Leaching Zn, Cd, Pb, and Cu from Wastewater Sludge Using Fenton Process

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Abstract

Background: High amount of heavy metals in sludge is one of the major obstacles to its use on farms. The present study aimed to investigate the possibility of leaching heavy metals from wastewater sludge by Fenton method and determine the optimum level of parameters, such as iron, hydrogen peroxide, time, and pH for Fenton reaction.

Methods: The effects of various parameters, such as pH (2-9), hydrogen peroxide concentration (0.5-6 g/l), Fe concentration (0.5-4 g/l), and leaching time (5-60 min), were studied.

Results: The results showed that the optimal condition for leaching of heavy metals occurred at pH of 2-3, hydrogen peroxide concentration of 3 g/l, iron concentration of 2 g/l, and leaching time of 15 min. Under these optimal conditions, 92% of Zn, 100% of Cd, 100% of Pb, and 80% of Cu were leached from the wastewater sludge.

Conclusions: Fenton method can leach heavy metals from wastewater sludge through decomposition of organic materials at H_2O_2/Fe ratio of 1.5:2.

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Introduction

The methods used for wastewater treatment produce high amounts of sludge that need to be disposed of. One of the main methods for disposal of wastewater sludge is to recycle its valuable materials (N, P, organic matter, etc.) to be used on farms. However, the presence of large amounts of heavy metals in the sludge is one of the major obstacles to its application in the field of agriculture.[1] Large quantities of these metals negatively affect ecosystems and human health.[2] As a result, safe disposal of heavy metals from wastewater sludge is essential.

Up to now, several techniques have been used for removal and recovery of heavy metals from wastewater sludge, including chemical precipitation, electrochemical methods, ion-exchange, and membrane filtration.[3] Most chemical methods are based on using organic and inorganic acids to dissolve metals. Chelating agents, such as EDTA, and inorganic chemicals, like $FeCl_3$, are also used for this purpose.[4] In the recent years, in an attempt to improve sludge conditions, advanced oxidation methods have been used, including sludge dewatering and removing the organic content from the sludge, leading to release of heavy metals from the sludge clots. Among various processes of advanced oxidation, Fenton process is recommended because of its low leaching time, use of coagulation and flocculation, producing non-toxic compounds, and the possibility of being used in various scales.[5] Pretreatment by Fenton reduces the amount of sludge, increases the bio-degradability of biological sludge, and can lead to a decrease in volatile solids.[6,7]

Yi Zhu and colleagues carried out a study to explore the possibility of combining bioleaching and Fenton reaction. The results showed that using Fenton reaction for bioleached sludge decreased Zn, Cu, Pb, and Cd by 75.3%, 72.6%, 34.5%, and 65.4%, respectively.[8] Fu and colleagues also found that Fenton process was effective in removal of nickel from wastewater (98%).[9] Moreover, Zeng and colleagues combined biological and Fenton-like method and removed 99% of Cd, 39% of Pb, and 70% of Cu and Zn.[10] In another study by Raf Dewil and colleagues., thermal acid hydrolysis decreased the content of heavy metals, except for Cu, Hg, and Pb in the sludge layer.[11]

The present study aimed to investigate the possibility of leaching heavy metals, including Zn, Cd, Pb, and Cu, from wastewater sludge by Fenton method and determine the optimal parameters for this reaction.

Methods

Samples of Wastewater Sludge

This study was carried out at the main laboratory of environmental sciences at Shiraz University of Medical Sciences in 2014. It was conducted using an experimental method at the laboratory scale. Random samples were taken from the wastewater treatment plant in Shiraz for testing once a week for 12 weeks. The sludge sample used in this study was taken from Shiraz wastewater treatment plant and was a 50:50 combination of primary and secondary sludge. Wastewater sludge samples were stored in closed polyethylene containers at 4 °C until use. To investigate the effects of different parameters on the removal efficiency, at each stage, one of the parameters was changed and the others were kept constant. The experiments were conducted twice, and the results are the average of these twice independent trials. The results were analyzed statistically using Excel software.

Treatment with Fenton Method

In Fenton test, 30% hydrogen peroxide and $FeSO_4.7H_2O$ was used. Besides, H_2SO_4 and NaOH (1 N) were used to adjust the pH. Moreover, heavy metals stock solution (manufactured by Merck, Germany) was used to provide the standards of Zn, Cd, Pb, and Cu.

At all stages, 100-ml samples of wastewater sludge in 250-ml flasks were used. The effects of various parameters, such as pH (2-9), hydrogen peroxide concentration (0.5-6 g/l), Fe concentration (0.5-4 g/l), and leaching time (5-60 min), were studied. To investigate the effects of different parameters on the removal efficiency, at each stage, one of the parameters was changed and the others were kept constant. The samples were mixed using a shaker at 200 RPM. The samples were then dewatered using a Buchner pump and the remaining layer on the filter paper was dried in the oven at 105°C.

Analysis

The dried samples were first turned into powder. Next, 250 mg of the sample (dry weight) was weighed and added to the furnace. Afterwards, 4 ml of 96% sulfuric acid was added to the sample and the mixture was heated to 200 °C. When all the water was evaporated and the color became brown, 1 ml of 30% hydrogen peroxide was added to the mixture. In case of browning of the digestion mixture, hydrogen peroxide was added again until a colorless mixture was obtained. After cooling of the crucible, the volume of the remaining mixture was increased to 100 ml by adding distilled water and some of the digested sample was taken for determining heavy metals. Polarography (Metrohm) and analysis method No. 113/2 e were used to measure heavy metals (digestion and analysis methods were based on Application Bulletin No. 113/2 e).[12] Gravimetric method was used to measure the percentage of solids and pH meter and EC meter were used to measure pH and EC, respectively (Metrohm).

Results and Discussion

Samples were taken from the wastewater treatment plant in Shiraz for testing once a week for 12 weeks. The characteristics of the used sludge are presented in Table 1 and the amounts of heavy metals in the raw sludge are displayed in Table 2.

The Effect of pH

One of the main factors affecting the efficiency of Fenton process is pH. It plays an important role in controlling the activity of the oxidizing agent and the substrate, formation of iron species, and hydrogen peroxide stability. pH also affects hydroxyl radicals production and, therefore, influences the efficiency

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

Parameters	Unit	Minimum	Mean	Maximum
EC	Ms/cm	3.04	3.48	3.86
pH	----	5.3	5.94	6.74
Solids in sludge	٪	1.93	2.52	2.98

Table 2: The amounts of heavy metals in the raw sludge

Metal type Item	Zn mg/kg	Cd mg/kg	Pb mg/kg	Cu mg/kg
Minimum	2646.4	0	84.8	412
Mean	4908.2	48.9	291.6	821.6
Maximum	7481.6	183.6	564	1407.2

of oxidation.[13-15] As shown in Figure 1, the highest removal efficiency of heavy metals was observed at pH of 2 and 3. At pH 2, the leaching efficiency of Zn, Cd, Pb, and Cu was 96.7%, 100%, 64.8%, and 70.18%, respectively. At pH 3, the removal efficiency of these metals was 94.4%, 100%, 41.2%, and 82.8%, respectively. Thus, increasing pH significantly reduced the removal efficiency. According to Figure 1, at pH of 9, the leaching efficiency of Zn, Cd, Pb, and Cu was 43.2%, 70.6%, 4.8%, and 20%, respectively. At low levels of pH, iron forms a stable complex with H_2O_2, which neutralizes the iron catalyst and significantly reduces oxidation efficiency.[16] At alkaline pH, Fe^{+2} changes into Fe^{+3} and deposits as $Fe(OH)_3$, which exits the catalytic cycle. As a result, sufficient catalyst does not remain in the environment. This causes degradation of H_2O_2 and reduces the efficiency of the process.[5] Also, studies have shown that oxidative potential of OH radicals decreases with increasing pH.[17] According to Figure 1, leaching of Pb was less than that of other metals. The reason is that although oxidation may speed up decomposition of organic matter (because Pb in inclined to organic matters) and dissolution of sulphides (e.g. sulphates), the released Pb can be re-deposited in the form of sulfate, Pb carbonate, or lead absorbed by iron oxides or manganese.[11]

The Effect of Iron Concentration

Iron ions affect the efficiency of the Fenton process. Without iron ions, hydroxyl radicals are not formed. The concentration of iron ions is effective in reducing metals both in terms of increasing the production of hydroxyl radicals and helping the occurrence of coagulation.[5] In samples with low iron content in the raw sludge, when no iron is added along with the peroxide, dissolution of metals is very low in the Fenton method.[18] Based on Figure 2, at the iron concentration of 2 g/l, the leaching efficiency of Zn, Cd, Pb, and Cu was 91%, 99.3%, 100%, and 78.3%, respectively. With increasing the iron content up to 4 g/l, the leaching efficiency of these metals changed into 88%, 100%, 100%, and 70.6%, respectively. Based on Reaction 1, adding too much Fe^{2+} leads to consumption of hydroxyl radicals reduces the efficiency of the process.

Reaction 1: $OH^0+Fe^{+2}\rightarrow Fe^{+3}+OH^-$

In technical applications, the concentration of iron ions is kept less than that of H_2O_2 to prevent formation of large amounts of iron sludge.[19] Andrews found that an iron/hydrogen peroxide ratio of 1:4 was required for removing more than 70% of Cu and Zn from raw sludge.[18]

One limitation of the Fenton method is related to iron concentration in sludge after treatment with Fenton process. The results of the present study showed that the remaining iron after treatment with Fenton method was about 15164 mg/kg, which exceeded the allowed amount of iron for use on farms (11000 mg/kg).

The Effect of H_2O_2 Concentration

The effect of hydrogen peroxide concentration at leaching times of 15 and 30 min is shown in Figure 3 (a, b). As the Figure depicts, increasing H_2O_2 concentration increased heavy metals' leaching efficiency. This can be attributed to the increase in the amount of hydroxyl radicals. According to Figure 3a, the removal efficiency of Zn, Cd, Pb, and Cu in H_2O_2 concentration of 3 g/l was 91.6%, 100%, 100%, and 80%, respectively. Also, increasing the concentration

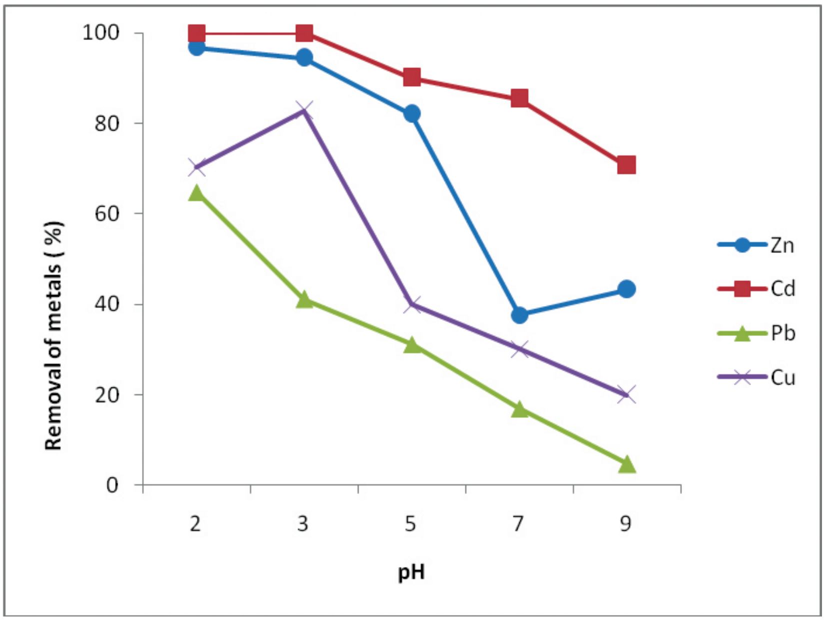

Figure 1: The effect of pH on the removal of Zn, Cu, Pb, and Cd from wastewater sludge (Fe=1 g/l, H_2O_2=2 g/l, and t=30 min)

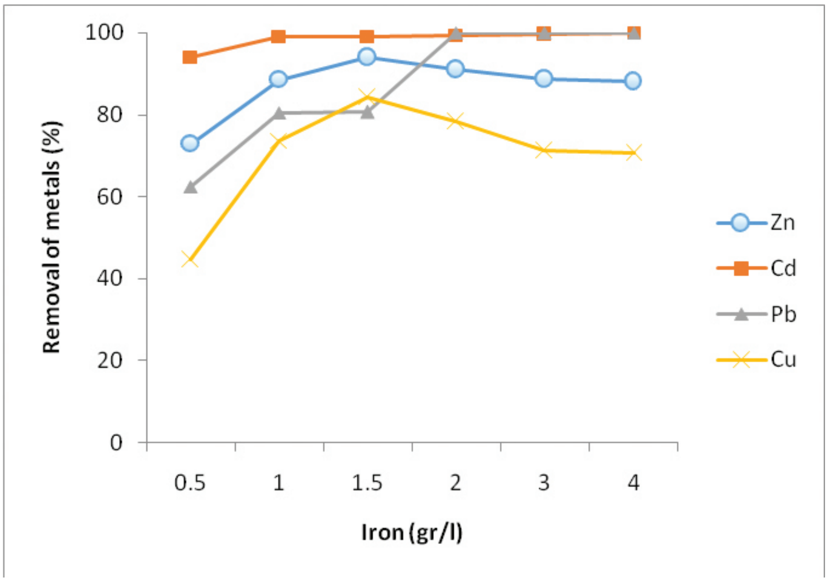

Figure 2: The optimal concentration of Fe for removal of Zn, Cu, Pb, and Cd from the sludge (pH=3, H_2O_2=2 g/l, t=15 min)

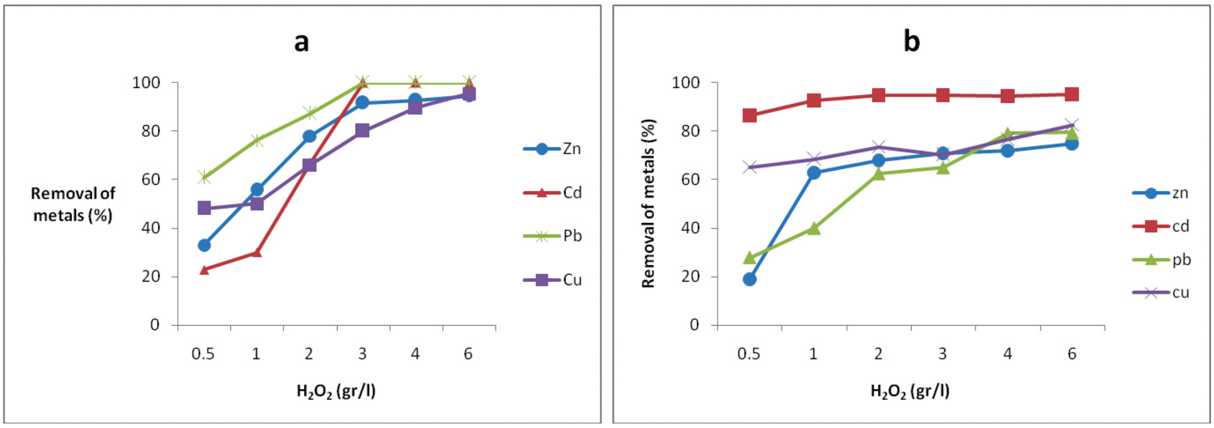

Figure 3: The optimal H_2O_2 concentration for removal of Zn, Cu, Pb, and Cd from wastewater sludge (a: pH=3, Fe=2 g/l, t=15 minutes and b: pH=3, Fe=2 g/l, t=30 minutes)

of hydrogen peroxide to 3 g/l increased the leaching of metals. However, no significant change occurred in the leaching efficiency beyond this concentration. This is due to decomposition of H_2O_2 to oxygen and water and combination of hydroxyl radicals, which prevent formation of hydroxyl radicals.[20,21] Additionally, since a high concentration of hydroxyl radicals is produced in the first few min of Fenton reaction, at constant H_2O_2, increasing the leaching time from 15 to 30 min had no effect on leaching of metals. Increasing the leaching time in small quantities of hydrogen peroxide can cause metals to enter the solid phase from the solution phase. Fenton method at H_2O_2/Fe ratio of 1.5:2 can significantly leach heavy metals from wastewater sludge through decomposition of organic materials. Wong's study suggested that the efficiency of Cu and Pb emissions increased rapidly with increasing the concentration of H_2O_2 up to 0.2 M. Besides, Cd had the highest emissions at H_2O_2 concentration of 0.1 M.[22] Furthermore, Zang suggested 5 g/l as the optimal concentration of heavy metals. His results showed that H_2O_2 concentration did not have a significant impact on metal removal.[8] According to Figure 3, Cu leach rate increased rapidly in the presence of hydrogen peroxide. In fact, by increasing the H_2O_2 concentration from 0.5 to 6 g/l, Cu removal efficiency increased from 48% to 95.5%. Cu has a great affinity to organic matters and is released when Fenton breaks the organic matters down. Cu is mostly present in sulfide parts of the sludge, which have strong connections with organic materials. In the activated sludge, Cu is connected to extracellular polymeric materials that contain a large number of complex organic positions. Degradation of extracellular polymeric materials by Fenton agent helps one to wash some of the connected Cu. Cu removal also occurs through degradation of extracellular polymeric materials, contributing to sludge dewatering.[18,23]

Zn leaching efficiency increased by increasing the hydrogen peroxide concentration in such a way that by increasing the concentration from 0.5 to 6 g/l, Zn leaching efficiency increased from 33% to 94.6%. At higher Zn amounts in the carbonate phase, its leaching rate increased because it entered the aqueous phase at pH 3.[24] The Fenton method increased decomposition of organic matters; therefore, the ions were combined with sludge clots. Oxidation also changed the insoluble sulfide to soluble sulfate.

Studies have indicated that Cd in solutions is dominant in the form of free cation, which does not have a strong link with organic matters. Thus, Cd is leached from the sludge relatively easily.[18] In the current study, the concentrations of Cd and Pb in the sludge were less than those of Zn and Cu. Thus, by addition of 2 g/l hydrogen peroxide, the concentrations of these two metals reached a level undetectable by the device. Although Pb is often present in the form of Pb (II) or Pb (IV), which have affinity to organic matters,[18] and oxidation can increase decomposition of organic matters and dissolution of sulphides (e.g. sulphates), the released Pb can be re-deposited in the form of sulfate, Pb carbonate, or lead absorbed by iron oxides or manganese.[11]

The Effect of Leaching Time

Oxidation time is one of the parameters affecting the Fenton process efficiency. To determine the best time and its impact on the Fenton process, the tests were conducted at different times from 5 to 60 min. The effect of various leaching times on the leaching efficiency of the metals has been presented in Figure 4. At 15 min, the leaching efficiency of Zn, Cd, Pb, and Cu was 84.3%, 95.2%, 67.3%, and 77.7%, respectively. In advanced oxidation reactions other than Fenton, hydroxyl radical is produced continuously. In Fenton method, however, high production of hydroxyl radicals occurs in the first few minutes of the reaction. As Figure 4 depicts, the highest leaching efficiency of Zn, Cd, and Cu occurred at reaction time of 15 minutes. Only the removal efficiency of Pb increased with increase in leaching time. This can be attributed to its high initial concentration in the raw sludge (in the tests of time, greater amounts of Pb were observed in the raw sludge samples compared to other samples) as well as its lower mobility compared to the other metals.[24]

At optimal conditions, 92% of Zn, 100% of Cd, 100% of Pb, and 80% of Cu were leached from wastewater sludge. After treatment with Fenton method, the amounts of Cd and Pb reached an undetectable range. In addition, the remaining amounts of Zn and Cu in the sludge were respectively 359 and 188.5 mg/kg, which is suitable for use on farms. However, the iron content was higher than the allowed level and smaller amounts of sludge have to be used for agricultural purposes. The maximum limits for heavy metals recommended by Environmental Protocol Agency (EPA) are shown in Table 3.[25]

Table 3: The EPA's recommended maximum limits for heavy metals

Heavy metal	Concentrations (mg/kg)
Cd	39
Cu	1500
Pb	300
Zn	2800
Iron	11000

Conclusions

The present study investigated the effect of Fenton method on leaching of heavy metals from wastewater sludge. The optimum condition occurred at pH of 2-3, hydrogen peroxide concentration of 3 g/l, iron concentration of 2 g/l, and reaction time of 15 min. Increasing the leaching time in this method showed no significant effect on leaching of the metals, except for Pb. This can be attributed to lower mobility of Pb compared to the other

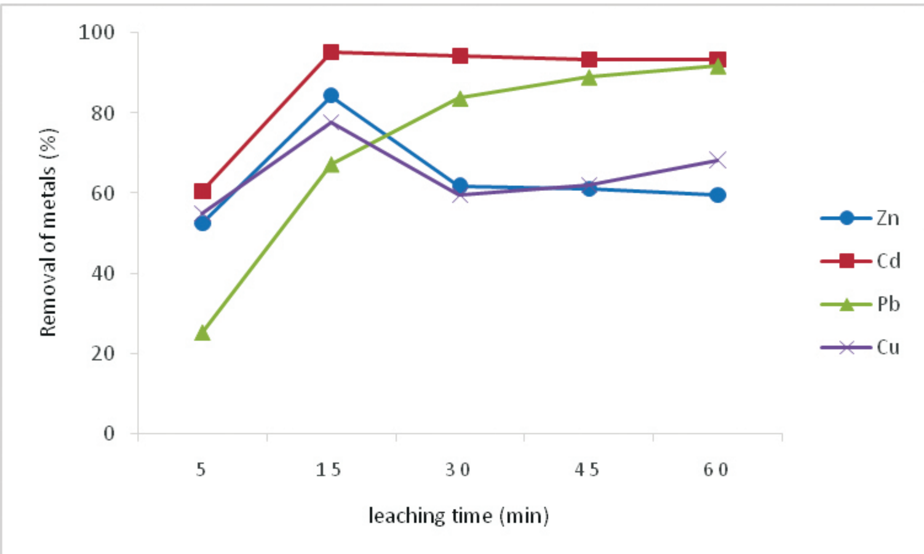

Figure 4: The optimal reaction time for removal of Zn, Cu, Pb, and Cd from wastewater sludge (H_2O_2=4 g/l, PH=3, and Fe=2 g/l)

metals. After treatment with Fenton, the amount of Cd and Pb reached an undetectable range. Additionally, the remaining amounts of Zn and Cu in the sludge were respectively 359 and 188.5 mg/kg, which were within the EPA standards for disposal on farms. However, the iron concentration in the sludge exceeded the allowed level. Combining this method with bioleaching techniques can help reduce iron in the sludge.

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Conflict of Interest: None declared.

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