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CO-APPLICATION OF COAGULATION AND ELECTROCHEMICAL PROCESSES TO REMOVE FLUORIDE FROM WATER

Davarkhah Rabbani,[a,b] Zeinab Parmoozeh,[a] Amir Hossein Mahvi,[c,d] Atieh Salem[a,*]

Kashan and Tehran, Iran.

ABSTRACT: Fluoride at more than the standard level in drinking water can result in health hazards. Therefore, different technologies are used to remove it. The aim of this study was to examine fluoride removal from water with the co-application of alum-coagulation and an electrochemical processes. A bench scale study was conducted in a batch system on 138 water samples with fluoride concentrations of 5, 12.5, and 20 mg.L^{-1}. First, in the coagulation process, the effects of run time and alum dosage on fluoride removal were investigated. Then, the effect of an electrochemical process using aluminum electrodes was studied. Finally, the co-application of the electrochemical and the coagulation processes was investigated. The results showed that the average fluoride removal using the coagulation process, with 15 minutes run time and pH =6, was 86.63%. Under the same conditions, the average fluoride removal efficiency with the electrochemical process was 86.70%. The co-application of both processes resulted in 91.33% removal. The co-application of chemical coagulation and an electrochemical process to remove fluoride from polluted water is significantly more efficient than the application of each of them alone.

Keywords: Coagulation process; Electrochemical process; Fluoride; Water treatment.

INTRODUCTION

Fluoride is a contaminant that can remain in soil, plants, and the human body.[1] Fluoride intake usually occurs through the daily consumption or use of air, water, food, drugs, cosmetics, and toothpaste.[2] Therefore, fluoride adjustment in drinking water is one of the most important ways to improve human health. Excessive amounts of fluoride can result in different health problems.[3-11] Various technologies which are used to reduce the fluoride level in water include coagulation-sedimentation, ion exchange electro-coagulation, an electrochemical process, membrane filtration, and absorption.[12-16]

All of these techniques have some advantages and disadvantages that limit their use. In the coagulation-sedimentation method, alum (aluminum sulfate) is commonly used as a non-toxic chemical coagulant. Alum coagulation can remove fluoride in the pH range of 5.5–7.5, but the high dosage of alum used in the process results in the formation of a lot of sludge with a high aluminum concentration which is harmful to human health. It is accordingly not recommended as being a suitable method for water de-fluoridation.[17-19] The electrochemical method seems to be an easy clean process with many advantages, such as being able to be used in drinking water and wastewater treatment, having a simple system design, having low operation and maintenance costs, and having a low rate of sludge production.[20] Therefore in this study we investigated the co-application of chemical coagulation and an electrochemical process for the removal of fluoride from water.

[a]Department of Environmental Health Engineering, Faculty of Health, Kashan University of Medical Sciences, Kashan, Iran; [b]Social Determinants of Health (SDH) Research Center, Kashan University of Medical Sciences, Kashan, Iran; [c]Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran; [d]Center for Solid Waste Research, Institute for Environmental Research, Tehran University of Medical Sciences, Tehran, Iran. *For correspondence: Atieh Salem, Department of Environmental Health Engineering, Faculty of Health, Kashan University of Medical Sciences, Kashan, Iran.

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MATERIAL AND METHODS

Firstly, pure sodium fluoride powder was added to double-distilled water for preparing a fluoride stock solution (1,000 mg.L^{-1}). The synthetic wastewater samples with 5, 12.5, and 20 mg.L^{-1} fluoride were prepared by using dilutions of the stock solution. The alum purity was 99.3% and the containers were made of polyethylene.

The effect of the chemical coagulation process was investigated. In this stage, the jar-test was applied to determine the optimum alum dosage at pH=6, which was selected of the basis of previous studies.[21,22] Four dosages (50, 100, 200, and 400 mg.L^{-1}) of alum were added to the water samples. Rapid mixing (100 rpm) was applied on all samples for 1 minute and gentle mixing (40 rpm) was continued up to 15, 30, and 45 minutes.

After that, the electrochemical process was done to determine the optimal current intensity. The pilot included eight submerged aluminum electrodes, 1 cm apart from each other. In this stage, four electrical current intensities (0.156, 0.31, 0.63, and 0.94 mA/cm^2) were studied. The reaction time was 15 minutes, based on the first stage findings. In all the runs, the contents was blended during the reaction by a magnetic stirrer at 300 rpm.

The optimum values for the co-application of the chemical coagulation and electrochemical processes were found by considering the alum dosages and current intensities obtained from the previous stages. Generally the run conditions were same as used for the electrochemical process apart from the addition of the coagulant to the process. The electrical current intensities and the alum dosages were trimmed down step by step to 10% of their optimum values. A multi-meter (Mi 160 Milwakie, Taiwan) fluoride ion selective electrode (SENTEK, England) was used to measure the fluoride concentration before and after the processes.

Finally, the descriptive statistical analysis was conducted to determine the mean and standard deviation (SD) of the results. The normality of data was studied by the Kolmogorov-Smirnov Test. A variance analysis, with repeated measurements, was conducted to investigate the effect of the alum concentration and the current intensity with regard to run time. A linear multiple regression model was developed based on the factors which affected the results.

RESULTS AND DISCUSSION

1. The effect of run time on F removal in the coagulation process: The optimum run times for the different initial fluoride concentrations (5, 12.5, and 20 mg.L^{-1}) were determined by a jar-test. The maximum ratio of removed fluoride/run time (mg/min) for all the concentrations was obtained at 15 minutes (Table 1) and the difference between this reaction time and the others was meaningful ($p<0.001$). In this run time, the fluoride content reduced to less than the WHO standard for fluoride in drinking water (1.5 mg.L^{-1}). So, 15 minutes was considered to be the best run time which was in agreement with a similar study.[23]

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Table 1. The removed fluoride/run time (mg/min) in chemical coagulation for 54 samples (Values are mean±SD)

Run time (min)	Removal speed (mg/min)	p value
15	0.77±0.38	
30	0.38±0.19	<0.001
45	0.25±0.12	
Total	0.47±0.34	

2. The effect of alum dosage on fluoride removal in the coagulation process: In this stage, the effect of different dosages of alum (50 to 400 mg.L^{-1}) on different initial concentrations of fluoride was investigated. The results showed the removal efficiency increased with increasing the dosage of alum for all the concentrations of fluoride. The optimal alum concentration was determined based on the reduction of fluoride content to below the WHO guideline of 1.5 mg.L^{-1}. At an initial fluoride concentration of 5 mg.L^{-1}, the optimal dosage of alum was less than 50 mg.L^{-1}, while for initial fluoride concentrations of 12.5 and 20 mg.L^{-1}, the optimal dosages of alum were 100 mg.L^{-1} and 200 mg.L^{-1}, respectively (Figure 1).

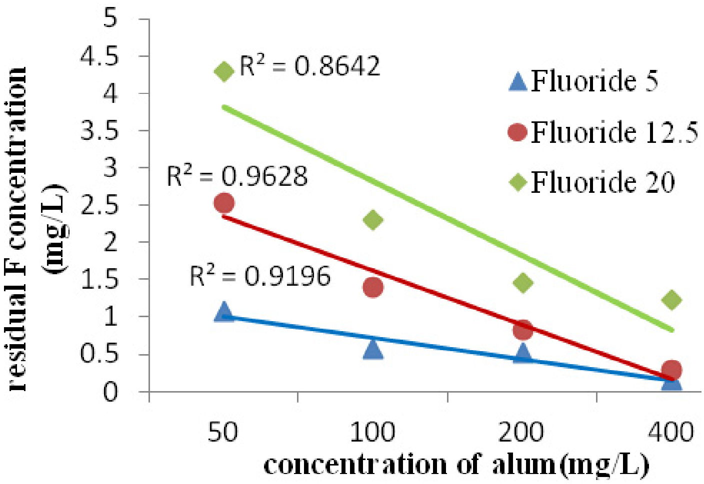

Figure 1. The mean of the residual fluoride concentrations as a function the alum dosage in the coagulation process.

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3. The effect of current density on fluoride removal in the electrochemical process: In this stage, the effects on fluoride removal of the current density, adjusted to be in the range of 0.156 to 0.94 mA/cm^2, was examined for all fluoride concentrations while the reaction time was fixed at 15 minutes. The findings showed that increasing the current density in the electrochemical process resulted in increases in the fluoride removal efficiency. The lowest current densities which could reduce the fluoride concentrations below the WHO guideline (1.5 mg.L^{-1}) were 0.156, 0.63, and 0.94 mA/cm^2 for the fluoride concentrations of 5, 12.5, and 20 mg.L^{-1}, respectively (Figure 2). Other studies have shown similar findings. [24]

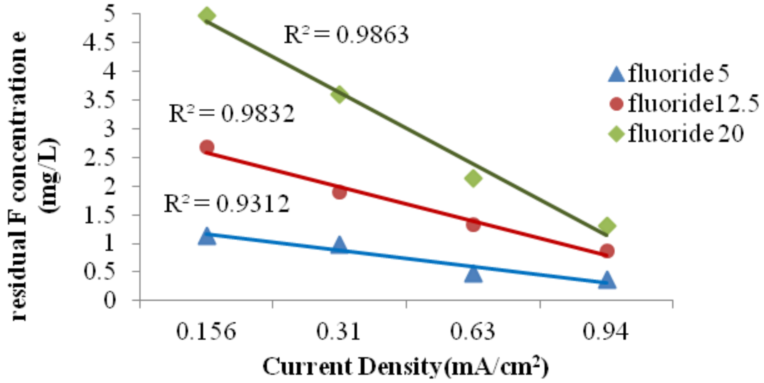

Figure 2. The mean of the residual fluoride concentration as a function of the current density in the electrochemical process

4 The effect of the co-application of alum coagulation and the electrochemical processes: At this stage, according to the findings of the previous stages the optimal alum dosage and optimum current density were combined and applied to all the samples with different concentrations of fluoride. In this combination for all the runs, the run time was controlled at 15 minutes. Also, various fractions, down to 10%, of the optimal dosage of alum and the lowest current densities which could reduce the fluoride concentrations below the WHO guideline (1.5 mg.L^{-1}) were applied to all the samples with the different F concentrations based on the previous findings.

A study showed that adding the electrochemical process by aluminum electrodes, could reduce the amount of coagulant by half and keep the remaining turbidity at the standard level.[25]

In another study, the addition of polyaluminum chloride to the electrochemical process for fluoride removal increased the efficiency from 87% to 100%.[26] It should be noted, however, that the electrode type was copper and the coagulant was different.

Table 3 shows the optimum values of the investigated parameters in the coagulation and electrochemical processes in competition with their optimum values in the co-application of these reactions. The aim was to achieve the WHO fluoride standard (1.5 mg.L^{-1}).

Table 2. The effect of combined electrochemical and coagulation processes on fluoride removal

Initial F concentration ($mg.L^{-1}$)	Alum concentration ($mg.L^{-1}$)	Current density (mA/cm^2)	Residual F concentration ($mg.L^{-1}$)	The average removal efficiency (%)	p value
5	10	0.03	1.24	75.04± 0.51	<0.001
	20	0.06	1.15	76.96 ± 1.17	
	31.5	0.09	1.02	79.63± 0.89	
	50	0.156	0.83	83.32 ± 1.71	
12.5	10	0.06	3.56	71.53 ± 5.12	<0.001
	15.7	0.09	3.0	76.01 ± 3.01	
	25	0.16	2.25	81.96 ± 3.04	
	40	0.25	1.76	85.90 ± 0.16	
	63	0.41	1.28	89.73 ± 1.15	
	100	0.63	0.68	94.53 ± 3.93	
20	20	0.09	3.72	81.42 ± 1.59	<0.001
	31.5	0.16	3.46	82.70 ± 0.17	
	50	0.22	2.54	87.29 ± 0.48	
	80	0.37	1.60	92.02 ± 0.26	
	126	0.59	1.17	94.13 ± 0.47	
	200	0.94	0.77	96.14 ± 0.22	

Table 3. The optimum values of the studied parameters to achieve the fluoride standard level of 1.5 $mg.L^{-1}$

Process	Initial F concentration ($mg.L^{-1}$)		
	5	12.5	20
Chemical coagulation	50 $mg.L^{-1}$ alum (78.4% removal)	100 $mg.L^{-1}$ alum (88.8% removal)	200 $mg.L^{-1}$ alum (92.7% removal)
Electrochemical	0.05 A (77.3% removal)	0.2 A (89.4% removal)	0.3 A (93.4% removal)
Combined	10 $mg.L^{-1}$ alum + 0.01 A (75.4% removal)	63 $mg.L^{-1}$ alum +0.13 A (89.7% removal)	126 $mg.L^{-1}$ alum + 0.19 A (94.1% removal)

5. Regression analysis: A multiple linear regression model for fluoride removal by the co-application of the coagulation and the electrochemical processes shows that the most effective factors on fluoride removal are the electrical energy ($p<0.001$) and the alum dosage ($p<0.001$), while the initial concentration of fluoride has less effect on the F removal efficacy ($p=0.014$). The final model to which the collected data was fitted had a strong explanatory power ($R^2=0.847$).

Equation 1 was developed to determine the fluoride removal efficiency as a function of the electrical energy, the alum dosage, and the initial fluoride concentration:

$$R = 70.791 + 0.306\,E - 0.014\,A + 0.211\,F_{\text{initial}} \quad \text{..............................Equation 1}$$

Where:

R = Fluoride removal efficiency

E = Electrical energy (kWh)

A = Alum dosage (mg/L)

F_{initial} = Initial fluoride concentration (mg/L)

CONCLUSIONS

Generally, the co-application of the alum-coagulation and the electrochemical processes could improve the fluoride removal efficiency by about 3% to 6%. With this combined process, in the case of samples with an initial fluoride concentration of 5 $mg.L^{-1}$, the current intensity and alum dosage were reduced from 0.156 mA/cm^2 and 50 $mg.L^{-}$ to 0.03 mA/cm^2 and 10 $mg.L^{-1}$, respectively. The aim was the reduction of the fluoride concentration below the WHO standard of 1.5 $mg.L^{-1}$.

Also, the co-application of the two mentioned processes on samples with an initial fluoride concentration of 12.5 $mg.L^{-1}$, decreased the current intensity from 0.63 to 0.41 mA/cm^2 and the alum dosage from 100 to 63 $mg.L^{-1}$. At the initial concentration of 20 $mg.L^{-1}$-F^{-}, the current intensity was decreased from 0.94 to 0.59 mA/cm^2 and the alum dosage from 200 to 126 $mg.L^{-1}$.

For treatment plants engaged in fluoride removal using the coagulation process, adding the electrochemical process with aluminum electrodes to the rapid mixing tanks can significantly reduce the fluoride removal cost.

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REFERENCES

1 Yu Y, Yu L, Chen JP. Adsorption of fluoride by Fe–Mg–La triple-metal composite: adsorbent preparation, illustration of performance and study of mechanisms. Chemical Engineering Journal 2015;262:839-46.

2 Dobaradaran S, Fazelinia F, Mahvi AH, Hosseini SS. Particulate airborne fluoride from an aluminium production plant in Arak, Iran. Fluoride 2009;42(3):228-32.

3 Dhillon A, Soni SK, Kumar DJ. Enhanced fluoride removal performance by Ce–Zn binary metal oxide: Adsorption characteristics and mechanism. Journal of Fluorine Chemistry 2017;199:67-76.

4 Rahmani A, Rahmani K, Dobaradaran S, Mahvi AH, Mohamadjani R, Rahmani H. Child dental caries in relation to fluoride and some inorganic constituents in drinking water in Arsanjan, Iran. Fluoride 2010;43(4):179-86.

5 Karimzade S, Aghaei M, Mahvi A. Investigation of intelligence quotient in 9–12-year-old children exposed to high-and low-drinking water fluoride in West Azerbaijan Province, Iran. Fluoride 2014;47(1):9-14.

6 Rahmani A, Rahmani K, Mahvi AH, Usefie M. Drinking water fluoride and child dental caries in Noorabademamasani, Iran. Fluoride 2010;43(3):187-93.

7 Aghaei M, Derakhshani R, Raoof M, Dehghani M, Mahvi AH. Effect of fluoride in drinking water on birth height and weight: an ecological study in Kerman Province, Zarand County, Iran. Fluoride 2015;48(2):160-8.

8 Dobaradaran S, Mahvi AH, Dehdashti S, Abadi DRV. Drinking water fluoride and child dental caries in Dashtestan, Iran. Fluoride 2008; 41(3):220-6.

9 Dobaradaran S, Mahvi AH, Dehdashti S, Dobaradaran S, Shoara R, Correlation of fluoride with some inorganic constituents in groundwater of Dashtestan, Iran. Fluoride 2009;42(1):50-3.

10 Yousefi M, Ghoochani M, Mahvi AH. Health risk assessment to fluoride in drinking water of rural residents living in the Poldasht city, Northwest of Iran. Ecotoxicology and Environmental Safety 2018;148:426-30.

11 Mohammadi AA, Yousefi M, Yaseri M, Jalilzadeh M, Mahvi AH. Skeletal fluorosis in relation to drinking water in rural areas of West Azerbaijan, Iran. Scientific Reports 2017;7(1):17300.

12 Boldaji MR, Mahvi A, Dobaradaran S, Hosseini S. Evaluating the effectiveness of a hybrid sorbent resin in removing fluoride from water. International Journal of Environmental Science & Technology 2009;6(4):629-32.

13 Cui H, Qian Y, An H, Sun C, Zhai J, Li Q. Electrochemical removal of fluoride from water by PAOA-modified carbon felt electrodes in a continuous flow reactor. Water Research 2012;46(12):3943-50.

14 Bazrafshan E, Ownagh KA, Mahvi AH. Application of electrocoagulation process using iron and aluminum electrodes for fluoride removal from aqueous environment. Journal of Chemistry 2012;9(4):2297-308.

15 Chen J, Shu C, Wang N, Feng J, Ma H, Yan W. Adsorbent synthesis of polypyrrole/TiO_2 for effective fluoride removal from aqueous solution for drinking water purification: Adsorbent characterization and adsorption mechanism. Journal of Colloid and Interface Science 2017;495:44-52.

16 Zazouli MA, Mahvi AH, Dobaradaran S, Barafrashtehpour M, Mahdavi Y, Balarak D. Adsorption of fluoride from aqueous solution by modified Azolla filiculoides. Fluoride 2014; 47(4)349-58.

17 Drouiche N, Aoudj S, Lounici H, Drouiche M, Ouslimane T, Ghaffour N. Fluoride removal from pretreated photovoltaic wastewater by electrocoagulation: an investigation of the effect of operational parameters. Procedia Engineering 2012;33:385-91.

18 Waghmare SS, Arfin T, Fluoride removal from water by various techniques. Int J Innov Sci Eng Technol 2015;2:560-71.

19 Razbe N. Various options for removal of fluoride from drinking water. IOSR Journal of Applied Physics 2013;3:40-7.

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20 Mumtaz N, Pandey G, Labhasetwar PK. Global fluoride occurrence, available technologies for fluoride removal and electrolytic defluoridation: a review. Critical Reviews in Environmental Science and Technology 2015; 45(21):2357-89.

21 Gong WX, Qu JH, Liu RP, Lan HC. Effect of aluminum fluoride complexation on fluoride removal by coagulation. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2012;395:88-93.

22 Ingallinella AM, Pacini VA, Fernández RG, Vidoni RM, Sanguinetti G. Simultaneous removal of arsenic and fluoride from groundwater by coagulation-adsorption with polyaluminum chloride. Journal of Environmental Science and Health, Part A. 2011;46(11):1288-96.

23 Pińón-Miramontes M, Bautista-Margulis RG, Pérez-Hernández A. Removal of arsenic and fluoride from drinking water with cake alum and a polymeric anionic flocculent. Fluoride 2003; 36(2):122-8.

24 Aliannejad S, Kashi G, Khezri S, Mashinchian A. Removal of fluoride from drinking water using an electrocoagulation reactor, batch experiments. Journal of Safety Promotion and Injury Prevention 2014;2(5):291-8.

25 Rabbani D, Bigdeli M, Ghadami F. Comparing the effect of electrochemical process and alum coagulation in removing turbidity and coliform bacteria from the synthetic wastewater. Kashan University of Medical Sciences Journal (KAUMS Journal) (FEYZ) 2012;16(3):273-81.

26 Kashi G, Nasehi N. Fluoride removal from drinking water using the combination of electro and chemical coagulation processes. Journal of Health in the Field 2017;2(2):43-52.