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Stabilization of Excess Sludge From Poultry Slaughterhouse Wastewater Treatment Plant by the Fenton Process

Zeinab Masoumi [1]; Reza Shokoohi [1]; Zeinab Atashzaban [1]; Nahid Ghobadi [1]; Ali Reza Rahmani [1,*]

[1]Department of Environmental Health Engineering, Faculty of Health and Research Center for Health Sciences, Hamadan University of Medical Sciences, Hamadan, IR Iran

*Corresponding author: Ali Reza Rahmani, Department of Environmental Health Engineering, Faculty of Health and Research Center for Health Sciences, Hamadan University of Medical Sciences, Hamadan, IR Iran. Tel: +98-8138381641, Fax: +98-8138381641, E-mail: rahmani@umsha.ac.ir

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Abstract

For stabilization of excess sludge in activated sludge process, the Fenton process was applied as a safe technique and its effectiveness was experimentally examined. In order to carry out experiments, a batch reactor with the effective volume of 0.5 L was used. Effect of hydraulic retention time, pH, H_2O_2, and Fe concentrations on sludge stabilization were investigated. Before and after the process, the content of total solids (TS), volatile solid (VS), chemical oxygen demand (COD), and color were measured. The study showed that, the best efficiency was obtained when iron concentration was 60 mg/L, duration of the process was 150 minutes, pH = 3, and H_2O_2 concentration was 4000 mg/L. The Fenton process can reduce the values of TS, VS, COD, and color to 50%, 61%, 53% and 61%, respectively. By analogy to conventional methods, the Fenton process is an effective method that can be suggested to stabilize excess sludge.

Keywords: Wastewater; Poultry; Slaughterhouse; Sludge

1. Introduction

During past decades, industrial development and urbanization have led to the production of the significant amount of sewage sludge and in the meantime the progress of wastewater treatment. This process is expected to continue in the future. Currently, lack of the principle management of sludge disposal from wastewater treatment has led to the release of some raw (untreated) sludge to the environment. This release has caused a lot of damage to the environmental resources and human health (1, 2). Slaughterhouses are industries that produce large amounts of wastewater and sludge containing a wide variety of organic compounds at very high amounts. Unless this wastewater manages and treats properly, it can cause environmental damage and has horrible effects on human health.

One of the systems used in the industrial livestock and poultry slaughterhouse wastewater treatment is activated sludge. Typically, the activated sludge system produces 15 - 100 L sludge per each 1 kg removed biochemical oxygen demand (BOD). Sludge from wastewater treatment contains 95% - 98% water. According to the provisions of sludge disposal, appropriate management of sludge is a great challenge for operators (3, 4). Generally sludge stabilization has several goals such as reducing pathogens, removing foul odors, and reduction or elimination of putrescible (5). Recently, advanced oxidation processes in sludge management are applicable with high efficiency. However, high investment costs and energy consumption are justifiable when there are no cheaper options (6).

The Fenton process is a suitable approach for sludge stabilization with high performance and low cost (7). Using Fenton reaction for minimization of excess sludge is based on this idea that a part of the activated sludge decomposes into carbon dioxide and water, and the other part is converted to solution biodegradable material (8). The high efficiency of the process is due to the presence of hydroxyl radicals. Hydroxyl radicals are produced from interaction between hydrogen peroxide and ferrous sulfate at atmospheric pressure and in the absence of heat. Oxidation potential of OH° is dependent on pH. In neutral pH, E° = 1.8 v and in acidic conditions E° = 2.7 v. Therefore, the Fenton process is managed in acidic conditions (7, 9). Principles of advanced oxidation processes performed by Fenton's reagent (H_2O_2/Fe^{2+}) can be summarized in the following equations (10):

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

$$OH + H_2O_2 \rightarrow H_2O + HO_2 \quad (2)$$

(3) $$Fe^{3+} + HO_2 \rightarrow Fe^{2+} + H^+ + O_2$$

(4) $$Fe^{2+} + HO_2 \rightarrow Fe^{3+} + HO_2^-$$

(5) $$Fe^{3+} + OH^- \rightarrow Fe^{2+} + OH$$

The produced hydroxyl radicals can quickly degrade the extracellular material and destruction of the sludge flocs increases the sludge stabilization. Effect of the Fenton process strongly depends on the reaction temperature, pH, hydrogen peroxide concentration, contact time, and concentration of iron (11-13).

Ease of use, applicable in ambient temperature, material availability, ease of storage and inexpensive materials are the advantages of the Fenton process. Erden and Filibeli applied the Fenton reaction to biological sludge for dewatering and noted that 4 g Fe (II)/kg TS and 60 g H_2O_2/kg TS was efficient for floc disintegration (14). The purpose of this study was stabilization and reduction of the amount of excess sludge slaughterhouse wastewater treatment plant. For this purpose, the excess sludge of treatment plant of the poultry slaughterhouse of Hamadan City was used. Activated sludge is the system, used for wastewater treatment of this slaughterhouse, which produces large amount of excess sludge with COD higher than 20000 mg/L. This is considered a problem for this industry. Therefore, the Fenton process was investigated in order to reduce the amount of COD, solids, and color in this slaughterhouse.

2. Materials and Methods

All investigations carried out in a lab-scale reactor in a batch system. Samples were collected during summer and autumn 2014 in Hamadan poultry slaughterhouse wastewater treatment plant with a random approach from returned sludge to the aeration tank. Samples were transported to the laboratory at 4°C. Physical and chemical characteristics of raw sludge are presented in Table 1. A plexiglass reactor with useful volume of 0.5 liter (15 cm height and 10 cm diameter) was used for testing. Chemicals such as ferrous sulfate ($Fe_2(SO_4)_3.7H_2O$), hydrogen peroxide (H_2O_2), sulfuric acid, sodium hydroxide 0.1 M (to adjust pH) with purification of 99.5% from Merck Co (Germany) were used. After adjusting the pH of the samples, several concentrations of iron (30-80 mg/L) and hydrogen peroxide (1000 - 5000 mg/L) were supplied in separate steps and added to the reactor. The contents of the reactor during the reaction stirred with the speed of 200 rpm for 0 - 180 minutes and samples were collected from a depth of 10 cm at time intervals of 30 minutes. Measurements were done in accordance to the standard methods (15). The samples were diluted for COD test and in order to determine its amount, the closed reflux colorimetric method was used. Then, absorbance values at 600 nm were read. Before subjecting to the COD measurement, the samples were pretreated with Na_2SO_4 to remove residual H_2O_2. Color of the samples were measured through photometric method and TS and VS tests were carried out through gravimetric methods (8, 16). Data were entered, cleaned, and analyzed using SPSS version 16.0. Descriptive statistics were employed to report numerical summaries of the findings.

Table 1. Physical and Chemical Properties of Raw Sludge in This Study

Parameters	Values
pH	7 - 8.3
COD, mg/L	25000 - 32000
VS, mg/L	3310 - 9000
TS, mg/L	5320 - 11500
Total Coliform, MPN/100 mL	90 × 105
Fecal Coliform, MPN/100 mL	20 × 105
EC, µs/cm	550 - 900
TDS, mg/L	900 - 1000
Color, Pt/Co	800 - 1197
SVI, mL/g	900 - 950

3. Results and Discussion

3.1. Effect of Retention Time on the Fenton Process

In order to study the effect of retention time on the Fenton process, pH adjustment on 3 and then concentrations of iron (60 mg/L), and hydrogen peroxide (4000 mg/L) were added to the reactor. The sludge was sampled at intervals of 30 minutes. Results are shown in Figure 1. The most important part of the reaction occurs in the beginning of the reaction between iron and hydrogen peroxide, which leads to the production of hydroxyl radical. Organic materials were oxidized by radical OH and converted to CO_2 and H_2O (17). The observed foam on the sludge represents the formation of CO_2 (Figure 2). Maximum removal efficiencies for TS, VS, COD, and color during 150 minutes are 50%, 61%, 53%, and 61%, respectively. No significant change was observed with increase in retention time. This showed that, in 150 minutes, the reaction between hydrogen peroxide and iron is completed. In a study, Aliabadi et al. (18) have used the Fenton process for the treatment of sewage containing olive oil. They also used cracking operation for degradation of inhibitor compounds. At the condition of pH 3, four hours retention time, H_2O_2 as 0.5 M, and Fe as 0.02 M, this process removed 57% of COD.

3.2. Effect of pH on the Fenton Process

pH is an important parameter in Fenton process. According to Figure 3, with increasing pH, the removal efficiency of the process decreases. So, if pH increases from 3 to 9, then the efficiency of the process for TS, VS, COD, and color from 50%, 61%, 53% and 61% will be decreased to 9%, 13%, 20% and 10%, respectively. Gholikandi et al. in a study about the Fenton process in reduction of organic load in biological excess sludge, found that the best efficiency was obtained at pH = 3 (19). When pH is below 3, Fe $(OH)^{2+}$ reacts very slowly with hydrogen peroxide, which leads to the reduction of radical OH. Therefore, the efficiency of the process will decrease. Hydrogen peroxide is unstable in basic solution, and in pH level of above 7, it would decompose to yield oxygen and water. In addition, conversion of iron (II) to iron (III) occurs very fast and leads to sedimentation of iron as Fe $(OH)^{2+}$, which decreases the efficiency of the process (10, 15).

Figure 2. The Formation of Foam Due to the Presence of CO_2

3.3. Effect of H_2O_2 Concentration on the Fenton Process

In the Fenton process, the chemical efficiency of hydrogen peroxide is remarkable (17). Effects of the initial H_2O_2 concentration on sludge stabilization at different concentrations of H_2O_2 (1000 - 5000 mg/L), in the presence of a specified amount of iron (60 mg/L), pH = 3, and time period of 150 minutes are shown in Figure 4. It was found that, increase in initial H_2O_2 concentration would improve the sludge disintegration rate. Increase in the concentration of hydrogen peroxide to 4000 mg/L, leads to increase in the removal efficiency of TS, VS, COD and color to 50%, 61%, 53%, and 61%, respectively.

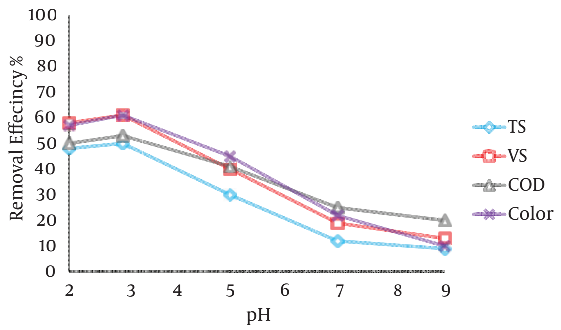

Figure 3. Effect of pH on the Removal Efficiency of Investigated Parameters in the Fenton Process (Iron = 60 mg/L, Retention time = 150 min, and H_2O_2 = 4000 mg/L)

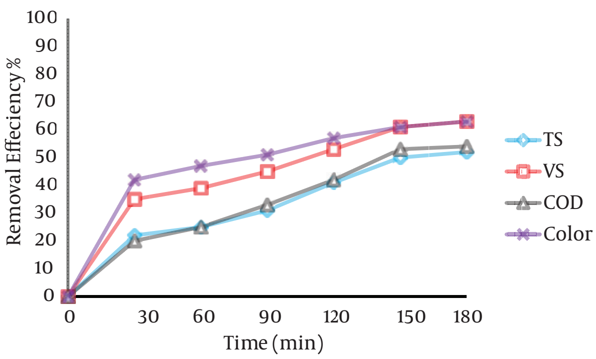

Figure 1. Effect of Retention Time on the Removal Efficiency of Investigated Parameters in the Fenton Process (iron = 60 mg/L, pH = 3, and H_2O_2 = 4000 mg/L)

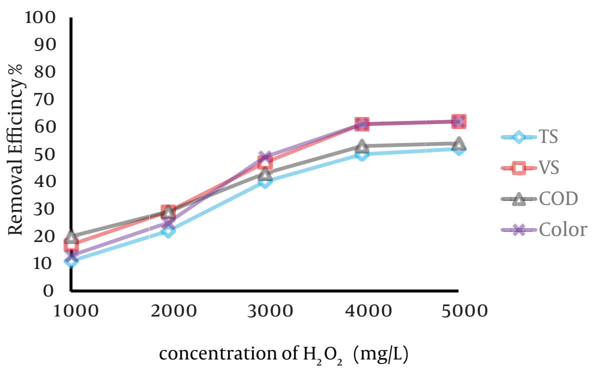

Figure 4. Effect of Concentration of H_2O_2 on the Removal Efficiency of Investigated Parameters in the Fenton Process (Concentration of iron = 60 mg/L, pH = 3 and Time = 150 minutes)

Hydrogen peroxide was not completely consumed during the reaction. The residual H_2O_2 can interfere with COD measurement because of its reaction with dichromate in the aqueous solution and hence a higher COD would be obtained when H_2O_2 was present. High concentration of H_2O_2 inhibits the production of hydroxyl radical and reduces the efficiency of the process. Also in the presence of excess hydrogen peroxide, according to the reactions 6 through 8, H_2O_2 acts as a consumer of hydroxyl radicals (Following Equations) (18, 20).

Lopez et al. in a study on landfill leachate showed that increase in H_2O_2 concentration up to an optimum amount can reduce the amount of COD, and with increase in hydrogen peroxide concentration more than optimum concentration, there will be no increase in efficiency (21).

$$H_2O_2 + OH \rightarrow H_2O + HO_2 \tag{6}$$

$$HO_2 + OH \rightarrow H_2O + O_2 \tag{7}$$

$$OH + OH \rightarrow H_2O_2 \tag{8}$$

3.4. *Effect of Fe Concentration on the Fenton Process*

The effect of different concentrations of iron (30 - 80 mg/L) on the Fenton process in the presence of optimum conditions (Period = 150 minutes, pH = 3, and concentration of H_2O_2 = 4000 mg/L) were investigated. Figure 5 shows the effect of iron concentration variance on the efficiency of the process. The results showed that, increasing iron concentration, can improve the efficiency of the process. This increase in efficiency was observed until 60 mg/L of iron were added. If iron concentration increased more than the optimum concentration, the efficiency of the process would reduce. Increasing concentration of Fe can limit the catalytic action of Fe. Because, the excess of this ion in the solution combine with hydroxyl radical and bring them out of the solution (22). Kochany and Lipczynska-Kochany (23) for pretreatment of landfill leachate, used the Fenton process with iron concentration of 56 mg/L, which reduced the 66% of COD in the solution. Iron in reaction with hydrogen peroxide is consumed. With increasing Fe (II), more hydroxyl radicals produce. Thus, reducing the amount of ferrous increases the hydraulic retention time. On the other hand, excessive amounts of iron can lead to an increase in the color and opacity (16, 18, 19).

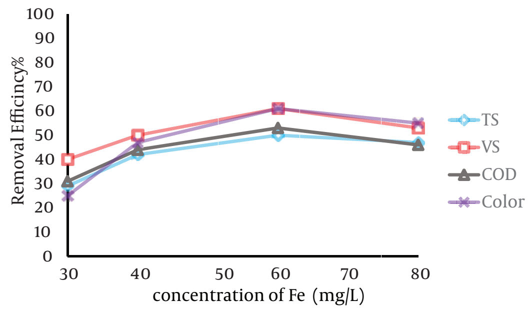

Figure 5. Effect of Concentration of Fe on the Removal Efficiency of Investigated Parameters in the Fenton Process (H_2O_2 = 4000 mg/L, pH = 3 and Time = 150 min)

4. Conclusions

According to the results of the experimental studies on sludge of slaughterhouse wastewater treatment plant, the Fenton process is an effective process for sludge stabilization. This is a simple, environmental, and economical process. Oxidation rate depends on many factors such as pH of sludge, concentration of hydrogen peroxide, ions of iron and time of reaction. The best efficiency will be obtained when the pH is 3, concentration of hydrogen peroxide is 4000 mg/L, concentration of iron is 60 mg/L, and duration of the process is 150 minutes. The disadvantage of the Fenton process is the production of Fe $(OH)_3$ that must be collected and disposed properly. According to these results, the Fenton process is an effective process for sludge management.

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