Investigation of heavy metal (lead) removal from aqueous solution by using advanced oxidation process (Fenton)

Abstract:

Background and Aim: Undoubtedly, controlling the maximum entry of heavy metals into the food is one of measures which should be taken into account in order to maintain the food consumers' health and achieve the food safety. The sensitivity and importance of this issue are doubled due to the irreparable, acute and chronic complications of heavy metals which are classified according to the effects on the nervous system until the carcinogenesis in the human body. On the other hand, this issue is significantly important since these metals differently enter to crops such as tea, water, and rice and generally the food and beverage that are widely consumed. Therefore, the aim of this study is to remove heavy lead metal from aqueous solution by Fenton method. This study is an experimental study. The samples are synthesized in a collection of laboratories at the Faculty of Health, and the pH parameters, contact time and lead elimination rate and the optimal Fenton ratio are investigated. Results are analyzed using SPSS software and Charts are plotted by excel. The results showed that the best pH for removal of lead 5 and its best concentration is 30 mg/ L, and the optimal Fenton ratio is 1 to 5, as well as the best contact time for removal of lead from aqueous media for 10 minutes. The present study showed that the pH factor, contact time, Fenton concentration and lead in all four were effective in removing lead from aquatic solution.

Keywords: Heavy metals, Lead, Fenton, Water Solutions

Introduction:

When an allowed amount of wastewater containing heavy metals enters into the environment, they are condensed under the influence of physical, chemical and microbial factors and pollute the underground and surface water [1]. Heavy metals constitute a group of metals which have different chemical and biological properties. This group of metals has specific weights greater than 5 grams per cubic centimeter. They cannot be easily decomposed in the environment, and they cause severe disorders and illnesses by accumulation in living organisms [2]. Heavy metals are put in the group of the first grade toxic pollutants [3]. Lead is applicable in the battery manufacturing industry (waste), water tanks, roof coatings, production of metal wires, weapon and ammunition manufacturing, welding, soldering, crystal production, paintings, food industry, pesticides and petroleum production industry [3,4]. Lead is very toxic and causes diseases such as Anemia, hepatitis and kidney syndrome in the case of entry to water (drinking). Lead causes abortion and premature births [5]. Heavy metals tend to accumulate in the food chain; hence, they can seriously threaten the animal and plant life [6]. The World Health Organization (WHO) recommended the standard amount of lead equal to 0.01 mg per liter in drinking water [7, 8]. Various methods have been offered for removing heavy metals from aqueous media including chemical deposition, Ion exchange, membrane processes, evaporation, and other processes [9, 10]. Given the population and industry growth, the uncontrolled increase in use of underground water is one of the basic needs of society. Both the increasing agricultural activities and the lack of attention to environmental standards have led to the entry of most pollutants into the water sources, but the treatment of this water is expensive and requires advanced equipment [11]. In recent years, the advanced oxidation processes such as ozonation, Ultrasound and Fenton oxidation are introduced for treating wastewater containing non-biodegradable materials as well as wastewater with high concentrations of pollutants [12, 13]. Fenton process is one of the most effective processes for removal of pollutants due to the advantages such as high oxidation capacity, rapid oxidation, cost effectiveness, material transferability, and production of toxic and hazardous by-products in comparison with other methods, as well as reduced energy consumption due to the catalytic properties of iron [14, 15]. Disadvantages of Fenton method include the production of color, deposition and clogged pores of facilities [15]. In Fenton process, iron ions, especially ferrous ion, produce hydroxyl radicals due to their catalyst roles in an acidic medium and reaction with hydrogen peroxide [15]. Different studies have been conducted on the role of Fenton in removing metals and elements. For instance, Nakhzari-Moghadam et al studied the removal of Cadmium by Fenton and found that the removal percentage of Cadmium was 75% [16]. Wang et al reduced the amount of LAS in detergent factory wastewater to less than 5mg/l through pretreatment with Fenton oxidation and biological treatment [17]. The aim of this study was to determine the optimum conditions for Fenton removal in lead by studying the effect of various parameters such as pH, H_2O_2 on Fe, contact time and various concentrations of lead.

Method and Material:

This is an experimental study that was conducted to remove lead from aqueous solutions. The needed water samples prepared synthetically and the required tests were done instead of the method of work, accuracy and accuracy according to standard methods for water tests. In this study, the stockok solution is prepared using a lead acetate compound. And appropriate solutions were prepared using these solutions. In this study, a solution of H_2O_2 with a weight percent of 35%, a volumetric mass of 1.31 kg / l and iron sulfate ($FeSO_4$, 7 H_2O_2) was used. This test has 4 variables (Fenton concentration, lead concentration, amount, and duration of contact) and the percentage of deletion of each of the variables was determined in this experiment. It should be noted that each of the tests mentioned above was repeated 3 times. The concentration of lead in the initial solutions and analyzed by the spectrophotometer 5000-DR was measured. And used for drawing charts from Excel software.

Step 1: **Determine optimal lead concentration:** The concentration of lead in the range of 10, 15, 20, 25 and 30 mg /l, pH rang was 3, 5, 7 and 12, H_2O_2: Fe ratio was between 1: 1 and 1:10, and the contact time was 5 to 30 minutes. In the first part, the average value of each of these variables was considered constant (to obtain the optimal parameter value). This means that the lead content was 20 mg, pH = 7, H_2O_2: $FeSO_4$ ratio was 1: 5, and the contact time was 20 minutes. In the first step, different concentrations of lead (10, 15, 20, 25, 30 mg / L) and time, PH, and constant time were assumed and each of the time variables, pH, and the Fenton ratio are considered to be mid-range. After preparation of the samples are stirred with around 300 RPM. The numbers obtained are plotted on the chart, which is derived from the plotting of the percentage of optimal lead elimination.

Step 2: Determine of optimal pH: In the second step, pH varies. At this stage, the optimum lead concentration was assumed to be constant (as defined in the previous step) and adjusted their pH to 3, 5, 7 and 12 using acid and open solutions (NaoH and Hcl). And the Fenton A ratio and the duration as in the previous step are constant. Finally, the specimens are placed on the spectrophotometer and the results are read.

Step 3: Determine the optimal Fenton ratio: At this stage, using the previous experiments (lead concentration and pH specified in the previous steps), at this stage, the optimal Fenton ratio is determined in the range of 1/1, 1/5 and 1/7 and 1/10.

Step Four: Determine the optimal call time: In the final stage, the contact time is optimized**.** In this way, the concentration of lead, pH and Fenton ratios increased from previous experiments and performed at 5, 10, 15, 20, 25 minutes, and the results were read by spectrophotometry. Finally, finally, using the obtained results, the diagrams are plotted.

Finding:

Efficiency of the Fenton Process Depending on the various pollutants, pH, hydrogen peroxide concentrations, ferrite ion concentration, and initial concentrations of the pollutant are relevant [15]. In this study, the effects of pH parameters, lead concentration, H_2O_2 to Fe ratio and contact time on the efficiency of the Fenton process were tested. Figure 1 shows the percentage of optimal lead elimination by the Fenton process. This graph shows that the percentage of lead elimination by increases with increasing concentrations and the highest percentage of lead elimination at 30 mg /l. The highest percentage of lead removal was observed at a concentration of 30 mg /l in about 90%. Figure 2 shows the effects of pH changes on the removal of lead from aqueous solutions. This graph shows that with increasing pH in the solution, the percentage of elimination lead decreases. On the other hand, the highest percentage of lead removal occurs at pH 5 and the lowest percentage of lead removal at pH 12 was observed at 40%. Figure 3 shows the Fenton's ratio of lead elimination. This figure shows that by increasing the proportion of H_2O_2: FeSO4, the removal rate of lead decreases. In addition, the maximum percentage removal of lead in the 1:5 ranges of H_2O_2: FeSO4 ratio was 70%. Figure 4 shows the effects of contact time on lead elimination in aqueous solutions. In this figure, it was observed that with increasing contact time, the percentage of lead elimination increased to ten minutes and then decreased. Also, the analysis of this figure showed that reducing the efficiency at lower oxidation times is more than longer oxidation time.

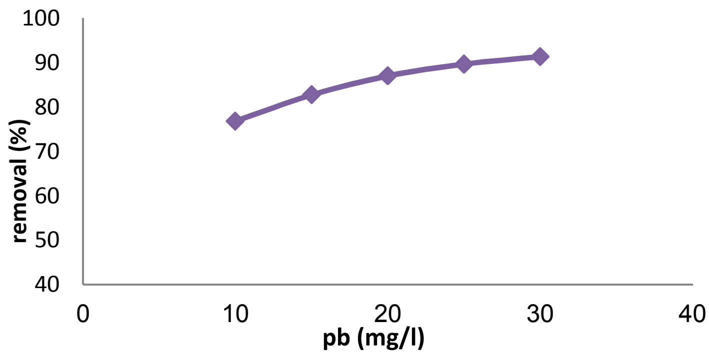


Figure1: The effect of primary concentration on lead elimination by the advanced Fenton oxidation process.

pH=7, T=20 MIN, $_{H2O2}$/Fe=1/5

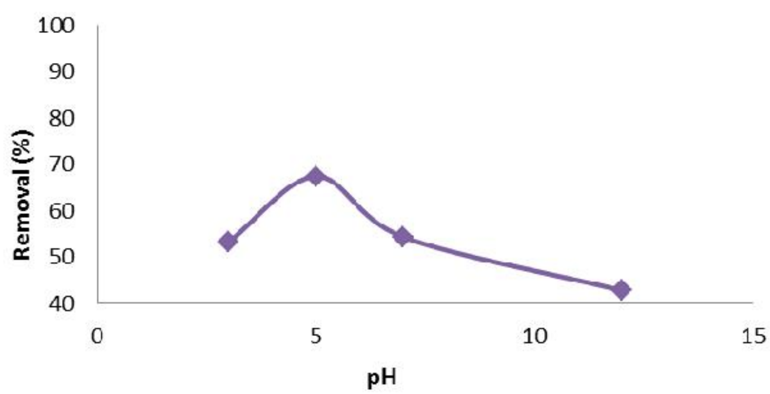
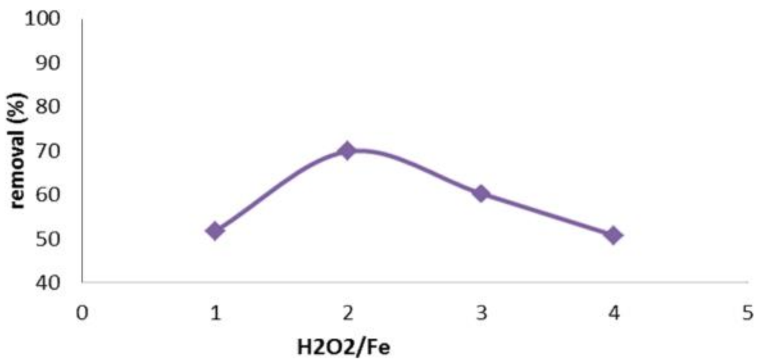


Figure2: The effect of pH on lead elimination by the advanced Fenton oxidation process

H_2O_2/Fe=1/5, T=5Min, Pb Concentration=30



Figurer3: The effect of H_2O_2 / Fe ratio on lead elimination from aquatic environments by advanced oxidation process.

pH=5,T=5 min, pb concentration=30

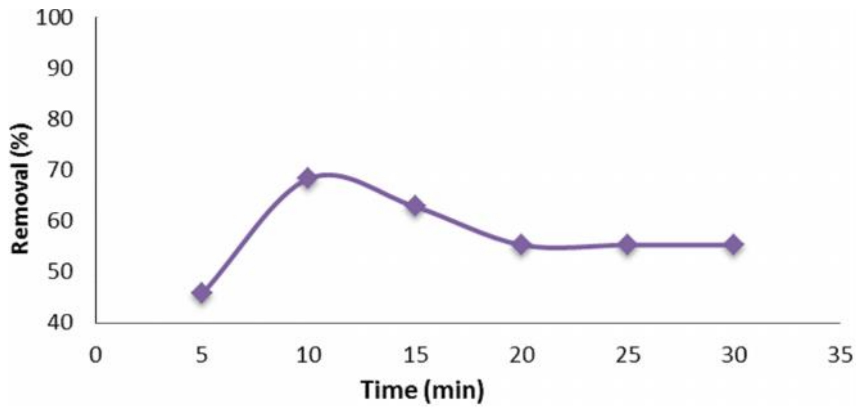


Figure4: The effect of time on the removal of lead from aquatic environments by the advanced Fenton oxidation process

pH=5 , H_2O_2/Fe=1/5,Pb concentration=30

Result:

Removal of heavy metals including lead with Fenton process is affected by various factors such as oxidant concentration, catalyst, contaminant concentration, pH and reaction time. These factors play a significant role in radical hydroxyl production and Fenton process efficiency. These factors have a great influence on the production of hydroxyl radicals and the efficiency of the Fenton process. Higher pH results in reduced radical hydroxyl production, rapid decomposition of H_2O_2 into water and oxygen. Higher pH results in reduced radical hydroxyl production, rapid decomposition of H_2O_2 into water and oxygen, and Fe^{2+} sedimentation with Fe^{3+} formation, and prolonged contact times increase the cost of treatment. In general, the lead elimination rate in this experiment is 79%. As a result, this method, along with low pH, is an effective way to remove lead from aqueous solutions.

Discussion and conclusion:

Effect of optimal lead concentration:

The diagram of effect of optimum lead concentration indicates that an increase in the concentration of Lead increases the percentage of Lead. The highest percentage of Lead removal (90%) occurs in the concentration of30 mg/l. numerous studies have investigated the effect of increasing the initial concentration of pollutants on the efficiency and potential of Fenton process performance. For instance, according to Al-Ananzeh et al's study entitled "A study on the advanced oxidation processes", due to the increased concentrations of pollutants, they react with hydrogen peroxide and reduce the effect of hydrogen peroxide; hence, increasing the initial concentration of a target pollutant in the early stages of oxidation leads to the lower removal efficiency [18]. As shown in Figure 1 of the present study, Lead removal efficiency was increased from 10 to 30 mg/l according to the constant parameters (pH, time and H_2O_2/Fe). Therefore, the concentration of 30 mg/l was selected as the appropriate concentration of test at this stage.

Effect of optimal pH:

The effect of pH was measured for samples based on the Lead removal mechanism and its role in the environment. pH is one of the most important variables in removal of metals and elements. We measured the effect of pH at the ranges of 3, 5, 7, and 12. According to the examined effect of pH on Lead removal efficiency by Fenton, the best Lead removal efficiency occurred at pH=5 in which the percentage of removal was about 69% (Figure 2). At higher pH, the removal efficiency was reduced to 40%. Fenton process properly occurred in acidic conditions due to the complete solubility of Iron ion (Fe^{2+}) and stability of H_2O_2 and Fe^{2+} [19]. The highest percentage of Lead removal in acidic conditions may be due to an increase in the maximum amount of dissolved hydroxyl ions in water in this situation. The hydroxyl radical is formed in this case [20]. Therefore, pH=5 is determined as the optimal pH in this test. In Fenton reaction, hydroxyl radical acts as the main oxidizing agent. On the other hand, the lowest removal percentage may be due to the low exchange between Pb and OH. It should be noted that the low pH results in the production of a good amount of hydroxyl radical. In addition, the lower removal percentage in higher pH may be due to the formation of Ferrous and Ferric hydroxyls which reduce the production of hydroxyl radical in a reaction [21]. Meijuan et al obtained the similar results in this regard [22].

The effect of Fenton:

The present study investigated various effects at the range of 1:1 to 1:10. According to the diagram of Figure 3, an increase in the ratio of Fenton leads to the reduced Lead removal percentage in all ratios except for the ratio of 1:5. In other words, the removal percentages of ratios of 1:10 and 1:7 of H_2O_2:Fe at contact time of 20 minutes were equal to 60.1%, and 50.28% respectively. In Lead removal at high ratios of H_2O_2:Fe, as the produced hydroxyl radicals are not enough to remove Lead from the solution, the hydroxyl ion appears as the sediment. Therefore, the ratio of 1:5 of H_2O_2:Fe has the highest Lead removal percentage, and thus it is selected as the optimal ratio.

The effect of Time:

We studied the effect of another parameter on Lead removal at contact time within the range of 5-30 minutes in lead concentration of 30mg/l, pH=5 and ratio of H_2O_2: Fe= 1:5. Figure 4 shows the Lead removal percentage at contact time. This figure shows that an increase in the contact time leads to the increased Lead removal percentage to the amount of higher than 70% at the time of 10 minutes and it may be due to the entry of hydroxyl radical into the solution [22]. This time is thus selected as the equilibrium time. The contact time initially removes the available hydroxyls in the lead solution, and finally reduces the efficiency of process due to the lack of hydroxyl ion. Argun et al found similar results about the removal of heavy metals [23]. Tomar et al also found that the removal of Fluoride increased at higher contact time [21].

Reference:

1-A. Johnson, N. Jain, Joshi H, Prasad S. Agricultural and agroprocessing wastes as low cost adsorbents for metal removal from wastewater: a review. J Sci Ind Res 2008; 67(9): 647-58.

2- Futalan CM, Tsai WC, Lin SS, Hsien KJ, Dalida ML, Wan MW. Copper, Nickel and Lead Adsorption from Aqueous Solution using Chitosan Immobilized on Bentonite in a Ternary System. Sustain Environ Res 2012; 22(6): 345-355.

3- Ponder SM, Darab JG., and Mallouk TE. Remediation of Cr (VI) and Pb(II) aqueous solutions using nano scale zero-valent iron. Environ Sci Technol 2000; 34(12): 2564-2569.

4-Tangahu BV, Abdullah SRS, Basri H, Idris M, Anuar N, Mukhlisin M. A Review on Heavy Metals (As, Pb, and Hg) Uptake by Plants through Phytoremediation. Int J Chem engin 2011; 8: 21-30.

5-Yu B, ZhangY, Shukla A, ShuklaSS, Dorris KL.The removal of heavy metal from aqueous solutions by sawdust adsorption removal of copper. J Hazard Mater B 2000; 80(1-3): 33-42.

6-Zahra N. Lead Removal from Water by Low Cost Adsorbents: A Review. Pak J Anal Environ Chem 2012; 13 (1):1-8.

7-Mehrasbi M, Farahmandkia Z. Heavy Metal Removal from Aqueous Solution by Adsorption on Modified Banana Shell. Heal Environ J 2008; 1(1):17-25.

8. Javanbakht V, Zilouei H, Karimi K. Effect of pH on Lead Removal from Aqueous Solution by Fungus Mucor Indicus. Water weast 2010; 1:76-84.

9- Esalah JO, Weber ME, Vera JH. Removal of lead, cadmium and zinc from aqueous solutions by precipitation with sodium di-(n-octyl) phosphinate. Cana J Chem 2000; 7(5)8:948-954.

10. Shukla SR, Pai RS. Adsorption of Cu (II), Ni (II) and Zn (II) on modified jute fibers. Biores technol 2005; 96(13): 1430-1438.

11-Bailey SE, Olin TJ, Bricka RM, and Adrian DD. Areview of potentially low-cost sorbents for heavey metals. Water Res 1999; 33(11): 2469-2479.

12-Meriç S, Kaptan D, Ölmez T. Color and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process. Chemosphere. 2004, 54(3):435-41.

13-Sun J, Sun S, Sun R, Sun JY, Sun RX, Qiao LP, Guo HQ, et al. Degradation of azo dye Acid black 1 using low concentration iron of Fenton process facilitated by ultrasonic irradiation. Ultra sonics sono chemistry 2007; 14(6):761-6.

14-Farrokhi M, Kouti M, Mousavi G. The study on Biodegradability Enhancement of landfill leachate by Fenton oxidation. Journal of Health and Environment 2009; 2(2):114-23. [Persian].

15-Khodadadi DA, Shahmansouri A, Ganjidost H. Fenton remediation of methyl tertiary butyl ether (MTBE) and effects of reaction conditions on the byproducts formed. J Water and Waste Water. 2009; 4: 36-43.

16- Nakhzari moghadam, F; bagheri, S; Shahreki, A, janikol, N. Investigating the Removal of Cadmium from Water Using Chemical Oxidation (Fenton). International Journal of Innovative Science, Engineering & Technology June 2017; 4(6):291-295.

17- Wang XJ, Song Y, Mai JS. Combined Fenton oxidation and aerobic biological processes for treating a surfactant wastewater containing abundant sulfate. Journal of Hazardous Materials 2008; 160(2–3):344–48.

18-Al-Ananzeh NM. Oxidation processes: experimental study and theoretical investigations. [Disertation]. Faculty of the Worcester Polytechnic Institute 2004. pp: 445.

19-Neyens E, Baeyens J. A review of classic Fenton's peroxidation as an advanced oxidation technique. Journal of Hazardous Materials 2003; 98(1-3):33-50.

20- Poinern GEJ, Ghosh MK, Ng Y-J, Issa TB, Anand S, Singh P. Defluoridation behavior of nanostructured hydroxyapatite synthesized through an ultrasonic and microwave combined technique. Journal of hazardous materials 2011; 185(1):29-37.

21-.Tomar V, Prasad S, Kumar D. Adsorptive removal of fluoride from water samples using Zr–Mn composite material. Microchemical Journal 2013; 111:116-124.

22- Xu M, Wang Q, Hao Y. Removal of organic carbon from wastepaper pulp effluent by lab-scale solar photo-Fenton process. Journal of Hazardous Materials 2007; 148(1-2):103-109.

23-.Argun ME, Dursun S, Karatas M, Gürü M. Activation of pine cone using Fenton oxidation for Cd (II) and Pb (II) removal. Bioresource technology 2008; 99(18):8691-8698.