Stabilization and Dewatering of Wastewater Treatment Plants Sludge Using the Fenton Process

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Received:3 Agu. 2015, Revised: 15 Sep. 2015, Accepted: 26 Oct. 2015

ABSTRACT
Wastewater sludge typically contains large amounts of water and organic materials; therefore, its stabilization and dewatering is of particular importance. In this study, Fenton oxidation process is used for stabilization and dewatering of sludge in the output of a wastewater treatment plant. To evaluate the sludge stabilization and dewatering, specific resistance to filtration (SRF), volatile organic compounds (VSS), total suspended solids (TSS), soluble chemical oxygen demand (SCOD) and heterotrophic bacteria were measured. During the experiment, the optimal values of various parameters such as pH (2-9), hydrogen peroxide (0.015-0.18 mol/L), Fe2+ (0.008-0.1 mol/L) and time (5-60 minutes) for optimum sludge dewatering and stabilization were investigated. The results showed that the highest percentages of SRF reduction and removal rates of SCOD, VSS and TSS were 99.48, 61, 42, and 41 percent respectively. These results were obtained in optimum pH 5, 0.05 mol/l Fe2+, 0.12 mol/l hydrogen peroxide, and the retention time of 15 minutes. The removal rate of heterotrophic bacteria increased with increasing dose of hydrogen peroxide, so that a removal rate of 84 percent was observed at a dose of 0.18 mol/l. In general, Fenton process can reduce volatile organic materials and chemical oxygen demand of the sludge resulting in its significant stabilization and dewatering. In general, Fenton process can reduce volatile organic materials and chemical oxygen demand of the sludge resulting in its significant stabilization and dewatering.

Key words: Sludge, Fenton, stabilization and dewatering, organic materials

INTRODUCTION
Wastewater sludge is a by-product of wastewater treatment in wastewater treatment plants [1] and include metals, macronutrient and micronutrient, trace elements, organic pollution, microorganisms and various parasites eggs [2]. In recent decades, there has been increasing focus on the treatment and control of large quantities of sludge produced and the negative effects that may be associated with the disposal of sludge in the environment [1]. Sewage sludge is a complex mixture including of inorganic compounds, microorganism, certain undigested materials and moisture [3]. In addition, the presence of pathogens in sewage sludge is really dangerous for the environment and can create serious problems related to health [4]. Treatment and disposal of sludge generated in the process may account for up to 60% of the total operation expenses [5]. Wastewater sludge contains about 94-99% water and its dewatering is the most challenging and expensive parts of the wastewater treatment plants [6]. Sludge dewatering significantly depends on sludge properties, such as particle size, extracellular polymeric substances, etc. [7, 8]. Dewatering is very important due to the reduction volume of sludge and reducing the cost of transferring and disposing of the subsequent sludge processing [9]. As a result, treatment of large amounts of sludge is one of the basic requirements of wastewater treatment plant and accounts for much of the costs related to treatment [10]. New methods such as microwave conditioning, electrolysis, and chemical oxidation have been developed to disrupt extracellular polymeric substances (EPS) or to release the bound water, which both increase sludge dewaterability. Pre-treatment using Fenton and Fenton-like processes have served as alternative approaches for sludge conditioning [11-17]. In recent years, the advanced oxidation techniques have been used a lot in order to improve sludge conditions such as dewatering and remove the content of organic sludge, which causes the release of heavy metals from the sludge clots. Among the various processes of advanced oxidation using Fenton process is a good way because of the low response time, utilization of the coagulation process and flocculation, non-toxic compounds, and the possibility of using it in a different scale [18].
Pretreatment by Fenton reduces the amount of sludge, increases the biodegradability of biological sludge, and can lead to a decrease in volatile solids and an increase in the biogas [19, 20]. The effects of Fenton treatment largely depend on reaction conditions such as the H$_2$O$_2$ and Fe$^{2+}$ concentrations, and pH value [21]. Previous studies have rarely investigated stabilization and dewatering of a mixture of primary and secondary sludge simultaneously. Thus, the aim of this study was the simultaneous investigation of sludge dewaterability, degradation of organic materials in the sludge, and elimination of microorganisms from wastewater sludge using Fenton process.

MATERIALS AND METHODS

Sludge properties

Samples were taken from sludge output of Shiraz wastewater treatment plant (a mixture of primary and secondary sludge), which were designed and collected using activated sludge method and stored at 4 °C in polypropylene containers.

Laboratory methods

In this study, the effects of parameters such as pH, reaction time, Dosage of H$_2$O$_2$ and Fe$^{2+}$ were investigated. To determine the amount of oxidation and sludge stabilization, soluble chemical oxygen demand (SCOD) and the removal of heterotrophic bacteria (HPC) were tested. At each stage, constantly keeping all the variables and changing one variable, the optimal amount of each variable was determined. The first, 100 ml of the sample was poured in a 250 mL container and the pH was set to desired values (2, 3, 5, 7 and 9), Fe$^{2+}$ (0.008, 0.02, 0.03, 0.07, 0.09 and 0.11 mol/l) was added to the sludge and the Fenton reaction was launched to adding H$_2$O$_2$ (0.01, .029, .058, 0.12, 0.15 and 0.18 mol/l) at room temperature, to evaluate sludge stabilization and dewatering. To have uniform materials, sludge samples were continuously mixed by a shaker for specific reaction periods (5, 15, 30, 45 and 60). To provide Fe$^{2+}$ and H$_2$O$_2$ in the Fenton reaction, FeSO$_4$.7H$_2$O and H$_2$O$_2$ solution with a weight percentage of 30% as Fenton reagent were used. Normal sulfuric acid and sodium hydroxide were used to set the pH. All materials such as sulfuric acid and hydrogen peroxide were purchased from Merk. The 42 Whatman filter paper was used. The experiment was repeated twice to control the errors.

Analysis

Sludge cake was dried at 105 °C for 24 hours and then the weight difference before and after drying was measured as the amount of sludge water. Sludge stabilization and mineralization were done via determining the VSS/TSS ratio. The amounts of SCOD, VSS, TSS and HPC were measured by standard methods [22]. Vacuum filtration method was used to measure SRF [23]. In this method, 100 ml of the sample was poured into standard Buchner funnel equipped with filter paper and the sample was filtered at pressure of 75 Kilopascal. Finally, the SRF value was determined by creating a volume-time.

Sludge filtration capability was determined based on the following formula (mkg-1):

$$SRF = \frac{2PAb}{\mu w}$$

Where, SRF = specific resistance of filtration, (m/kg); P = pressure of filtration (N/m$^2$); A = area of filter (m$^2$); b = slope of filtrate discharge curve (sm$^{-6}$); $\mu$ = viscosity of the filtrate (N.s/m$^2$) and $w$ = weight of cake solids / volume of filtrate (kg/m$^3$).

RESULTS AND DISCUSSION

The basic description of sludge

Sludge used for the experiments was the raw sludge which had gone through a biological process. Some information about the raw sludge is presented in Table 1.

Table 1: Characteristics of raw sludge taken from Shiraz wastewater treatment plant

<table>
<thead>
<tr>
<th>parameter</th>
<th>Unit</th>
<th>Min.</th>
<th>Max.</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydration</td>
<td>[%]</td>
<td>95.29</td>
<td>96.83</td>
<td>96.06</td>
</tr>
<tr>
<td>SRF</td>
<td>[m·kg$^{-1}$]</td>
<td>88×10$^3$</td>
<td>16×10$^4$</td>
<td>12.4×10$^3$</td>
</tr>
<tr>
<td>Reaction</td>
<td>[pH]</td>
<td>5.73</td>
<td>6.90</td>
<td>6.31</td>
</tr>
<tr>
<td>TSS</td>
<td>[g·L$^{-1}$]</td>
<td>31.69</td>
<td>39.42</td>
<td>35.55</td>
</tr>
<tr>
<td>VSS</td>
<td>[g·L$^{-1}$]</td>
<td>17.29</td>
<td>31.54</td>
<td>24.41</td>
</tr>
<tr>
<td>COD of Filtrate</td>
<td>[mg·L$^{-1}$]</td>
<td>3710</td>
<td>5200</td>
<td>4455</td>
</tr>
<tr>
<td>HPC</td>
<td>Cfu/ml</td>
<td>1067  × $10^3$</td>
<td>1225 × $10^3$</td>
<td>1146 × $10^3$</td>
</tr>
<tr>
<td>TDS</td>
<td>[g·L$^{-1}$]</td>
<td>2.210</td>
<td>11.040</td>
<td>6.625</td>
</tr>
</tbody>
</table>

The effect of pH on sludge dewatering and stabilization

Fig. 1 indicates the effect of pH on sludge samples in reaction time of 30 min, 0.058 mol/l hydrogen peroxide and 0.03 mol/l Fe$^{2+}$. As showed in the figure, at pH 5, maximum removal efficiency of SCOD, VSS, TSS and maximum reduction of SRF obtained 26, 21, 20 and 53 percent respectively. In alkaline conditions, the formation of OH radicals is prevented due to Fe$^{3+}$ conversion into Fe(OH)$_2$ deposits. In addition, research shows that the oxidative potential of OH radicals decreases with increasing pH [24]. Therefore, at pH more than 5, due to instability of hydrogen peroxide and its
conversion into water and oxygen, the removal rate is reduced [25]. At pH less than 3 decomposing organic matter is reduced due to a decrease in free iron ions in the solution. This can be due to formation of the Fe3+ ions and buffering or the precipitation of oxy-hydroxy ferric in the reaction environment. Theoretically, at a very low pH (less than 2.5), the formation of Fe(H2O)52+ which reacts with hydrogen peroxide very slowly, can reduce the amount of hydroxyl radicals and thus reduces the efficiency of the process [26].

In this study, the effect of pH alone without adding Fenton reagents to the sludge was also studied. In this situation, dewatering was not changed significantly. He et al. investigated activated sludge dewatering via acid treatment and concluded that the amount of dewatering does not improve significantly via pretreatment with acid [27]. There are not the convincing conclusions on the optimum pH for the oxidation with Fenton. For example, Lu et al. claimed that pH values ranging from 2.5 to 7.0 have no significant effect on sludge dewatering that modified with Fenton process [28]. On the other hand, Mo et al. reported that the amounts of optimum pH are for modifying sludge 3 [12]. Also Zhao et al. found that sludge dewatering is better at pH= 4-5. This can be attributed to the release of metal ions such as iron and aluminum, which improve the sludge flocculation [13].

Low reaction time facilitates the operation and reduces the reactor volume and the related costs. In order to determine the best time and its effect on the Fenton process, tests were performed at different retention times of 5, 15, 30, 45, and 60 minutes, Fe2+= 0.03 mol/l, H2O2= 0.058 mol/l, and pH=5. The results showed that dewatering improved at lower times, but with the passage of time, it showed no significant change. As shown in Fig. 2, maximum removal efficiency of SCOD, VSS, TSS and maximum reduction of SRF was 43, 30, 28 and 61.66 percent respectively which occurred in retention time of 15 minutes, which indicated that sludge was easy to be dewatered and stabilized. Thus, the optimal reaction time was selected to be 15 min. In advanced oxidation reactions other than Fenton, hydroxyl radical produces continuously. However, in Fenton method, high production of hydroxyl radical occurs in the first few minutes of the reaction [29]. Therefore, according to the figure, increasing time more than 15 minutes did not significantly affect SCOD, VSS and TSS removal rates. Tony et al. showed that Fenton method rapidly oxidizes part of the organic matter in the sludge flak and increases sludge dewatering capacity at low reaction time [13]. Mo et al. also showed that the Fenton reaction time can be reduced to 5 minutes [12].

**Fig. 1:** The effect of pH on removal of SCOD, VSS, and TSS and reduction of sludge SRF (at retention time= 30 minutes, Fe2+= 0.03 mol/l and hydrogen peroxide= 0.058 mol/l).

**Fig. 2:** The effect of time on removal of SCOD, VSS, and TSS and reduction of sludge SRF (pH=5, Fe2+=0.03 mol/l and hydrogen peroxide= 0.058 mol/l).

**The effect of H2O2:**

Figure 3 (a and b) indicates the effect of different concentrations of H2O2 on the removal of SCOD, VSS, and TSS, at pH 3 and 5, Fe2+=0.03 mol/l and
t=15 minutes. As Fig. 3a shows, removal efficiency increased with an increase in hydrogen peroxide dose. The highest removal efficiency occurred at a hydrogen peroxide dose of 0.12 mol/l, but higher doses of H$_2$O$_2$ did not have a significant effect on the removal efficiency. Fenton process produced active hydroxyl radicals which attack and destroy organic matters. The amount of H$_2$O$_2$ directly affects the hydroxyl radical production and plays a critical role in sludge dewatering [7, 23, 30]. Thus, when H$_2$O$_2$ concentrations increased from 0.015 to 0.12 mol/l, the removal rate of SCOD, HPC, TSS and VSS from the sludge refined by Fenton reached 55, 84, 29 and 31 percent respectively and sludge dewatering increased to 96.72 percent. As showed in Fig. 3a, the lower SRF indicated the higher sludge dewaterability. At the beginning, the SRF decreased obviously with the increase in H$_2$O$_2$ dosage, but later there was no significant change. The minimum SRF was achieved at the H$_2$O$_2$ dosage of 0.12 mol/L. Thus, the sludge became easy to be dewatered at the H$_2$O$_2$ dosage of 0.12 mol/L. At high levels of hydrogen peroxide, due to consumption of hydroxyl radicals, the removal efficiency decreased based on reactions 1 and 2[31].

\[ \text{OH}^\cdot + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^\cdot + \text{H}_2\text{O} \]  
\[ \text{OH}^\cdot + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \]  

Thus, even when the H$_2$O$_2$ dose increases, as the Fenton reaction reaches an equilibrium, the Fenton oxidation efficiency remains unchanged [32]. Also, when OH increases, Fe$^{2+}$ converts into Fe(OH)$_2$, while the high concentration of H$^+$ prevents the formation of FeOOH$^{2+}$ and OH. This reduces Fe$^{2+}$ concentration resulting in decreased Fenton oxidation efficiency [32, 33]. An important factor in sludge stabilization is reducing the amount of microorganisms. To this end, Heterotrophic bacteria (HPC) were used. As showed in Fig. 3, the HPC removal rate increases with increasing doses of hydrogen peroxide so that at the level of 0.18 mol/l hydrogen peroxide, the removal rate is 83%. This can be attributed to the reaction of free hydroxyl radicals with structural particles of the cells and damage to biological structures. These findings are consistent with that of Debowksi et al. study on using Fenton for raw sludge disinfection [34].

The effect of Fe$^{2+}$ on sludge stabilization and dewatering

Fig. 4 shows the effect of different concentrations of Fe$^{2+}$ on the removal of SCOD, VSS, TSS and reduction of SRF. As showed in this figure, the highest removal efficiency of VSS, TSS and SCOD was 41, 42 and 61 percent respectively and occurred in Fe$^{2+}$ concentration of 0.05 mol/l. SRF also reduced by 99.48 percent. But, beyond this concentration, Fe$^{2+}$ concentration had no effect on removal efficiency. The concentration of Fe$^{2+}$ ions has a significant effect on the efficiency of the Fenton process. In the absence of Fe$^{2+}$ ions, hydroxyl radicals are not formed; therefore, the concentration of Fe$^{2+}$ ions increases the production of hydroxyl radicals and causes clotting [35]. In addition, Fe$^{2+}$ acts as a catalyst in Fenton reaction that leads to production of more hydroxyl radicals. Organic material of microorganisms and minerals in the sludge prevents the Fenton oxidation cycle; therefore, enough amount of Fe$^{2+}$ is required for the reaction [32].

In technical applications usually iron in fewer concentrations is used than H$_2$O$_2$ to prevent the formation of large amounts of iron sludge [36]. At the H$_2$O$_2$/ Fe$^{2+}$ ratio of 2.26, sludge dewatering reaches the highest value, but did not change significantly beyond that level. Buyukkamaci et al. found H$_2$O$_2$ / Fe$^{2+}$ ratio of 1.2 as the optimum ratio in Fenton process[11]. When Fe$^{2+}$ is more than H$_2$O$_2$, Fenton reagent is most inclined to chemical flocculation after oxidation. Therefore, improvement in sludge dewatering is mainly attributed to chemical flocculation [12]. On the other hand, based on reaction 3, excessive Fe$^{2+}$ leads to consumption of hydroxyl radicals which reduce the removal efficiency [37]. However, H$_2$O$_2$ dose is the most important factor affecting the decomposition of EPC and microbial cells.

\[ \text{OH}^\cdot + \text{Fe}^{2+} \rightarrow \text{Fe}^{2+} + \text{OH}^- \]  

a
Removal TSS(%)  
Removal VSS(%)  
Reduction of SR(%)  
Removal SCOD(%)  
Removal Efficiency(%)  
H2O2(mol/l)  
b

Fig. 3: The effect of different concentrations of H2O2 on removal of SCOD, VSS, and TSS and reduction of sludge SRF (a: pH = 5 and b: pH = 3, Fe2⁺ = 0.03 mol/l and t = 15 min).

CONCLUSION
In this study, simultaneous dewaterability and stabilization of wastewater sludge via Fenton was investigated. The results showed that sludge dewatering significantly improved in lower reaction times. Under optimal conditions of pH=5, reaction time=15 minutes, and H2O2 and Fe2⁺ concentrations of 0.12 and 0.05 mol/l, SRF reduced by 99%. Thus, according to the results, we can say that since the Fenton process acted as an antioxidant and anticoagulant and destructed extracellular polymers, was effective in sludge dewatering and could significantly increase removal of microorganisms (84%) and stabilization of organic matter (40-60 percent). However, it is recommended that further studies be carried out to find more economical methods and compare them with the biological methods.

ETHICAL ISSUE
In this study, Shiraz University of Medical Sciences ethics committee approved the study protocol and researches explained all procedures and requirements to participants. They voluntarily signed a consent form before enrolling in the study.

COMPETING INTEREST
Authors of this manuscript declare that we have no significant competing interests that might have influenced the performance of the work described in this manuscript.

Funding/support
This study was financially supported (No 7331) by the Deputy of Research and Technology of Shiraz University of Medical Sciences.

AUTHORS’ CONTRIBUTIONS
All authors equally help to write this manuscript.

ACKNOWLEDGEMENTS
The authors would like to appreciate the Deputy of the Research and Technology of Shiraz University of Medical Sciences for its financial support for the research project of (No 7331).

REFERENCES