\text{VSS}$). The best results were achieved in R-3 reactor. Whereas in R-0, VSS concentration was only reduced by 28.2%. In all the cases, during aerobic digestion process, VSS changes were also reflected in TSS changes.

Sludge hydration was in range of $99.2 + 99.5\%$. No relationship between sludge hydration and efficient dose of H_2O_2 was observed.

Changes of Putrescibility and COD

Application of H_2O_2 apparently influenced the duration of supernatant putrescibility. At standard conditions (reference reactor R-0) after 15 days of process, supernatant putrescibility was not observed for 5 days and more. Such good results were not obtained in reactors R-1, R-2 and R-3. Using H_2O_2 resulted in putrescibility not to be observed only for several hours. Generally, the higher the dose of H_2O_2 , the longer time of supernatant putrescibility was observed, not to exceed, however, 14 hours.

The observed results were due to the fact that application of H_2O_2 once a day did not ensure sufficient concentration of dissolved oxygen in the reactors. In most cases, on the following day of the experiment, prior to the addition of a new dose of H_2O_2 , dissolved oxygen concentration was 0.0 mg dm^{-3} . Simultaneously, the redox potential (ORP) was about $-25 \div -30 \text{ mV}$; not high enough, rising rapidly to $50 + 120 \text{ mV}$ after addition of H_2O_2 (depending on dose of hydrogen peroxide).

Periodical deficiency of aerobic conditions may have affected COD changes in the reactors. The best results of COD removal were observed in the reference reactor (up to 50%). On the other hand, at the end of the process an increase in COD was observed, most likely because of

microorganisms to undergo lysis processes and cell metabolites to be released into medium (Fig. 1). In working reactors R-1 to R-3 the COD removal effects were lower. For initial 2 ÷ 6 days a decrease in COD was observed, while after that constant increasing in COD was noticed. The most probable reason was due to appearance a digestion products as a result of periodical deficiency of aerobic conditions. The highest COD values were observed in R-1, while the lowest - in R-3, where the highest doses of H_2O_2 were added.

Changes of Capillary Suction Time

Capillary suction time (CST test) is a simple and easy method to promptly evaluate some properties of sludge, e.g. its tendency to dewatering [20]. Moreover, the CST test is widely applied to select sludge processing agents, determine doses and analyze several factors that influence filtration properties of sludge.

Generally, aerobic digestion deteriorated sludge tendencies to dewatering. The least visible decreasing of sludge dewatering was observed in R-0. In this reactor CST progressively varied from 23 seconds up to 50 seconds at the end of the digestion. On the 13th day the maximum value of CST (62 sec) was observed (Fig. 2).

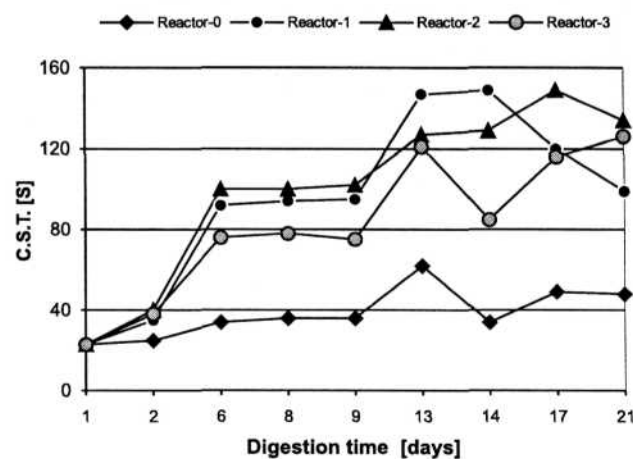


Fig. 2. CST changes of sludge during aerobic digestion in the presence of H_2O_2 .

In working reactors for 13 days almost simultaneously changes of capillary suction time were observed. In this time CST results were increased, reaching values from 121 sec (R-3) to 146 sec (R-1). Then, CST changes were different for various reactors. In R-1 CST, after momentary stagnation, was decreased up to 99 sec, whereas in R-3 it was initially decreased up to 85 sec, and then increased up to 126 sec. For R-2, CST was almost continuously increased up to 134 sec. All the results are shown in Figure 2.

The results of our experiments, showing that aerobic digestion reduces sludge tendency to dewatering, are in accordance with observations that this process results in

a gradual increase in the amount of the finest range flocs [2]. According to Karr and Keinath [20] and Olboter and Vogelpohl [22], floc size and particle size distribution are considered two of the most important factors in the dewatering of sludge. Novak et al. [21] showed that especially the amount of small particles in a sludge is responsible for poor dewatering, because the small particles tend to blind the sludge cake during filtration.

Settling and Sludge Volume Index Changes

The initial sludge was poorly settled and dewatered. After the addition of two doses of H_2O_2 the settling properties of sludge began to differentiate (see Figs. 3 to 6). After 13 days of experiments, sludge from R-3 shown the best tendencies to settling (especially to thickening after 60 min). Moreover, this sludge had the highest tendency to dewatering. On the contrary, sludge from R-0 had the lowest tendency to settling. After 8 days, settling properties of sludge in R-1 and R-2 were highly improved. After that time no visible settleability changes were observed in those reactors.

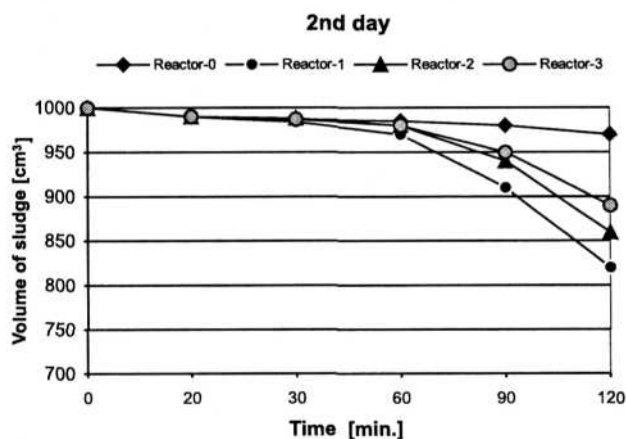


Fig. 3. Settling changes during aerobic digestion - day 2.

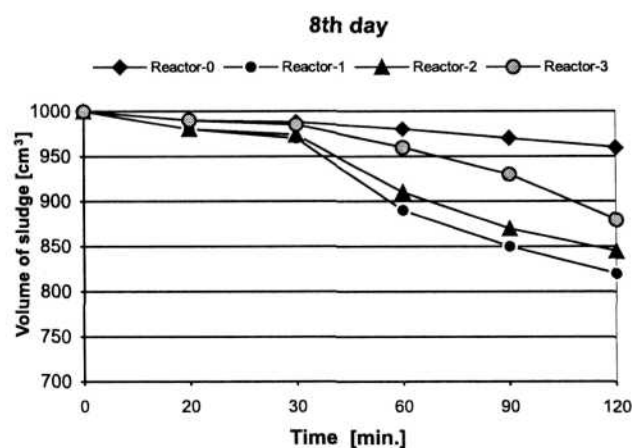


Fig. 4. Settling changes during aerobic digestion - day 8.

In all examined reactors an increase in sludge volume index was observed. It was proportional to added amounts of H_2O_2 . The lowest increase in SVI (sludge volume index) was observed in R-0, whereas the most apparent in R-3, where the highest doses of H_2O_2 were added. It may thus be assumed that settling and thickening changes in R-3 were only due to TSS decrease and cannot be attributed to improvement of settling properties as a result of flocs structure and sludge properties changes. Such conclusion is supported by SVI changes, increasing from $240 \text{ cm}^3/\text{g}$ to $412 \text{ cm}^3/\text{g}$ in the course of experiment in R-3. Generally, in all the cases, the longer reaction time the higher SVI.

pH Changes

In most cases pH values were in the range $7.2 \div 8.2$, while relatively high decrease in pH (up to $6.0 \div 6.1$) was observed at the end of experiment (17 \div 21 day) in the reference reactor R-0. It was most likely a reason for observed flocs decomposition and mentioned earlier lysis of microorganisms cells and was partly connected with increase in COD for supernatants.

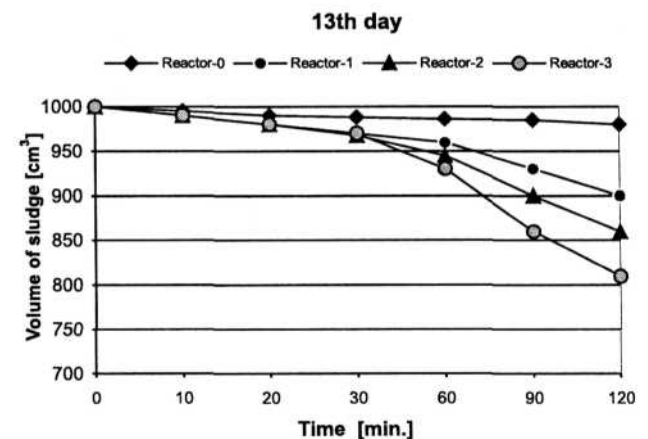


Fig. 5. Settling changes during aerobic digestion - day 13.

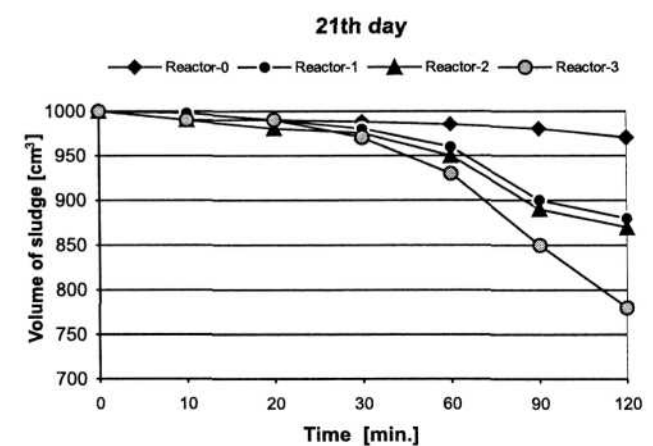


Fig. 6. Settling changes during aerobic digestion - day 21.

Conclusions

The addition of H₂O₂ was followed by increasing in organic mass decay in comparison with standard stabilization process. Moreover, when the higher H₂O₂ doses were applied the longer putrescibility time of supernatant was obtained. The results were, however, not good enough in comparison with those observed in the standard conditions.

It should be noticed that application of H₂O₂ to improve aerobic sludge digestion must be accompanied by keeping constant aeration conditions in the reactors, i.e. permanent addition of H₂O₂. It was assumed that periodical deficiency of aerobic conditions and negative values of redox potential were partly a reason for insufficient results of COD removal. Therefore, the more appropriate way is to combine the addition of H₂O₂ with continuous aeration of digestion chambers or to apply the stronger oxidant, for example Fenton's reagent.

The clear disadvantage of H₂O₂ application is decreasing in sludge tendencies to dewatering and thickening. The use of H₂O₂, however, may be advantageous to improve properties of putrefied sludge. It may take place for aeration system failure or when sludge is to be stored for a long time before dewatering.

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