Original Article

Performance evaluation of Fenton process removing fluoride from aqueous solution

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ABSTRACT

Aims: This study was conducted to determine the Fenton performance on the fluoride removal efficiency from aqueous solutions.
Materials and Methods: The removal efficiency of fluoride from aqueous solutions by the Fenton was carried out by preparation of the water solutions. The studied concentrations of fluoride were in the range of 1.5-3.5 mg/L, pH 2-11, contact times 1-17 min, and the Fenton ratios in the range of 1:1-1:10. The SPADNS method was used for fluoride determinations.
Results: The optimum obtained values of the studied parameters to maximum 67% removal of the fluoride from the solutions were, the fluoride concentration 2.5 mg/L, pH = 3, Fenton ratio (H_2O_2:Fe) = 1:2 and the contact time of 15 min.
Conclusion: The proposed material has successfully been applied to the removal of fluoride in different aqueous solutions having a broad concentration range of fluoride. The simplicity of the proposed fluoride removal material, high removal efficiency, a short time and the use of safe chemicals demonstrate the high potential of the proposed method for routine fluoride removal from water samples. The obtained results showed that Fenton process in the removal of fluoride concentration could be an effective method for the removal of fluoride.

Key words: Aqueous solutions, Fenton, fluoride removal

INTRODUCTION

Fluorine is one of the four elements that are essential for animal life; there is a considerable amount in all tissues and body fluids of humans and animals.[1] This compound is abundant in the environment and exists only in combination with other elements as fluoride compounds, which are constituents of minerals in rocks and soil. Therefore, fluoride is commonly associated with volcanic activity.[2] People living in places where water has high concentrations of fluoride ions may develop fluorosis.[3] This is one of the most frequently occurring endemic diseases and currently affecting millions of people worldwide.[4] Waters with high concentrations of fluoride are found mostly in alluvial aquifers, areas of geothermal activity, arid, and semi-arid regions. Fluoride, as a contaminant in ground/surface water, could be from either natural geological sources or industries that use fluoride-containing compounds as raw materials. Hence, it is an important task to supply water with safe fluoride levels. In Mexico, the excess of fluoride in drinking water affects 5 million people (about 6% of the population). Many efforts have been taken by various researchers to reduce the fluoride

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concentrations in water.[5] More than 95% of the rural and about 30-40% of the urban population in India depends on groundwater for its domestic requirements. Other studies have been observed fluoride levels in groundwater in America,[6] Africa,[7] and Asia,[8] ≥30 mg/L. In some parts of Turkey has been observed fluoride concentration in groundwater in the range of 5.1-13.7 mg/L.[9] In a study conducted by Ming *et al.*, it was shown that a high concentration of 5 mg/L fluorine that has been observed in Changzhou, China.[10] High concentration of contaminants such as fluoride and nitrate in groundwater render it unfit for drinking purpose. Fluoride contamination in groundwater has been recognized as a global problem and its concentration in drinking water at many places of the world exceeds the permissible limits.[11] Fluoride is known as both beneficial and detrimental to human health. It is well known that fluoride can effectively prevent dental caries when a relatively low level is constantly maintained in the oral cavity. On the contrary, an excessive fluoride intake leads to various diseases such as dental and skeletal fluorosis.[12,13] Fluoride concentrations in the range of 1.5-4.0 mg/L result in dental fluorosis whereas with prolonged exposure at still higher fluoride concentrations (4-10 mg/L) dental fluorosis progresses to skeletal fluorosis.[6] Therefore, the World Health Organization as well as many countries has set 1.5 mg/L of fluoride as the upper limit in drinking water.[14,15] Thus, fluorosis is one of the most frequently occurring diseases that develop in the population who depends on water containing high fluoride concentrations for their daily drinking.[16] Compared to its beneficial effect, fluoride is more detrimental. Thus, fluoride is a toxic chemical, and it is a risk factor for thyroid hormone production in children when the exposure to fluoride occurs during intrauterine growth period.[17] Interference of fluoride with carbohydrates, lipid, proteins, vitamins, and mineral metabolism are also to the presence of high concentrations of fluoride in water. Various technologies such as adsorption, ion exchange, precipitation, electro-dialysis, and reverse osmosis have been employed for the removal of fluoride from water resources.[17-23] Fenton about a 100 years ago was invented for the 1st time in 1914 by human growth hormone Fenton. However, its mechanism remained unknown until 1930s,[24] and until the 1960s, it was not experienced for destroying of any toxic compounds. Later, it was used in the oxidation-resistant organic matter in municipal wastewater and non-biodegradable material such as phenolic wastewaters.[25] The Fenton reaction causes the dissociation of the oxidant and the formation of highly reactive hydroxyl radicals that attack and destroy the organic components.[26] Some recent research has shown that the mechanism of Fenton oxidation of reactive hydroxyl radicals derived from H_2O_2 in acidic conditions and the presence of a catalyst.[27] So, in the Fenton process are used iron and hydrogen peroxide, two chemicals that are very important in terms of cost and efficiency. The other Fenton advantage in comparison with other advanced oxidation reactions is its short reaction time.[28] Fenton technique is classified to photo-Fenton, electro-Fenton, dark-Fenton, and pseudo-Fenton process. These methods are based on different operating conditions, but their reactions are the same. Reagents used in these processes are available, inexpensive, and environmentally safe.[29]

Since to date, a study on fluoride removal from aqueous solutions by Fenton process has not been reported, this study was designed to evaluate the removal efficiency of fluoride from aqueous solution by the Fenton method. In this regard, the optimum H_2O_2:$FeSO_4$ ratio, pH, fluoride concentration, and contact times were determined.

MATERIALS AND METHODS

Material used

In this study, all reagents and materials used had analytical grade and were purchased from Merck Co., Germany. The SPADNS reagent was provided by Hach Co., USA.

The F^-solutions were prepared using NaF powder with commercial purity of 98%. In this study, varying ratios of a solution of 35% (w/v) H_2O_2 and ferrous sulfate ($FeSO_4$, 7 H_2O_2) were used as Fenton. Fluoride concentrations in the initial and final solutions were analyzed by SPADNS method using a direct reading spectrophotometer, Dr-5000, Hatch-LANGE, USA. The study experiments had four variables, the Fenton ratio, and fluoride concentration of solutions, pH, and the contact times.

Design of experiments was as one variable at a time. All experimental tests were repeated 2 times and the mean of results is presented. The number of analyzed samples was 72.

Experiments

Effect of initial fluoride concentrations

In this section of the study, different initial concentrations of fluorine (1.5, 2, 2.5, 3, and 3.5 mg/L) were contacted by a H_2O_2:$FeSO_4$ ratio = 1:5. Other study parameters include of pH = 6, and the contact time = 10 min.

Effect of pH

In the second stage, the optimal pH was characterized. In this regard, 10 pH values of 2-11 were tested. It should be noted that the optimum concentration of fluoride (2.5 mg/L) was obtained from previous experiments was used as the fluoride concentration of the solution. Again, the contact time 10 min and the ratio of Fenton 1:5 were used.

Effect of Fenton ratios

In the following, a series of experiments were implemented to determine of optimum Fenton ratio. In the other word, using the optimal values of the F^-concentration and pH obtained in the previous experiments, the optimum ratio of Fenton in the range of 1:1-10:1 was determined. In this way, the fluoride concentrations of 2.5 mg/L and pH 5 were used. The contact time of these experiments was 10 min.

Effect of contact times

In this section, the previous obtained results of the experiments, F^-concentration = 2.5 mg/L, pH = 5, and the H_2O_2:$FeSO_4$ = 1:5 were applied for determination of the optimum contact time. The contact times of 1-17 min were tested.

RESULTS

Figure 1, shows the standard calibration curve of fluoride absorption in aqueous solutions. Figure 2 illustrates the effect of initial fluoride concentrations on the fluoride removal efficiency by Fenton process. As can be shown in this figure, the fluoride percentage removal was increased with increasing fluoride concentration and the most fluoride removal was occurring in the fluoride concentration of 2.5 mg/L. Figure 3 displays the effect of the pH changes on the fluoride removal from aqueous solutions. This figure indicates that by pH increasing of the solutions the fluoride removal efficiency was reduced. On the other hand, the maximum percentage of fluoride ions were removed at pH = 3. Figure 4, shows the influence of the Fenton ratios on the fluoride removal. This figure demonstrates that the increase of the H_2O_2:$FeSO_4$ ratio, the decrease the fluoride removal efficiency. In addition, the highest fluoride removal efficiency was obtained in the ratio of 1:2. Figure 5, displays the impact of contact time on the fluoride removal efficiency from aqueous solutions. As can be seen from this figure, it shows the fluoride percentage removal was increased with increasing contact time and the removal efficiency was constant after 15 min.

DISCUSSION

Effect of initial fluoride concentrations

The effect of initial fluoride ion concentration on the removal capacity of Fenton was studied by varying the initial fluoride

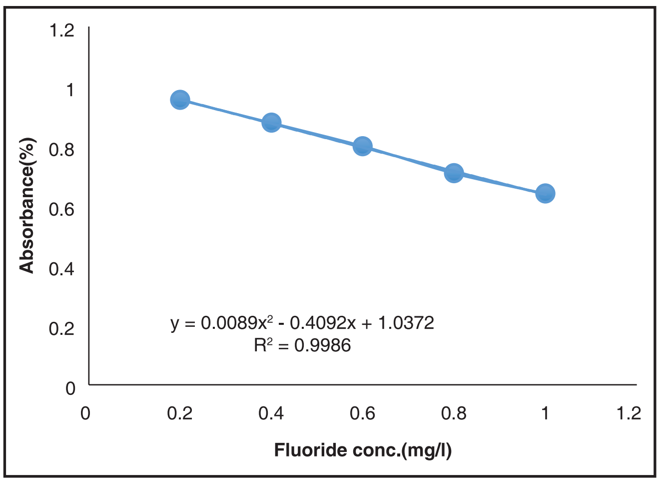

Figure 1: The standard calibration curve of fluoride absorption in aqueous solutions

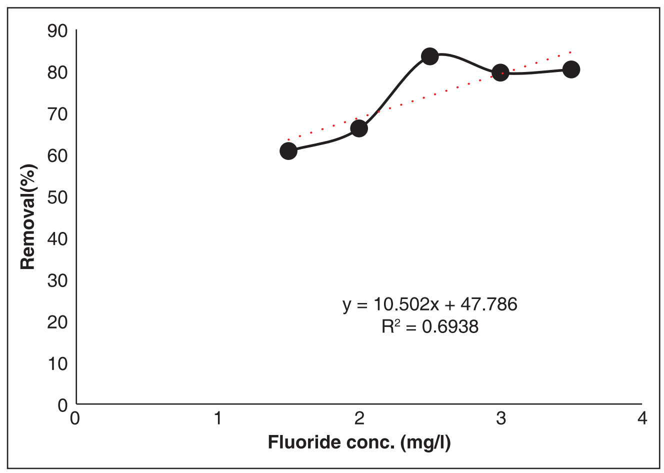

Figure 2: Effect of initial fluoride concentrations, (Time = 10 min, pH = 5, H_2O_2:Fe = 1:5)

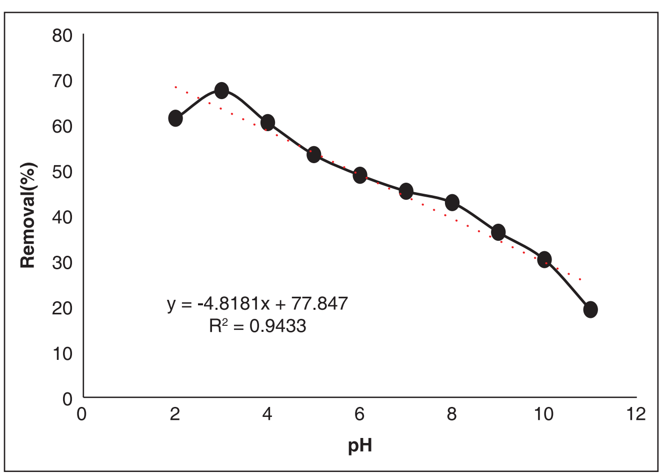

Figure 3: Influence of pH change on the fluoride removal, (time = 10 min, fluoride concentration =2.5 mg/L, H_2O_2:Fe = 1:5)

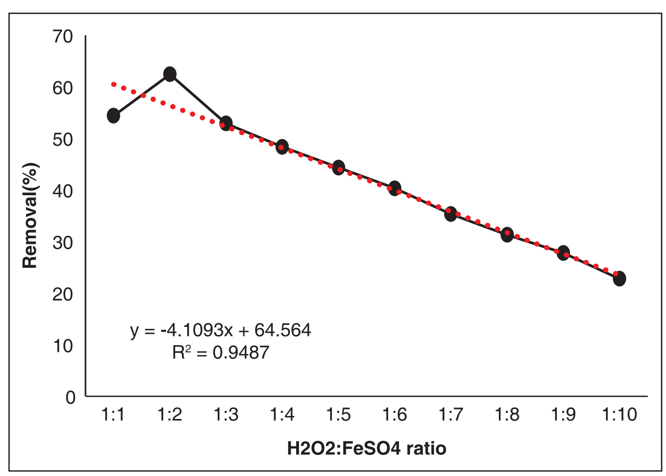

Figure 4: Impact of Fenton ratio on the fluoride removal, (time = 10 min, pH = 3, fluoride concentration =2.5 mg/L)

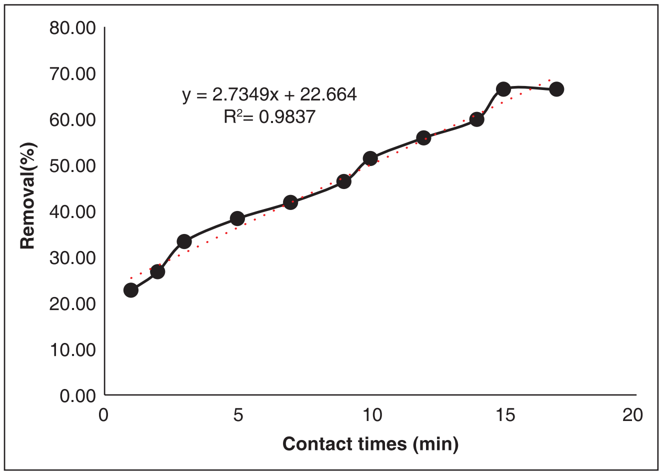

Figure 5: Contact time effect on the fluoride removal, (fluoride concentration =2.5 mg/L, pH = 3, H_2O_2:Fe = 1:2)

ion concentration in the range of 1.5-3.5 mg/L at pH 5, contact time 10 min, and the H_2O_2:Fe ratio of 1:5 [Figure 2]. It was observed that the fluoride removal efficiency (~88%) increased as the initial fluoride ion concentration increased to a specified level (2.5 mg/L) and then leveled off. However, totally the removal trend of the fluoride from the aqueous solutions was increased by increasing of the initial fluoride concentrations. As some references, the fluoride reaction with Fe^{2+} creates the Iron (II) fluoride (FeF_2). So, due to its k_{sp} of 2.3×10^{-6}, probably some of the solute fluorides could be removed from solution. However, some of the more insoluble compounds also may produce during this reaction, such as CaF_2 with k_{sp} 3×10^{-11}, and MgF_2 with k_{sp} 5.61×10^{-11}.[30,31]

Effect of pH

In order to understand the mechanism of fluoride removal from aqueous solutions by Fenton and the role of it, the pH of treated samples was measured. The pH of the solution is an important variable, which affect the removal of fluoride. Hence, the effects of the solution pH were studied in the range of 2-11. Results that are shown in Figure 3 indicates that with the increasing the solution pH, the fluoride removal efficiency was decreased. The superlative fluoride removal (67%) was occurring at the initial pH 3. Therefore, it is well established that the fluoride was highly removed in acidic conditions. The highest efficiency of fluoride removal at acidic condition may be related to the presence of the highest value of dissolved iron in water at such conditions. In this situation, the highest hydroxyl radicals are formed.[32] In this study, the pH 3 was chosen as the optimal pH in the Fenton reactions. In the Fenton reaction, the hydroxyl radicals are the main oxidation agents, which are produced by the decomposition of hydrogen peroxide catalyzed by metal ions, e.g., Fe^{2+}.

On the other hand, at the neutral solution pH 7, the obtained removal efficiency of the fluoride from aqueous solutions was only 45%. This lower removal efficiency may be due to the exchange interactions between F^- and OH^- groups in the solutions. It should be noted that, the lower the pH favors the generation of hydroxyl radicals. In addition, lower degradation at higher pH might be attributed to the formation of ferrous and ferric hydroxyl complexes, which will lead to a decrease in the production of hydroxyl radicals.[33]

At pH > 7, iron precipitations were visually apparent in yellow color at the bottom of the beaker. In this pH range, both Fe^{2+} and Fe^{3+} will precipitate as iron hydroxides. This limits the amount of iron available for Fenton reaction, which lead to decrease the amount of fluoride in the solution.[34] Xu *et al.*,[35] observed similar results.

Effect of Fenton ratios

In this part of the study, the effect of Fenton different ratios was analyzed in the range of 1:1-1:10 of H_2O_2:Fe. As can be seen in the Figure 4, in all studied ranges, except the 1:2 ratios, the trend line of the fluoride removal is decreasing by the increasing of the Fenton ratios. On the other word, under different H_2O_2:$FeSO_4$ ratios of 1:10, 1:5 and 1:2, the percentage of fluoride concentration removal at 10 min contact time was 22.74%, 44% and 62%, respectively. Fluoride removal in H_2O_2:Fe ratio of 1:10 and 1:9 was very low because hydroxyl radicals produced was not sufficient for fluoride removal from the aqueous solution, and the iron hydroxide precipitation was observed. So, in the 1:2 Fenton ratios, the highest removal efficiency of the fluoride was detected. Thus, this ratio was selected as the optimum value.

Effect of contact times

The effects of this parameter on the removal of fluoride were studied by varying the contact times in the range of 1-17 min under the fluoride concentration 2.5 mg/L, pH = 3, and the H_2O_2:$FeSO_4$ = 1:2. Fluoride removal efficiency as a function of contact time is shown in Figure 5. This Figure shows that by the increasing of the contact times, the fluoride removal efficiency was increased up to 66% at the contact time of 15 min. However, the fluoride was removed rapidly, reaching 38% removal during the first 5 min. This may be due to the diffusion of hydroxyl radical into the solution.[36] It is apparent that the fluoride removal rate was fixed and was stabilized at approximately 66%, after 15 min contact time. Argun *et al.*, observed similar results in a heavy metal removal study.[37] Tomar *et al.* shown that the removal of fluoride ions increased with increase in contact time.[33]

CONCLUSION

The proposed method has successfully been applied to the removal of fluoride in different aqueous solutions containing a wide concentration range of the fluoride. The simplicity of this method, high removal efficiency, a short time and the use of safer chemicals, demonstrate a high potential for routine fluoride removal from water samples. These values were then optimized individually double-tested and showed a maximum 67% fluoride removal. The obtained results showed that Fenton process could be an effective method for the removal of fluoride from aqueous solutions.

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