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Aerobic Sludge Digestion in the Presence of Chemical Oxidizing Agents Part II. Fenton's Reagent

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Abstract

Aerobic sludge digestion in the presence of Fenton's reagent and hydrogen peroxide was examined. Fenton's reagent considerably improved the aerobic digestion process in comparison with hydrogen peroxide as well as classical aerobic digestion. Application of Fenton's reagent also led to improvement of settling and dewatering properties of sludge and much better clarity of supernatant. Its drawback, however, is the formation of chemical precipitate and an apparent decrease in pH which might inhibit biochemical processes important for aerobic digestion efficiency.

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

Introduction

Activated sludge technology has been successfully applied in the effective treatment of municipal as well as industrial wastewater. However, utilization of excess sludges formed in the biological treatment still cause many serious problems. Aerobic digestion, considered the alternative method of excess sludge stabilization, is a process to be carried out in terms of endogenic respiration assisted by biochemical decomposition of organic substances included in sludge. The main disadvantage of the aerobic digestion process is its high energy-consumption [1, 2]. Thus, it is very important to find some possibilities to reduce time needed for sludge stabilization.

To this aim strong chemical oxidants have been used, as H_2O_2 or a Fenton's reagent, to assist microbiological processes of endogenic oxidation of organic matter contained in sludge. As a result shortening of digestion time and energy consumption reduction should be achieved. On the other hand, the careful elaboration of the process might be helpful in several emerging cases, e.g. for putrefied sludge digestion.

In this research, the influence of hydrogen peroxide and Fenton's reagent on aerobic sludge digestion was examined. In our experiments H_2O_2 was the only source of oxygen. The presented results are continuation of the experiments described in our previous paper [3].

Fenton's Process

Fenton's reaction is a very promising method for oxidation of compounds resistant to biodegradation. It is a radical reaction in which very reactive hydroxyl radicals are formed by the catalytic decomposition of H_2O_2 with ferrous iron (Fe^{2+}) according to the reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^*$$

Fenton's reaction destroys a wide variety of organic compounds without the formation of toxic by-products [4]. This method offers a cost-effective source of hydroxyl radicals, using easy-to-handle reagents. Hydroxyl radicals effectively react with nearly all contaminants. The main advantage of Fenton's process is that oxidation and coagulation take place simultaneously. Fentons's reaction is described in detail in literature [5-13].

Materials and Methods

Experimental Procedure

Experiments were carried out in four digestion reactors (R-0 to R-3) of 10 dm^3 each. The sludges in three reactors (R-l to R-3) were magnetically stirred without additional aeration, while the fourth reactor R-0 (a reference one) was only aerated with compressed air introduced in the bottom 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 litter) and was brought to laboratory batch reactors (R-0 to R-3). Various doses of 30% H_2O_2 (to R-l) and solid $FeSO_4 \bullet 7H_2O$ with H_2O_2 (to R-2 and R-3) were then added daily. Fe^{2+}:H_2O_2 (w/w) ratio in Fenton's reaction was 1:4. After 5 days of experiment H_2O_2 was only added to R-2 and R-3 reactors (without adding of $FeSO_4$). The reference reactor R-0 was aerated (without adding of H_2O_2), as in the standard aerobic digestion. Air flow intensity was adjusted with the aid of a precalibrated rotameter to maintain the content of dissolved oxygen concentration in the reactor at the range of 2.0-2.5 mg/dm^3. Although classical Fenton's reaction is carried out at low pH, no primarily acidification was done in our experiments. Evaporation losses in all reactors were made up each day with distilled water prior to sampling. Aerobic digestion was continued for 15 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 the aerobic digestion process. The changes of sludge hydration and putrescibility of supernatant (in the presence of methylene blue) were also analyzed. All above analytical procedures were measured in accordance with Standard Methods [14]. Diluted (1:1 with tap water) SVI determinations were performed in unstirred 1 litre graduated cylinder. The concentration of residual H_2O_2 was analyzed by the iodometric method. Because of residual H_2O_2 increases the COD value was calculated according to the formula described in [3, 15].

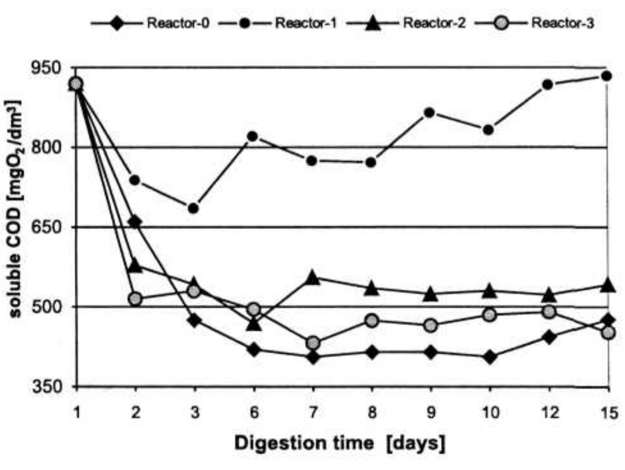

Fig. 1. COD changes for supernatants during aerobic digestion in the presence of H_2O_2 and Fenton's reagent.

Results and Discussion

The reagents were added according to the scheme presented below:

experimental day	reactor R-1 (H_2O_2)	reactor R-2 (Fenton)	reactor R-3 (Fenton)
1-5	5.0 g/dm^3	3.0 $g/dm^{3(1)}$	2.0 $g/dm^{3(1)}$
6-10	2.0 g/dm^3	1.0 $g/dm^{3(2)}$	1.0 $g/dm^{3(2)}$
11-15	1.0 g/dm^3	0.5 $g/dm^{3(2)}$	0.5 $g/dm^{3(2)}$

(1) $[Fe^{2+}]$:$[H_2O_2]$ ratio = 1:4 (2) H_2O_2 only was added

The examined sludge was taken from biological wastewater treatment plant in the chemical factory located in the south of Poland. Sludge consisted of 92% organic mass (VSS) and mostly of hardly biodegraded organic substances, was difficult to stabilize (see part I [3]). Therefore, the application of chemical oxidizing agents (e.g. Fenton's reagent and hydrogen peroxide) was thought to be highly recommended to intensify the aerobic digestion.

Examinations on Organic Mass Changes and Sludge Hydration

Organic mass (VSS) changes were different, depending on the method used. In a reference reactor (R-0) VSS concentration was decreased by 26.7% for 15 days experiment, while in R-l reactor, supplied with H_2O_2, concentration was decreased by 33.2%. The best results, however, were observed in R-2 and R-3 reactors, supplied with a Fenton's reagent and then with H_2O_2, and they were 43.4% and 50.1%, respectively.

The effects observed in R-l reactor, with 40 g/dm^3 of H_2O_2 added (on 1 dm^3 volume of reactor), were similar to those for reactor R-2 described in [3] and supplied with 120 g/dm^3 H_2O_2. Thus, it can be concluded that the final effect of sludge digestion depends not only on dosage but also on a way of a reagent addition. Better results are achieved when higher doses are applied at the beginning of the process, since highly concentrated biomass is easily mineralized.

The results obtained in reactors R-2 and R-3 show that hydroxyl radicals formed in a Fenton's reaction are more active than hydrogen peroxide. In R-2 and R-3 sludge was completely stabilized after 10 days of digestion, i.e. its organic mass (VSS) was reduced by at least 38%, according to Oleszkiewicz [16]. Thus, total amounts of H_2O_2 added to R-2 and R-3 (on 1 dm^3 volume of reactor) were 22.5 and 17.5 g/dm^3, respectively, and they were much lower than those for the R-l reactor.

Sludge hydration for reference R-0 and R-l reactors was about 99.5 - 99.7%, while for R-2 and R-3 reactors, after 5 days, sludge hydration was decreased to 99.1% and remained at this level to the end of the process.

Putrescibility and COD Changes

In the course of standard aerobic digestion (R-0) supernatant liquid did not putrefy for at least 5 days after 12 days of process, and for more than 5 days, after 15 days of process. When hydrogen peroxide was applied (R-l) (similar to part I of the experiments described in [3]) the supernatant putrefied after several hours. This was linked to the observed low level of dissolved oxygen in R-l reactor. Such problems did not appear in R-2 and R-3 reactors, most likely due to the high concentration of hydroxyl radicals (OH) and rapid decay of VSS in the initial phase of process improved by a Fenton's reagent. In R-2 and R-3 reactors supernatant stopped putrefying (for at least 5 days) after 5 days and 6 days' process, respectively. It was about two times lower time in comparison with standard aerobic digestion (R-0).

The highest efficiency in COD removal (up to 55.8%) was achieved in an R-0 reactor. In this reactor (similar to part I of the experiments described in [3]), further increase in COD as a result of microorganisms lysis and cells metabolites transfer into solution was observed at the end of the process (Fig. 1). COD removal was also satisfactory in R-2 and R-3 reactors and reached 49% and 53%, respectively. In a R-l reactor, supplied from the beginning with hydrogen peroxide, the effectiveness of COD removal was very poor and, because of periodical appearance of anaerobic conditions, nonregular increasing tendencies of COD were observed (Fig. 1).

pH and Redox Potential Changes

pH changes in R-2 and R-3 reactors, supplied with a Fenton's reagent, were different from those observed in other reactors, e.g. on the third day pH was decreased to 2.7 and 3.4 in R-2 and R-3, respectively. Because of Fenton's reaction pH was significantly reduced, therefore, after 5 days of the process, H_2O_2 was only added (without of $FeSO_4$). Final pH was 2.5-2.8 in both reactors (Fig. 2). In R-0 and R-l reactors an initial increase in pH was observed and it finally decreased up to 6.4 in R-0 reactor and remained at 8.3-8.4 in R-l reactor.

Redox potential (ORP) changes were reciprocal to those observed for pH. The highest values, 80-150 mV, depending on H_2O_2 dose, were observed in R-2 and R-3 reactors. This was confirmed by high oxygenation potential of OH radicals generated in Fenton's reaction.

Capillary Suction Time Changes

Unlike the results obtained in part I of experiments [3], worsening of sludge dewatering was observed not in all examined cases. It was first of all observed in R-l reactor, where H_2O_2 assisted digestion was carried out. CST value constantly increased from 23 to 54 seconds at the end of process. In a reference R-0 reactor, after initial worsening of filtration properties (3-6 day), they were then improved and CST reached 26.5-27 seconds.

The most efficient and rapid changes were observed in R-2 and R-3 reactors, where in three days experiments CST values were decreased and stabilized at 8.7-9.2 seconds, as it was shown in Fig. 3. Such effective dewatering was apparently due to synergetic combination of chemical oxidation and coagulation by Fe^{2+} salt addition. Similar observations were obtained by Mustranta and Viikari [17], treating different activated sludges from pulp and paper mills with hydrogen peroxide in the presence of ferrous sulphate in order to improve the sludge dewatering characteristics. The specific filtration resistance of the sludges studied were considerably enhanced by oxidative treatment.

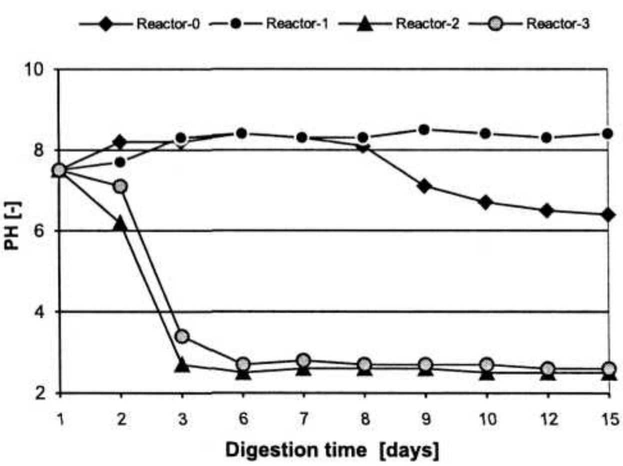

Fig. 2. pH changes in the R-0 + R-3 reactors during aerobic digestion in the presence of H_2O_2 and Fenton's reagent.

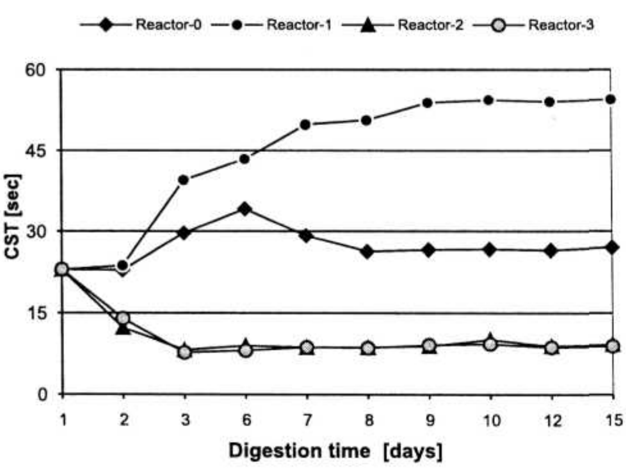

Fig. 3. CST changes of sludge during aerobic digestion in the presence of H_2O_2 and Fenton's reagent.

Settleability and Sludge Volume Index Changes

The first positive tendencies in settleability of sludge were observed after two days of experiments, where a Fenon's reaction was performed (R-2 and R-3), as it was shown in Figures 4 and 5. This tendency was continued up to the 9th day, however, from the 7th day thickening capacity was still very good, whereas settleability (to 30 minutes) was worsening (Fig. 6). After that both parameters in R-2 and R-3 were clearly decreased (Fig. 7) and it was also reflected in sludge volume index (SVI) increase (Fig. 4). One should note, however, that SVI changes, when a Fenon's reagent is applied, refer to activated sludge as well as chemical precipitate formed as a result of Fe^{2+} salt addition. It may thus happen that application of a Fenon's reagent is followed by total suspended solids (TSS) increase despite decay of organic suspended solids (VSS). It also affects the value of SVI.

The sludge treated by hydrogen peroxide (R-l) and the sludge from a reference reactor (R0) shown decreasing settleability tendencies for the first seven days and then, after slight improvement (8-9 day) were stabilized at levels much higher than initial value (Fig. 4).

Supernatant Liquid Appearance

In reference (R-0) and R-l reactors supernatant was initially very turbid and had intensive grey colour. After 7 days of the process, in a R-0 reactor supernatant became then slightly turbid and colourless. In a R-l reactor less decrease in supernatant turbidity (in comparison with R-0) was observed during aerobic digestion and slightly grey colour was maintained to the end of experiment.

In R-2 and R-3 reactor supernatant was at first also turbid and yellow-orange. Finally (from the 3rd day) it became clear, light yellow with a fine, noncoagulated fraction of suspended solids in upper layer of a cylinder. It can be presumed that this fine fraction appeared as a consequence of sludge floes breakup due to a high decrease in pH. To avoid high decrease in pH and floes decomposition it is recommended to add a Fenton's reagent to reactors supplied with aeration system. It enables decrease of reagents doses, demanded amounts of oxygen, energy consumption and duration of process.

Thus, the optimal procedure should be as follows: short-term addition of high dose of a Fenton's reagent,

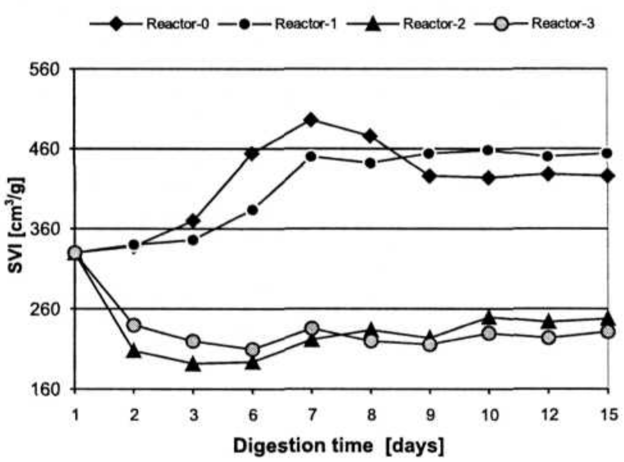

Fig. 4. SVI changes during aerobic digestion in the presence of H2O2 and Fenton's reagent.

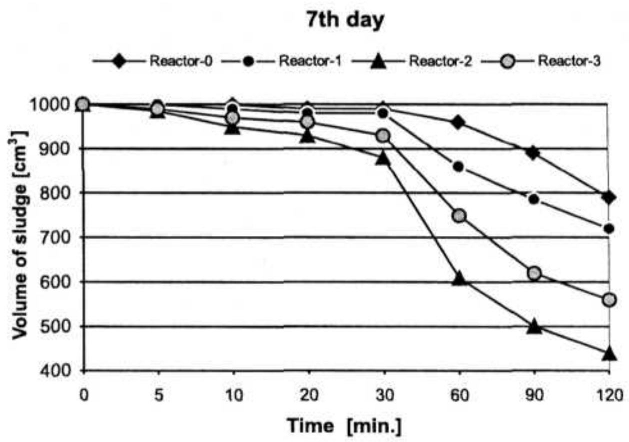

Fig. 6. Variation of settling characteristics during aerobic digestion – 7th day.

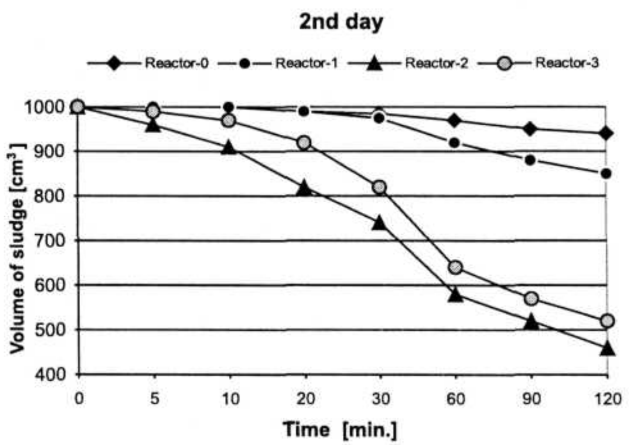

Fig. 5. Variation of settling characteristics during aerobic digestion – 2rd day.

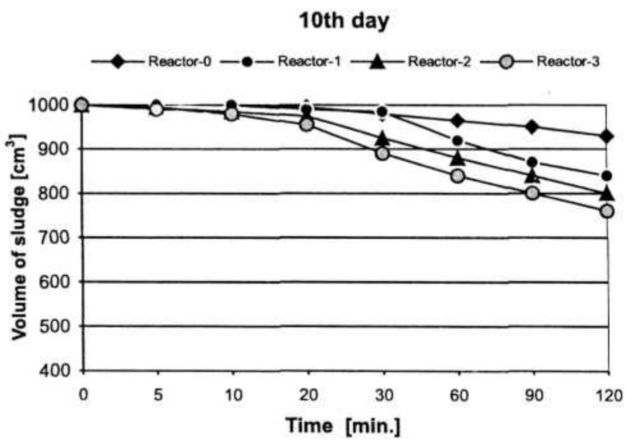

Fig. 7. Variation of settling characteristics during aerobic digestion - 10 th day.

then aeration or periodical addition of low doses of H_2O_2 and a final aeration without application of reagents. Frequency and doses of reagents should be estimated on the basis of monitoring the progress of the aerobic digestion process.

Conclusions

Application of a Fenton's reaction made aerobic sludge digestion more efficient than standard aerobic digestion and digestion assisted with application of H_2O_2. One of the disadvantages of a long-term Fenton's reaction application was, however, additional formation of chemical precipitate. Moreover, decrease in pH and increase of supernatant colouring induced as a result of Fe^{2+} salt addition, was observed. The main advantage of a Fenton's reaction is apparent improvement of sedimentation properties and dewatering capacity of sludge. Supernatant liquids are generally clear and transparent. To avoid high decrease in pH and floes decomposition it is recommended to add a Fenton's reagent to reactors supplied with aeration system. Fenton's process may be especially recommended for a putrefied sludge and for a sludge to be stored for a long time before dewatering. The next experiments are in progress.

Acknowledgement

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