Polish Journal of Environmental Studies Vol. 12, No. 1 (2003), 35-40

Aerobic Sludge Digestion in the Presence of Hydrogen Peroxide and Fenton's Reagent

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Received: 3 June, 2002
Accepted: 5 August, 2002

Abstract

The results of comparative experiments on aerobic digestion of excessive activated sludge using hydrogen peroxide and Fenton's reagent are described. Fenton's reagent was found to have a higher oxidation potential and, as a consequence, higher efficiency in a digestion process in comparison to hydrogen peroxide. Moreover, Fenton's reagent was shown to improve sedimentation properties of sludge and to decrease soluble COD more efficiently than H_2O_2. The main advantage of the Fenton's reagent application was the fact that oxidation processes took place even though Fenton's reagent was no longer added. On the other hand, the apparent disadvantage of its application is the formation of additional chemical sediments and possible decomposition of sludge flocs as a result of overdosage of reagents and, consequently, an increase in turbidity of supernatant liquid and some difficulties with sludge dewatering.

Keywords: Aerobic digestion, excess sludge, chemical oxidation, H_2O_2, Fenton's reaction

Introduction

Activated sludge process is the most common method for effective treatment of municipal as well as industrial wastewater. The excess sludges formed in the biological wastewater treatment plants are a source of many serious troubles due to their large volume, tendency to putrescibility and bacteriological hazard. The most widely spread methods of sludge digestion are biological processes consisting of degradation of organic matter present in excess sludges, by microorganisms in aerobic or anaerobic conditions. The advantage of aerobic digestion, as an alternative method, is the fact that low content of organic pollutions is observed in the supernatant phase, and the supernatant liquids, which turn back to the treatment system, have no influence at all on the wastewater treatment process. The main drawback of the process, however, is its high energy-consumption and problems connected with mechanical treatment of aerobic stabilized sludge. Thus, it is recommended to make efforts to increase the effectiveness of the process and decrease its duration.

Total suspended solids (TSS), volatile suspended solids (VSS) and at times biodegradable volatile suspended solids (BVSS) are usually the most often used parameters to determine degree of stabilization and digestion time [1–4]. In addition, the measurements of sludge activity [5–7]

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and the redox potential [8–9] as well as the floc size and sludge specific surface [10] represent widely used methods for optimization of aerobic digestion. The optimization has, however, only limited possibilities to intensify a process.

To accelerate aerobic digestion process it is advised to apply strong chemical oxidants as H_2O_2 or a Fenton's reagent (the mixture of hydrogen peroxide and ferrous iron) which have been found to be very important in industrial wastewater treatment [11–17]. A clear advantage of H_2O_2 application is the fact that the products of its decomposition are ecologically neutral oxygen and water, while in the Fenton's reaction very reactive hydroxyl radicals $OH^{\cdot}$ are formed by the catalytic decomposition of H_2O_2 with ferrous ions according to the reaction:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^{\cdot} \qquad (1)$$

The hydroxyl radicals could react rapidly and non-selectively with nearly all organic pollutants [18–20]. The main advantage of Fenton's reagent over other $OH^{\cdot}$ systems is its simplicity: the components are commonly available and there is no need for special equipment like UV lamps, complex reaction vessels, TiO_2 particles, or ozone generators [14]. Because of its simplicity, Fenton's reagent has the potential for widespread use in environmental protection technologies.

During the aerobic digestion considerable changes occur also in the structure and these physical properties of flocs which are directly connected with the settling properties and dewatering capacity [4, 10]. Generally, aerobic digestion often reduces sludge tendency to dewatering [3, 21–23]. However, the apparent advantage of Fenton's reaction is that oxidation and coagulation processes take place simultaneously. For that reason, this method may improve sludge tendencies to thickening and dewatering. These considerations have been confirmed by experiments carried out by Mustranta and Viikari [24], in which the dewatering characteristics of the sludges from pulp and paper mills were considerably enhanced by oxidative treatment with hydrogen peroxide in the presence of ferrous sulphate.

In our previous investigations [25, 26], aerobic sludge digestion in the presence of H_2O_2 and Fenton's reagent was examined. In these experiments, however, H_2O_2 was the only source of oxygen. Based on obtained results we concluded that in order to improve the aerobic sludge efficiency both H_2O_2 and Fenton's reagent should be introduced to digesters supplied with aeration system.

In the present study, the authors investigated the aerobic digestion process intensified by using H_2O_2 or Fenton's reagent with continuous aeration of digesters. The aim of the study was to point out the effectiveness of both reagent application and their influence on dewatering and sludge sedimentation properties.

Materials and Methods

Experimental Procedure

The aerobic digestion was performed in three laboratory scale batch reactors. Excess activated sludge was thickened to obtain initial total solids concentration of 12,000 mg/dm^3 and was brought to batch reactors with initial sludge volume of 8.0 dm^3 each. In order to aerate and mix the content, air was introduced in the bottom part of the reactor through a porous stone diffuser. The air supply was regulated so that the dissolved oxygen concentration in the reactor was always >2 mg O_2/dm^3, and aeration was sufficient to keep the solids in suspension. Evaporation losses were made up each day with distilled water, prior to sampling.

To the first reactor ($R_{H_2O_2}$) only hydrogen peroxide (30% w/w) was added, while a Fenton's reagent (H_2O_2 + $FeSO_4 \times 7H_2O$ in a solid state) was introduced to the second reactor (R_{Fenton}). In both cases the dose of H_2O_2 was 2.5 g/dm^3 per day. [Fe^{2+}] to [H_2O_2] ratio in a Fenton's reaction was 0.25. The third reactor, R_0, with standard stabilization process by aeration, was a reference one. Aerobic digestion was continued for 20 days. The reagents were added to $R_{H_2O_2}$ and R_{Fenton} for 8 days and then sludge in the reactors was aerated for 12 days. No primary acidification was applied in Fenton's reaction.

Analytical Methods

The measurements of soluble chemical oxygen demand (COD), total and volatile suspended solids (TSS, VSS), sludge volume index (SVI), capillary suction time (CST), microbial activity, pH and oxidation-reduction potential (ORP) as well as dissolved oxygen (DO), were performed to monitor the progress of the aerobic digestion process. Determination of microbial activity comprised measurements of oxygen uptake rate (OUR) and dehydrogenase activity (DHA). All above analytical procedures (except DHA) were measured in accordance with Standard Methods [27]. Diluted (1:1 with tap water) SVI determinations were performed in an unstirred 1 litre graduated cylinder. DO and pH were measured by an oximeter (OXI-196) and pH-meter (pH-196), respectively (both made by WTW, Germany). The oxidation-reduction potential was monitored by an ORP platinum electrode.

The DHA was determined with the help of TTC test similar to Oliveros *et al.* [19]. 2,3,5-triphenyl tetrazolium chloride (TTC) is a colourless water-soluble compound, which upon reaction with dehydrogenase forms the red coloured 1,3,5-triphenyl tetrazolium formazan. 8 ml samples of sludge taken from each reactor and 0.5 ml of TTC (2% in water) were added to the vials, the samples were then incubated for 0.5 h at room temperature in the dark and then centrifuged (2 min, 3000 rpm) and the water was decanted. 8 ml of methanol was added and the suspension was shaken and centrifuged. The methanol solution was separated, filtered and its absorption at 485

nm determined spectrophotometrically. Since TTC as well as other tetrazole salts kill the microorganisms when applied at high doses [28], optimum TTC concentration (at which highest dehydrogenase activity was obtained), and optimum incubation time were determined.

Putrescibility of supernatant was determined in accordance with Polish Standard [29]. In this method 0.05% solution of methylene blue was added to supernatant liquid and then the sample was tightly closed and incubated in 100 ml glass bottles at 20°C for 120 hours. Putrescibility is defined as a decolorization time. In the present study, the samples were incubated up to 10 days.

Concentration of residual H_2O_2 was analyzed by the iodometric method. Residual H_2O_2 increases COD value since it acts as a reductant, especially in the dichromate method of COD analysis. Thus, when the residual H_2O_2 was determined in the supernatant from $R_{H_2O_2}$ or R_{Fenton}, COD was calculated according to the following formula [30]:

$$COD\ (mg/dm^3) = COD_m - d \cdot f$$

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÷1000 mg/dm^3 H_2O_2)

Results and Discussion

VSS, TSS and Putrescibility Changes

TSS and VSS changes in $R_{H_2O_2}$ show almost the same tendencies, while in R_{Fenton}, because of chemical suspension formation, TSS concentration was continuously growing when the reagents were added, i.e. for 8 days. After having stopped a Fenton's reagent addition, TSS concentration was slowly reduced, see Fig. 1. In $R_{H_2O_2}$ VSS was decreased by 58.2% while in R_{Fenton} - by 80.6% in the whole process. During the addition of reagents, i.e. for the initial 8 days, the VSS reduction was 39.6% and 48.2% in $R_{H_2O_2}$ and R_{Fenton}, respectively. One may thus conclude that in aerobic digestion assisted with Fenton's reagent, biomass oxidation takes place after stopping reagents addition in a larger extent than in the case of H_2O_2 assistance.

In the reference reactor R_0, changes of TSS and VSS stabilized finally after 18 days of stabilization. The decrease in VSS and TSS values reached 48.0% and 42.5% (of its primary value), respectively. The rates of VSS and TSS changes were lower than those for $R_{H_2O_2}$ and R_{Fenton}, which supports the expected necessity of the chemical oxidants application in aerobic digestion.

The more efficient oxidation potential of Fenton's reagent was also observed in a process of putrescibility changes of supernatant liquid. In R_{Fenton} supernatant liquid putrefying stopped (for at least 5 days) after 3 days' process, while in $R_{H_2O_2}$ - after 7 days' process and, what is even more important, due to usage of two times higher amount

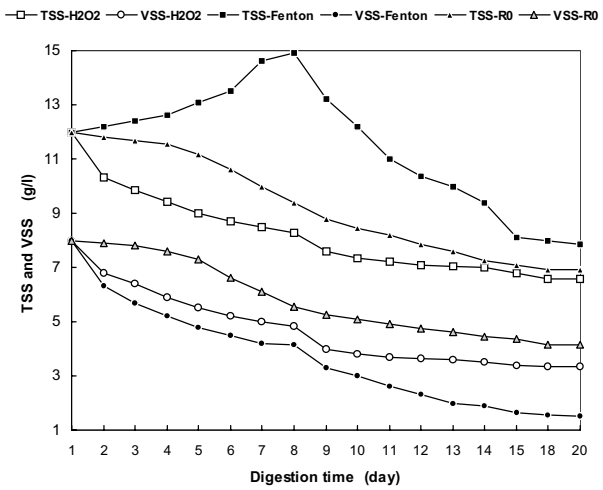

Fig. 1. Comparison of total (TSS) and volatile suspended solids (VSS) changes during aerobic digestion.

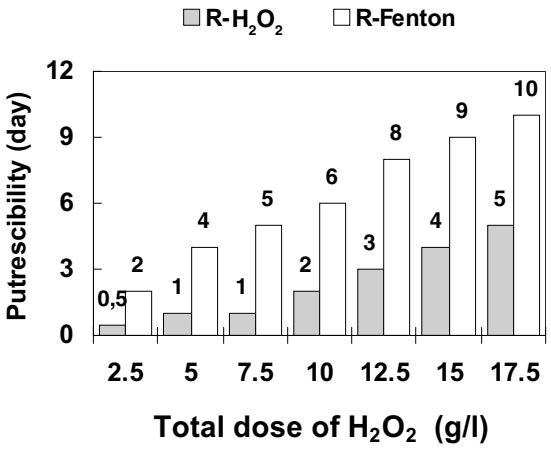

Fig. 2. Putrescibility as a function of H_2O_2 dose.

of H_2O_2, (Fig. 2.) On the other hand, in a reference reactor R_0 similar effect was observed after 12 days' aerobic digestion process.

Microbial Activity Changes

During aerobic digestion assisted with Fenton's reagent, both DHA and OUR activities decreased faster than the activities of sludge stabilized with H_2O_2. Moreover, the final values in R_{Fenton} were much lower than in $R_{H_2O_2}$ (Fig. 3 and 4). OUR and DHA in R_{Fenton} were reduced from 4.2 to 0.03 $mgO_2/g \cdot h$ and from 25 to 1.1 $mgTF/g \cdot h$, respectively, in 5 days' reaction, while in $R_{H_2O_2}$ OUR was decreased only from 4.2 to 0.88 $mgO_2/g \cdot h$ after 7 days' reaction and the final value was 0.77 $mgO_2/g \cdot h$. Enzymatic activity DHA in this reactor was reduced after the addition of the last dose of oxidant to 3.61 $mgTF/g \cdot h$ and it reached value of 3.1 $mgTF/g \cdot h$ at the end of the process.

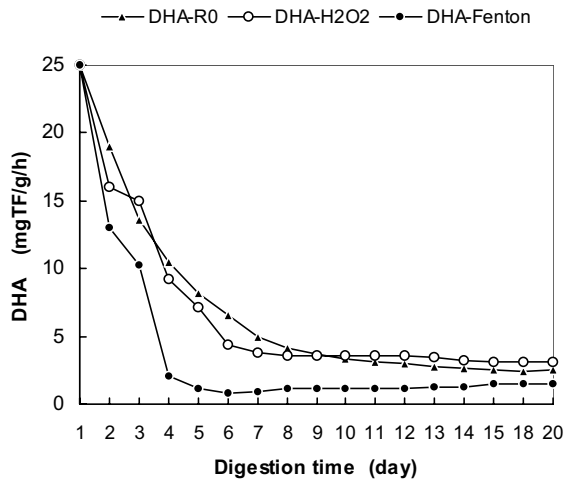

Fig. 3. Dehydrogenase activity (DHA) as a function of time.

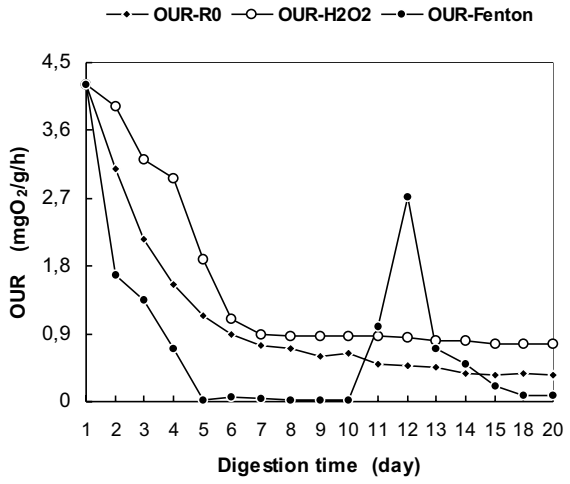

Fig. 4. Oxygen uptake rate (OUR) as a function of time.

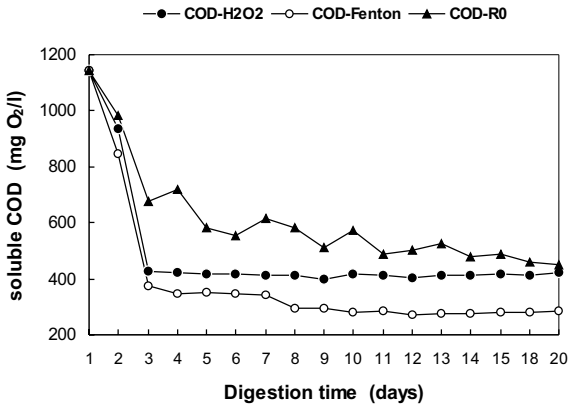

Fig. 5. Soluble COD as a function of time.

In the 11 and 12th day of experiments in R_{Fenton}, a difficult-to-interpret, rapid increase in OUR to 1.0 and then to 2.72 mg O_2/g·h took place (Fig. 4). It was most likely due to so-called oversensitivity, shown at extremal conditions, e.g. organic overloading or endogenous respiration, by microorganisms that increase their activity for a short time and then return to the initial state (transitional disturbance of homeostase) or is completely diminished (permanent disturbance of homeostase). This phenomena was observed by Barbusiński and Miksch [31] in relation to dehydrogenase activity.

In the reference reactor R_0, changes of DHA were closed to those observed in $R_{H_2O_2}$; however, decrease rate of OUR was faster than in $R_{H_2O_2}$. Slower rate of OUR changes in $R_{H_2O_2}$ could be due to the influence of residual hydrogen peroxide that might stimulate microorganism activity.

Changes of Soluble COD

The course of soluble COD changes was similar in both $R_{H_2O_2}$ and R_{Fenton} reactors (Fig. 5); however, rate and efficiency of COD removal were lower in $R_{H_2O_2}$ in comparison with R_{Fenton}. In $R_{H_2O_2}$ on the third day of aerobic digestion, COD was reduced to 425 mg O_2/dm^3 (62% removal) and remained at this level to the end of the experiment. In R_{Fenton} the corresponding COD value was 375 mg O_2/dm^3 (67% removal) and after 7 days was reduced to 340-350 mg O_2/dm^3. In the course of the next 10 days' aeration, without adding any oxidant, soluble COD in R_{Fenton} still decreased to 290 mg O_2/dm^3.

In the reference reactor R_0 some COD fluctuations with decreasing tendencies were observed, which indicates sorption and desorption of biomass destruction products. Similar fluctuations were observed by Barbusiński and Kościelniak [10]. At the end of the experiment COD in R_0 reached values closed to that from $R_{H_2O_2}$.

Changes of SVI and Sedimentation Properties

SVI changes in the course of the aerobic digestion process are shown in Figure 6. In R_{Fenton} SVI decreased from 64 to 30 cm^3/g after 11 days of process, whereas elongated aeration after finishing the addition of Fenton's reagent resulted in continuous increases in SVI up to 60 cm^3/g. Under these conditions from the 5th day considerable reduction of the floc size in R_{Fenton} (most likely due to unfavourable changes in their internal structure) was observed and supernatant liquid shown visible turbidity, which disappeared after 24 hours of sedimentation. This phenomenon indicated that a partial breakup of the flocs had taken place. The breakup of the activated sludge flocs was observed earlier by Barbusiński and Kościelniak [10, 32] under bidirectional organic loading changes as well as during aerobic digestion. When sludge digestion was assisted with H_2O_2 ($R_{H_2O_2}$), SVI dropped from 64 to 58 cm^3/g after the first four days and then was continuously rising up to 106 cm^3/g on the last day of aeration. The more H_2O_2 was added the flocs became larger and less coherent.

Similar increasing tendencies of SVI changes with values closed to that from $R_{H_2O_2}$ were observed in R_0, but the course of these changes was more "smooth" and an increase in SVI took place during whole experiment.

Thus, the application of Fenton's reagent apparently improved the sludge settleability and thickening capacity. It should be noticed, however, that the application of Fenton's reagent should be taken with care, taking into account H_2O_2 and Fe^{2+} doses. As mentioned above, too high doses may be followed by flocs breakup and worsening of sludge settleability and dewaterability. Other disadvantages of Fenton's reagent application are considerable pH decrease and colourization of supernatant liquid at large doses of H_2O_2 and Fe^{2+}. The colour could, however, easily be removed using CaO.

Changes of Capillary Suction Time

Capillary suction time (CST), as described by Vesilind [33], is a quick and easy test to determine filterability changes of sludge. In $R_{H_2O_2}$ CST was gradually increased from 86 s up to 130 s (Fig. 7). Similar tendencies were observed in the reference reactor R_0. In R_{Fenton}, however, CST was rapidly decreased for the first four days of the experiment and then reached value of 22-27 sec. It was most likely due to the synergetic effect of chemical oxidation and coagulation by the addition of iron salt. Earlier described unfavourable changes in floc structure and increase in SVI, observed from the 12th day were also reflected in growing CST value at the end of the aerobic digestion process (Fig. 7).

Changes of pH and ORP

During aerobic digestion in R_0 and $R_{H_2O_2}$ pH changes from 8.1 to 8.5 were observed. Only on the last day of experiment, pH in $R_{H_2O_2}$ rapidly decreased to 6.3. In R_{Fenton} pH was decreased from 8.3 up to 5.5 after 3 days' reaction. After that pH was corrected with Na_2CO_3 in order to enable biochemical reactions to run parallel in aerobic digestion. After stopping the addition of Fenton's reagent pH reached 8.3.

During the addition of reagents much faster increase in ORP and its higher values were observed in R_{Fenton} (up to 350 mV) in comparison with $R_{H_2O_2}$ and R_0 (up to 200 mV). However, after stopping the addition of Fenton's reagent, ORP was decreased and reached the final value lower than for $R_{H_2O_2}$. The similar effects were also observed for VSS and soluble COD. It may be attributed to the fact that despite stopping Fenton's reaction, the following oxidation reactions still occurred, what led to reduction of the residual amounts of H_2O_2 and, as a consequence, to further decrease of ORP potential values.

Conclusions

Application of a hydrogen peroxide and a Fenton's reagent is a method to intensify aerobic sludge digestion. It makes possible reduced duration time of the process and to improve mineralization of sludge.

Fenton's reagent showed higher oxidation potential in comparison with H_2O_2 and, as a consequence, better efficiency in aerobic digestion. Fenton's reagent also improved sedimentation properties of sludge and decreased soluble COD. The important advantage of Fenton's reagent application is that it may initiate the oxidation process more effectively than H_2O_2. Such a conclusion may be drawn on the basis of VSS, COD and ORP analysis.

The apparent disadvantage of Fenton's reagent application, however, is the additional formation of chemical sediment and the fact that overdose of a reagent may cause decomposition of sludge flocs and, as a consequence, increase of supernatant turbidity and some problems with sludge dewatering. When Fenton's reagent is applied for a long time or when high doses are applied, it is affected by colourization of supernatant liquid caused by iron salt addition.

On the basis of presented results the following improvement of a digestion process may be proposed:

- short-time addition of high doses of Fenton's reagent with simultaneous aeration, then

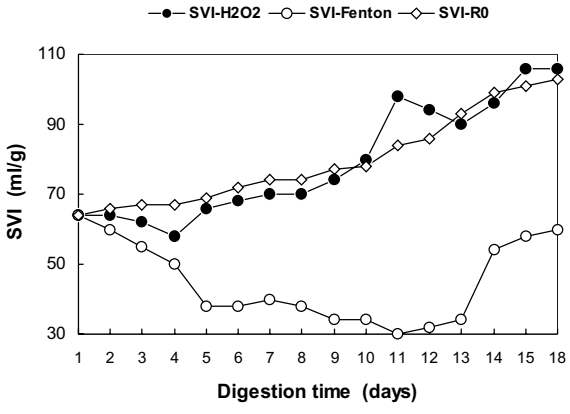

Fig. 6. Sludge volume index (SVI) as a function of time.

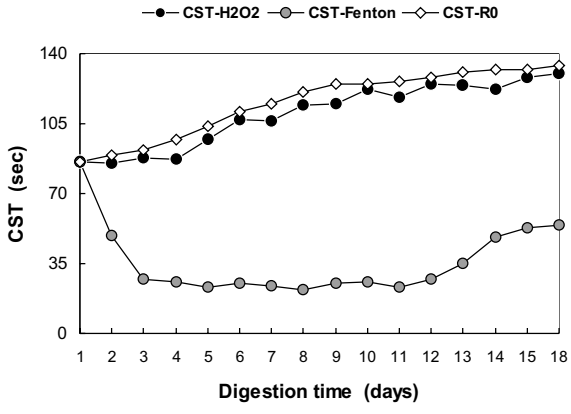

Fig. 7. Capillary suction time (CST) as a function of time.

- aeration with possible periodical addition of low doses of H_2O_2 (without Fe^{2+}), and finally
- aeration without any oxidation reagent.

The method of reagent addition should be monitored and based on the changes of basic aerobic digestion parameters as well as on redox potential changes. It is obvious that the doses of reagents need to be optimized for each sludge separately.

Intensification of aerobic digestion using H_2O_2 or especially a Fenton's reagent may be recommended to stabilize sludge from biological treatment plants for industrial wastewater consisting of resistant or non biodegradable pollutions.

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