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## Simultaneous Removal of Hardness and Fluoride from Water by Chemical and Electrocoagulation

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**ABSTRACT:** This paper presents studies on simultaneous removal of hardness and fluoride from water by chemical and electrocoagulation processes. Influence of parameters like pH, applied voltage and contact time were studied. Results obtained with synthetic solutions indicated a maximum hardness removal 67-78% for the concentrations of hardness of 700, 1000, 1200, and 1300 mgL<sup>-1</sup> and a fluoride removal of 74-90% for Fluoride concentrations of 2, 3, and 5 mgL<sup>-1</sup> investigated at an applied voltage of 15 V and a contact time of 5 hours. Chemical coagulation was found to be ineffective (5-8%) for removal of hardness but was effective for removal of fluoride up to 80-90%. When hardness and Fluorides are present together, fluoride removal reduced to 57-65% in the presence of hardness (1300 mgL<sup>-1</sup>) and hardness removal was negligible (around 10-15%). Alum coagulation was optimum at a pH of 6.5. Ferric salts are ineffective for removal of Fluorides and hardness from water.

**KEYWORDS:** Hardness and fluoride removal, chemical coagulation, electrocoagulation.

### I. INTRODUCTION

Safe and good quality drinking water supply in adequate quantity is a critical issue and is of paramount importance for the public health and well being of the society. Surface water acquires impurities through natural and anthropogenic activities while geological acquisition and microbial activities contribute impurities to groundwater. Presence of organic and inorganic impurities poses health risks in addition to other problems. Presence of Fluoride, Arsenic and minerals that cause hardness is a major issue in several parts of the world and India.

Geological and manmade sources contribute to the occurrence of fluoride in water. Countries such as Argentina, Brazil, China, Ethiopia, Germany, India, Sri Lanka, and Tanzania are reported<sup>(1)</sup> to have fluoride concentration higher than permissible limits in groundwater. In India, several areas in states like Andhra Pradesh, Bihar, Delhi, Gujarat, Haryana, Jammu and Kashmir, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Orissa, Punjab, Rajasthan, Tamil Nadu, and Uttar Pradesh have higher concentration of fluorides which are problematic<sup>(2)</sup>.

Fluoride is essential to prevent dental caries but an excess intake is detrimental to human health. The optimum level suggested by WHO<sup>(3)</sup> is 0.7 mg/L from infancy to 16 years and the maximum acceptable concentration of fluoride ions in drinking water specified by the World Health Organization is 1.5 mg/L to prevent dental and skeletal fluorosis<sup>(4)</sup>. Several methods of defluoridation of drinking water have been developed which include chemical precipitation<sup>(5)</sup>, membrane processes<sup>(6)</sup>, adsorption<sup>(7,8)</sup> and ion exchange<sup>(9)</sup>. However, in India precipitation and adsorption methods are most preferred. Precipitation methods depend on the addition of chemicals to the raw water, which leads to the formation of fluoride precipitates or adsorption of fluoride onto the formed precipitate<sup>(10-14)</sup>. Lime and alum are used either individually or in combination. The Nalgonda Technique, as developed in India in 1975, involves sequential addition of alum and lime<sup>(10)</sup> and is widely used at domestic as well as community levels<sup>(11)</sup>. Major limitations of

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Vol. 6, Issue 10, October 2017

Nalgonda Technique are: the daily addition of chemicals; large volume of sludge production; and not effective with water sources having high total dissolved solids (TDS) and hardness<sup>(15)</sup>.

Hardness in water refers to existing divalent ions, such as iron, manganese, calcium and magnesium. Among them, calcium and magnesium are known as the dominant species for water hardening<sup>(16)</sup>. Although it has been shown that water hardness doesn't have serious health impact, it has been demonstrated that hard water is responsible for the formation of deposits in boiler and household facilities, as well as diverse influence on cleaning performances of detergents<sup>(17)</sup>. High concentrations of magnesium in drinking water may induce a bitter taste<sup>(18)</sup>. Public acceptance of hardness differs remarkably. In general, water supplies with total hardness higher than 200 mg/L are tolerated by consumers but are considered as poor resources; while values higher than 500 mg/L are not acceptable for domestic consumptions. Hard water is found in several countries such as the United States, Canada, United Kingdom, Tanzania, England and Wales, and Australia. Hardest waters (greater than 1,000 mg/L) were measured in streams in Texas, New Mexico, Kansas, Arizona, southern California and Tonk district of Rajasthan, Uttara Khand, Uttar Pradesh, etc. In Andhra Pradesh, groundwater in districts like Guntur, Chittoor, East Godavari, Visakhapatnam and Krishna have high levels of hardness.

In water purification and treatment plant, lime and soda ash processes are used for the removal of hardness. One of the main drawbacks of this process is the resulting waste, namely the large amount of liquid sludge produced, as well as the need for re-carbonation of the softened water<sup>(19, 20)</sup>. In addition, the use of additional chemicals to prevent sludge production is restricted and hence in most cases water hardness species cannot be fully removed<sup>(21)</sup>. Ion exchange processes have been considered as an alternative<sup>(22-24)</sup> and used widely in industrial sector. Other methods like electrodeionization process<sup>(20)</sup>, electromembrane processes<sup>(21)</sup>, capacitive deionization<sup>(25)</sup>, membrane and fluidized pellet reactor<sup>(26)</sup>, and adsorption<sup>(27,28)</sup> were also investigated for removal of hardness from water.

Electrocoagulation is based on the in situ formation of the coagulant as the sacrificial anode corrodes due to an applied current, while the simultaneous evolution of hydrogen at the cathode allows for pollutant removal. This process combines three main interdependent processes, operating synergistically to remove pollutants namely, electrochemistry, coagulation and hydrodynamics. Chemical reactions occurring at the electrodes are:

At anode:  $4\text{Fe}^{2+}(\text{aq}) + 10\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) \rightarrow 4\text{Fe}(\text{OH})_3(\text{s}) + 8\text{H}^+(\text{aq})$

At cathode:  $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$

The iron hydroxide flocs normally act as adsorbents and/or traps for removal of hardness and fluoride ions from the solution<sup>(29)</sup>.

The objective of this study was to investigate the chemical and electrocoagulation for simultaneous removal of hardness and fluoride from water samples spiked with hardness causing and Fluoride ions and to determine the effects of alum dose, applied voltage, pH, initial concentrations and contact time on the removal efficiency.

## II. MATERIALS AND METHODS

### Chemicals and Glassware

All chemicals used were of analytical reagent grade. Chemicals like fused Calcium chloride ( $\text{CaCl}_2$ ), Magnesium chloride hexahydrate ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), Calcium sulphate dehydrate ( $\text{CaSO}_4$ ), Magnesium sulphate heptahydrate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and Sodium hydroxide ( $\text{NaOH}$ ) were used. Corning glassware of Borosil quality was used throughout the experiments. Tap water was distilled in an all glass distillation still and used.

Synthetic hard water was prepared by dissolving in 300 mL of distilled water of 20g calcium chloride ( $\text{CaCl}_2$ ), 14g magnesium chloride hexahydrate ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), 8g Magnesium sulphate heptahydrate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) and 8g Calcium sulphate ( $\text{CaSO}_4$ )<sup>(30)</sup>. Samples of various concentrations such as 700  $\text{mgL}^{-1}$ , 1000  $\text{mgL}^{-1}$ , 1200  $\text{mgL}^{-1}$  and 1300  $\text{mgL}^{-1}$  were then prepared by diluting appropriate quantity of synthetic hard water. Fluoride stock solution was prepared by dissolving 221 mg anhydrous sodium fluoride ( $\text{NaF}$ ) in 1000 mL distilled water<sup>(31)</sup>. Working dilutions of 2  $\text{mgL}^{-1}$ , 3  $\text{mgL}^{-1}$  and 5  $\text{mgL}^{-1}$  were prepared by appropriate dilution of the stock fluoride solution. Stock solution of aluminum

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Visit: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 10, October 2017

sulphate  $Al_2(SO_4)_3 \cdot 18H_2O$  was prepared by dissolving 10g in 1.0 L of distilled water; each mL of this stock solution equal to 10ppm<sup>(32)</sup>.

Electrocoagulation experiments were performed in a monopolar batch reactor, with two iron plate electrodes spaced at 1.5 cm. Laboratory scale experimental setup was made with the components involving - a power source, two iron electrodes (5×10 cm) and a glass beaker of capacity 1 L. Electrodes were connected as monopolar with the help of a piece of wood. Test solutions of desired concentrations of hardness and fluoride and fluoride with pH adjusted to required values were injected into the reactor. The pH of initial solution was adjusted (using 0.1N/1.0N  $H_2SO_4$  or NaOH). A DC power supply having a variable output of 0–32V (5, 10, and 15 V for this study) with maximum current of 1 ampere was used as direct current source. Desired electrical potential was applied and an aliquot of samples was withdrawn from the reactor at different time intervals of 30, 60, 120, 180, 240 and 300 minutes, filtered through Whatman 42 filter paper and analysed for residual total hardness and fluoride by EDTA titrimetric method and SPADNS method using UV-VIS Spectrophotometer at 570nm (APHA/AWWA/WEF, 1999)<sup>(31)</sup>.

Coagulation experiments were conducted by standard jar test procedures using a six place jar test apparatus (Biological Enterprises, Delhi, India). To a 500 mL sample of the test hardwater/Fluoride solution taken in a beaker, coagulant dose in the range of 100, 200, 300, 400, 500, 600, 700, 800  $mgL^{-1}$  was added and mixed for a typical rapid mixing time of 2 minutes at 120 rpm followed by slow mixing at 30rpm for 20 minutes. The contents were then sedimented for 2 hours and an aliquot of supernatant was withdrawn and analyzed for residual total hardness and fluoride concentration.

### III. RESULTS AND DISCUSSIONS

#### Removal of hardness by electrocoagulation:

Removal of hardness at an applied voltage of 5 V and at a solution pH of 6.0 is presented in Figure 3.1. It follows from the data presented in Fig.3.1 that removal of hardness was rapid during the initial 60 minutes (40-47%) for all the concentrations of hardness and the rate of removal decreased gradually reaching an almost constant value of 53-64%.

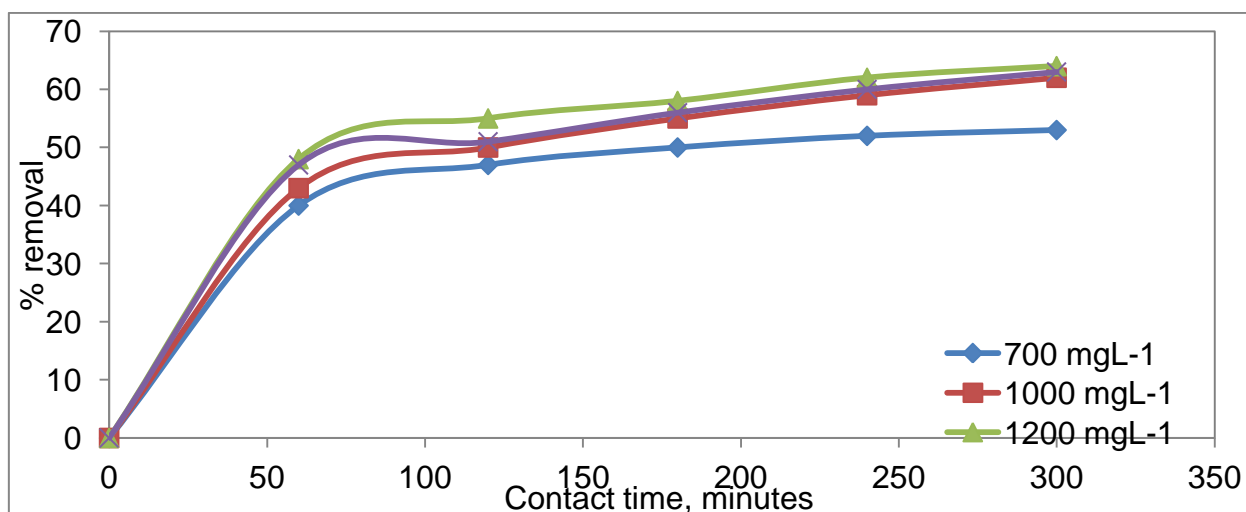


Figure 3.1 Removal of hardness at voltage 5V and contact times (pH=6).

In electrocoagulation processes, applied voltage is an important parameter that controls the rate of reaction and thus the overall efficiency of the process. At high voltages, more dissolution of the metal ions take place and this results in more release of the coagulant dosage, rate of bubble production, size and floc growth<sup>(33,34)</sup>. As the electrical potential increases, the amount of oxidized iron increases and consequently the amount of precipitate/hydroxide flocs with high

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Visit: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 10, October 2017

adsorption rate increases and this leads to an increase in the removal efficiency of hardness. In addition, it was demonstrated that as bubble density increases, their size decreases with increasing applied voltage, resulting in a greater upwards flux and a faster removal of hardness and sludge flotation. Also, as the applied voltage is increased, the time needed to achieve higher removal decreases and the results of this study is in conformity with that of the previous studies<sup>(35)</sup>. As the pH of the solution was increased, hardness removal also increased perhaps due to more hydroxide flocs with high adsorption capacity.

As the obtained values of removal of hardness was good, further experiments were conducted applying increasing voltages of 10 and 15 V and at solution pH of 7.0 and 8.0 and the results are presented in Table 1 and 2. It may be observed from the data presented in Table 1 and 2 that as the applied voltage value was increased, hardness removal also increased. Similarly, as the solution pH value was increased, hardness removal increased marginally.

Table 1. Values of removal of hardness (%) at different applied voltages and solution pH 7

Concentration of Hardness, mgL <sup>-1</sup>	Applied Voltage, V	Contact time, min					
		30	60	120	180	240	300
700	10	25	42	49	53	56	58
	15	29	46	54	57	60	61
1000	10	32	52	60	64	66	67
	15	33	52	59	63	66	68
1200	10	35	55	61	64	67	69
	15	37	56	62	66	69	70
1300	10	35	54	60	63	66	68
	15	40	59	64	67	69	71

Table 2. Values of removal of hardness (%) at different applied voltages and solution pH 8

Concentration of Hardness, mgL <sup>-1</sup>	Applied Voltage, V	Contact time, min					
		30	60	120	180	240	300
700	10	28	48	53	56	60	62
	15	30	49	59	62	64	66
1000	10	32	53	61	65	67	68
	15	34	55	64	68	69	70
1200	10	38	57	66	69	71	72
	15	36	57	68	70	72	73
1300	10	35	56	65	67	68	70
	15	39	59	66	68	70	72

### Simultaneous removal of hardness and fluoride by electrocoagulation:

Ground waters often contain hardness and fluorides in addition to few other quality parameters. In several water treatment plants, chemical coagulation that is employed also removes fluorides. However, not much data is available on removal of hardness. Therefore, electrocoagulation experiments were conducted to investigate simultaneous removal of hardness and fluorides employing different initial hardness of 700, 1000, 1200, 1300mg L<sup>-1</sup> and fluoride concentrations

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Visit: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 10, October 2017

of and 2, 3, 5 mgL<sup>-1</sup>. Different voltages of 5, 10 and 15 V were applied for different contact times of 30, 60, 120,180, 240 and 300 minutes. Experimental results of removal of hardness from a 700 mgL<sup>-1</sup> concentration and at different voltages of 5, 10, and 15V and at different contact times of 30, 60, 120,180, 240 and 300 minutes are presented in Figures 3.2.

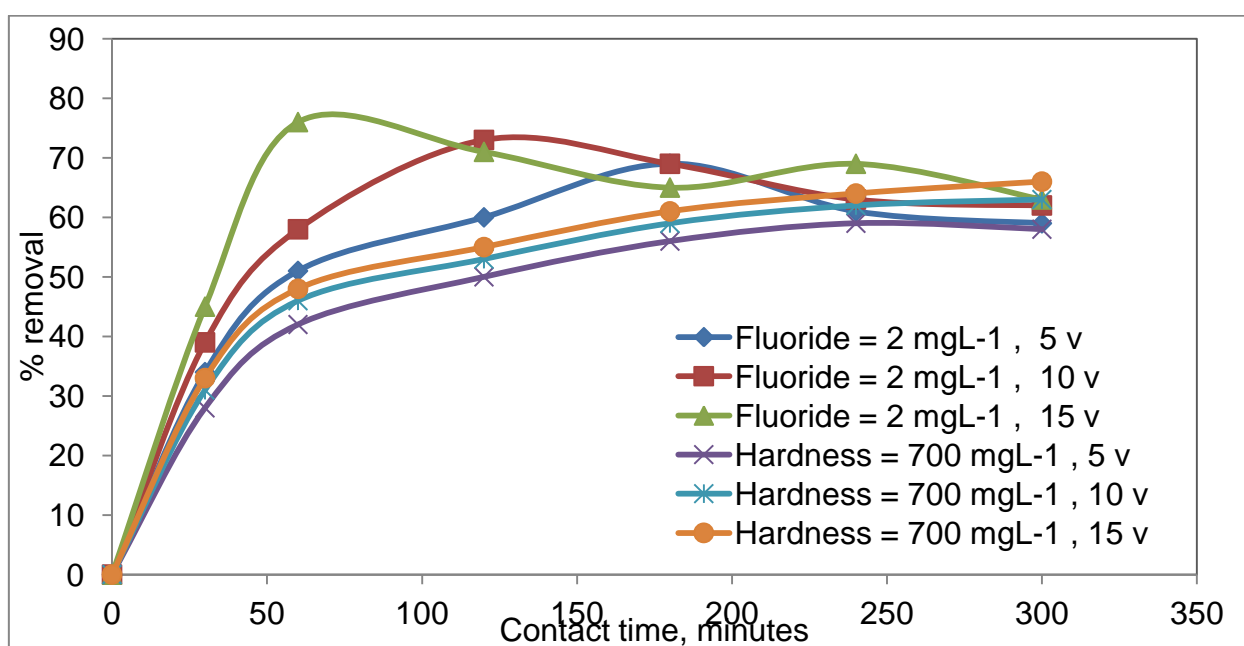


Figure 3.2 Removal of hardness and fluoride at different voltages and contact times (pH=8).

It may be observed from Figure 3.2 that as the contact time increases, hardness removal also increases. However in the case of Fluorides, removal increases upto certain contact time reaching an optimum contact time after which Fluoride removal decreases. As the applied voltage was increased to 10V and 15V, removal of both fluorides and hardness values increased at all contact times. As the simultaneous removal of hardness and Fluorides was good, further experiments were conducted employing higher concentrations of 1000, 1200 and 1300 mgL<sup>-1</sup> hardness and 3 and 5 mgL<sup>-1</sup> of Fluorides at a solution pH of 8 and the results are presented in Table 3.

## International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly, Peer Reviewed Journal)

Visit: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 10, October 2017

Table 3. Values of simultaneous removal of hardness and Fluorides at pH 8

Conc. of Hardness, mgL <sup>-1</sup>	Conc. of Fluorides, mgL <sup>-1</sup>	Applied Voltage, V	Contact time, min.					
			30	60	120	180	240	300
700	2	5	28,34	42, 51	50,60	56, 69	59,61	58,59
		10	31,39	46,58	53,73	59,69	62,63	63,62
		15	33,45	48,76	55,71	61,65	64,69	66,63
	3	5	26,38	43,69	50,73	57,76	60,72	61,73
		10	25,44	46,72	56,78	59,73	62,70	64,68
		15	28,54	50,83	58,80	62,72	65,73	67,70
	5	5	29,44	47,60	53,73	57,79	60,74	61,69
		10	33,53	51,77	57,88	60,85	62,82	64,79
		15	35,59	54,91	60,91	63,85	66,81	67,75
1000	2	5	30,39	51,56	60,67	63,71	66,66	67,62
		10	34,42	55,64	64,75	67,75	69,70	71,69
		15	36,45	58,78	66,76	68,72	71,66	73,65
	3	5	29,31	57,66	62,72	65,77	67,70	69,65
		10	33,51	59,79	64,81	67,78	69,82	73,76
		15	45,49	60,82	65,83	69,79	72,72	73,69
	5	5	30,42	56,59	60,75	64,82	66,78	67,72
		10	35,55	59,76	65,89	68,88	70,83	71,80
		15	41,62	63,90	69,93	71,89	73,83	75,77
1200	2	5	33,41	49,59	59,65	65,71	68,66	69,68
		10	37,47	56,63	65,76	69,75	72,70	73,72
		15	39,53	59,80	67,81	72,74	74,70	76,69
	3	5	32,36	52,66	56,72	60,76	63,71	66,65
		10	35,47	59,78	66,80	69,81	74,73	76,68
		15	43,51	61,84	69,82	74,78	76,79	79,69
	5	5	30,41	50,61	58,76	65,80	66,76	68,70
		10	36,52	55,75	66,86	69,85	71,78	72,79
		15	38,55	63,89	71,90	76,86	77,80	75,78
1300	2	5	33,35	52,49	60,62	63,72	65,68	66,64
		10	38,41	59,66	68,75	73,72	76,70	77,65
		15	41,46	62,79	70,78	75,80	78,72	79,68
	3	5	32,36	51,63	56,69	60,73	63,72	67,70
		10	36,46	54,72	66,77	72,73	75,70	77,68
		15	41,58	59,87	68,86	75,82	81,76	78,71
	5	5	31,40	49,60	57,75	61,81	63,80	65,72
		10	37,53	55,74	66,88	69,86	72,80	74,75
		15	42,60	63,89	70,92	76,90	78,86,	78,80

Note: Values in the Table denote removal % of hardness and Fluoride respectively.

It follows from the data presented in Table 3 that removal of hardness gradually increased as the contact time was increased from 30 minutes to 60, 120, 180, 240, and 300 minutes and also as the applied voltage was increased from 5V to 10 and 15 V. Whereas in the case of fluoride, removal of fluoride also increased with increasing contact time and reached a maximum value and thereafter removal of fluoride decreased.

## International Journal of Innovative Research in Science, Engineering and Technology

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Visit: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 10, October 2017

### Effect of pH on simultaneous removal of hardness and fluoride:

It has been established in previous studies that initial solution pH has a considerable effect on the efficiency of the electrocoagulation process<sup>(36,37)</sup> and also, the pH of the solution changed during the process depending on the type of electrode material and initial pH. Though, electrocoagulation process exhibits some buffering capacity, significant a change in solution pH occurs with a shift to alkaline medium<sup>(38)</sup>. As observed by other investigators<sup>(29,39,40)</sup>, a pH increase occurs when the initial pH is low. Vik et al. (1984)<sup>(39)</sup> ascribed this increase to hydrogen evolution at cathodes. In addition, if the initial pH is acidic, reactions would shift towards a pH increase. In alkaline medium (pH > 8), the final pH does not vary very much and a slight drop was recorded.

In the present study, electrocoagulation experiments were conducted to determine the effect of pH on hardness and fluoride removal efficiency at an applied voltage of 15V and varying pH (6, 7, 8). Hardness and Fluorides concentrations of 700 mgL<sup>-1</sup> and 2 mgL<sup>-1</sup> respectively were used and the results are presented in Figure 3.3.

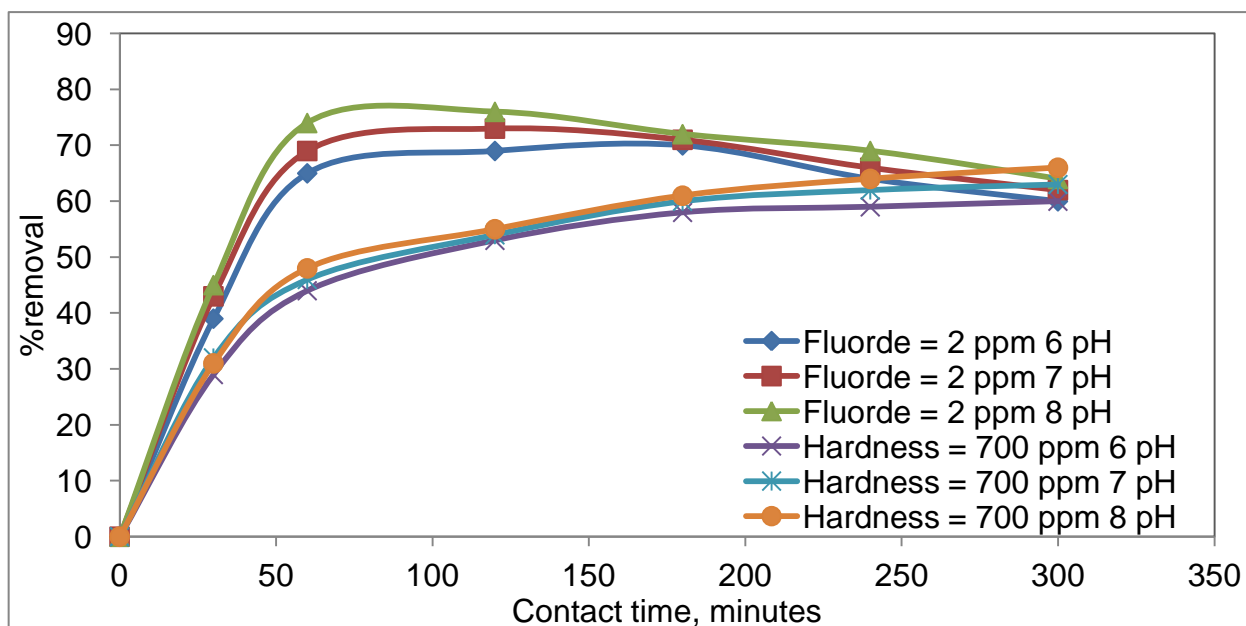


Figure 3.3 Simultaneous removal of hardness and fluoride at 15 V and at different pH.

It may be observed from the Figure 3.3 that, removal of hardness was rapid in the first 60 minutes (45-50% for 700 mgL<sup>-1</sup>) and thereafter, removal was gradual to 58-61% up to 180 minutes. Further increase in contact time up to 300 minutes resulted in a more or less constant removal. In the case of fluoride, within the first 60 minute period, 65-75 % removal was accomplished for a fluoride concentration of 2 mgL<sup>-1</sup> and at an applied voltage of 15V. Thereafter, fluoride removal increased slightly to 69-76% up to 120 minutes and reduced thereafter. In the electrocoagulation process, simultaneous removal of hardness and fluoride occurs on the electrode surface and flocs generated from the iron plate electrode determine the extent of removal. Adsorption on to the flocs and electrodes appears to be the primary removal mechanism.

As there was a good simultaneous removal of hardness and fluoride at 15V and at different pH values of 6, 7 and 8, further electrocoagulation experiments were conducted at Hardness values of 1000, 1200 and 1300 mgL<sup>-1</sup> and Fluorides concentrations of 3 and 5 mgL<sup>-1</sup> and the results are presented in Table 4.

## International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly, Peer Reviewed Journal)

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Vol. 6, Issue 10, October 2017

Table 4. Values of simultaneous removal of hardness and Fluorides (%) at 15 V

Conc. of Hardness, mgL <sup>-1</sup>	Conc. of Fluorides, mgL <sup>-1</sup>	Solution pH	Contact time, min.					
			30	60	120	180	240	300
700	2	6	29,39	44,65	53,69	58,70	59,64	60,60
		7	32,43	46,69	54,73	60,71	62,66	63,62
		8	31,45	48,74	55,76	61,72	64,69	66,64
	3	6	33,40	49,66	58,69	60,68	62,65	63,66
		7	31,49	47,77	55,80	59,79	64,76	67,71
		8	35,54	50,80	58,84	62,82	65,79	67,74
	5	6	29,53	45,81	52,81	56,78	58,74	60,70
		7	32,56	47,87	54,89	59,88	62,82	64,77
		8	35,59	54,87	60,91	63,89	66,85	67,80
1000	2	6	35,40	53,75	62,73	64,69	66,65	68,60
		7	37,43	55,77	64,74	67,70	70,66	71,62
		8	36,45	58,78	66,75	68,76	71,71	73,65
	3	6	30,40	52,72	59,71	63,72	65,69	67,66
		7	34,43	61,79	66,77	69,80	73,76	75,72
		8	37,49	60,82	65,83	69,80	72,76	73,75
	5	6	30,49	56,81	60,80	64,79	66,76	67,78
		7	35,55	59,85	65,83	68,84	70,82	71,80
		8	41,57	63,87	69,85	71,82	73,80	75,79
1200	2	6	35,48	51,76	59,73	64,71	66,67	68,65
		7	38,51	56,78	64,75	69,74	71,70	73,69
		8	39,53	59,80	67,76	72,75	74,72	76,70
	3	6	30,44	52,70	57,68	64,69	66,65	69,66
		7	34,46	60,79	66,80	69,77	73,75	76,74
		8	37,51	61,84	69,82	74,80	76,76	79,75
	5	6	31,48	53,80	59,79	63,75	66,71	67,70
		7	36,53	60,86	68,87	71,85	72,82	73,80
		8	38,55	63,89	71,88	76,85	77,81	75,79
1300	2	6	35,40	53,72	61,70	64,66	67,60	69,61
		7	38,43	56,76	65,75	68,77	72,71	74,65
		8	41,46	62,79	70,76	75,72	78,70	79,67
	3	6	30,46	55,74	61,75	67,70	70,67	72,66
		7	32,51	56,82	69,80	73,81	77,77	78,70
		8	35,58	59,85	68,86	75,87	81,80	78,74
	5	6	32,51	54,81	60,83	65,80	67,76	69,73
		7	37,58	59,86	66,87	71,82	73,80	74,76
		8	42,60	63,92	70,91	76,85	78,80	78,81

Note: Values in the Table denote removal % of hardness and Fluoride respectively.

It follows from the data presented in Table 4 that fluoride removal increases as contact time increases up to a certain contact time and thereafter fluoride removal decreases. In the anodic adsorption layer, the concentration of OH<sup>-</sup> ions is



## International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 6, Issue 10, October 2017

higher than the concentration of  $F^-$ , so the production of the complex  $Fe(OH)_3.F^-$  ion becomes difficult; and this results in the reduction of fluoride removal from water<sup>(36)</sup>.

In the case hardness, removal increase gradually and reaches a more or less maximum value and remains constant thereafter. Similarly as the applied voltage and solution pH is increased, there is a marginal increase in hardness removal. The influence of pH on adsorption can explain the slower rate of pollutant removal with increasing pH. The present study confirms this fact, wherein in the beginning of the process the removal was rapid and thereafter becomes slower due to the continuous evolution of  $H^+$  ions from the cathode; hence pH increase over the time<sup>(41)</sup>.

### Simultaneous removal of hardness and fluoride by chemical coagulation:

To find favorable pH for fluoride removal, coagulation experiments were conducted at three pH values of 5.0, 6.5 and 7.0 and the Fluoride removal data is presented in Figure 3.4.

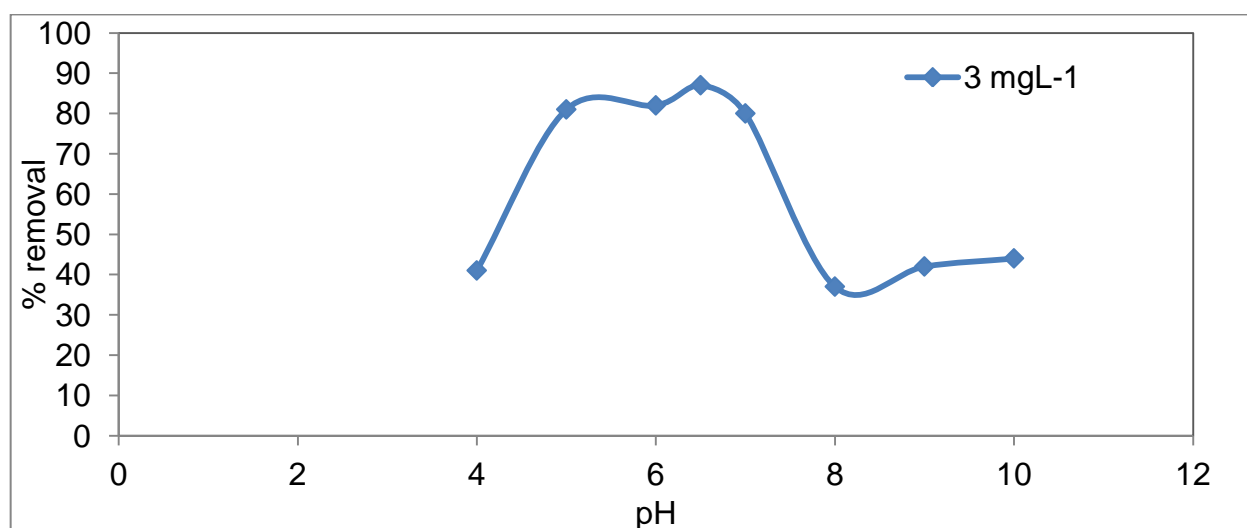


Figure 3.4 Effect of pH on Fluoride removal (alum dose=500 mgL<sup>-1</sup>, F=3 mgL<sup>-1</sup>).

Solution pH is an important factor for the chemical coagulation process. The favourable pH was in the range of 5 - 7 as shown in the figure 3.4 and this range agreed with the optimal defluoridation range expected due to aluminum solubility. Based on the solubility of aluminum with respect to an amorphous aluminum hydroxide, optimum removal for fluoride is expected to occur when the system pH is 6.5 because this is where the highest degree of oversaturation occurs regardless of alum dose. At circumneutral pH, the surface charge of the aluminum hydroxide precipitate is positively charged. The negatively charged fluoride ions in solution are attracted to the positive surface charge of the precipitate and therefore adsorb or complex with the surface of the precipitate. At lower pH values, positively charged, soluble fluoro-aluminum complexes form, decrease the amount of fluoride removal, and scavenge available aluminum to form a precipitate. In addition, the solubility of aluminum increases at low pH values, therefore reducing the overall degree of aluminum oversaturation in solution. Under pH conditions greater than pH 8, the solubility of aluminum increases and therefore reducing the overall degree of aluminum oversaturation in solution.

Chemical coagulation experiments employing standard jar tests were conducted to assess removal of fluoride alone by alum coagulation using alum dosages of 400, 500 and 600 mgL<sup>-1</sup>. Fluoride concentrations of 2, 3 and 5 mgL<sup>-1</sup> were investigated and the results are shown in Figure 3.5. It may be observed from the figures that Fluoride removal was 80-90% for all fluoride concentrations investigated.

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Vol. 6, Issue 10, October 2017

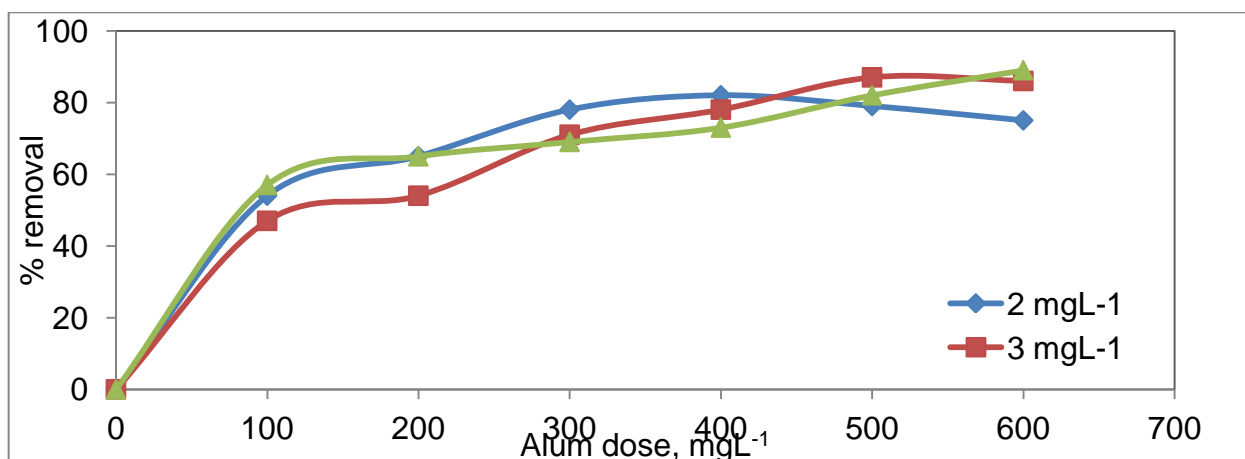


Figure 3.5 Removal of Fluoride by chemical coagulation at pH 6.5

It may be noted from the Figure 3.5 that for an alum dose of 100mgL<sup>-1</sup>, fluoride removal was 47-57% for all concentrations of Fluoride and at a constant pH 6.5. Fluoride removal increased as the alum dosage was increased to 400mgL<sup>-1</sup>, 500mgL<sup>-1</sup>, and 600mgL<sup>-1</sup> for all concentrations investigated. A subsequent increase in alum dosage resulted in a marginal decrease in fluoride removal perhaps due to increase in the overall degree of aluminum oversaturation in solution.

Several coagulation experiments were conducted to investigate removal of hardness alone from a 1300 mgL<sup>-1</sup> solution employing alum dose in the range of 10-1000 mgL<sup>-1</sup> and a hardness removal of 5-8% was obtained which is negligible. Thus chemical coagulation is ineffective for removal of hardness. However, further chemical coagulation experiments employing standard jar tests were conducted to investigate simultaneous removal of hardness and fluoride employing alum as a coagulant. A hardness concentration of 1300 mgL<sup>-1</sup> and a Fluoride concentration of 5 mgL<sup>-1</sup> were used and the results are presented in Figure 3.6

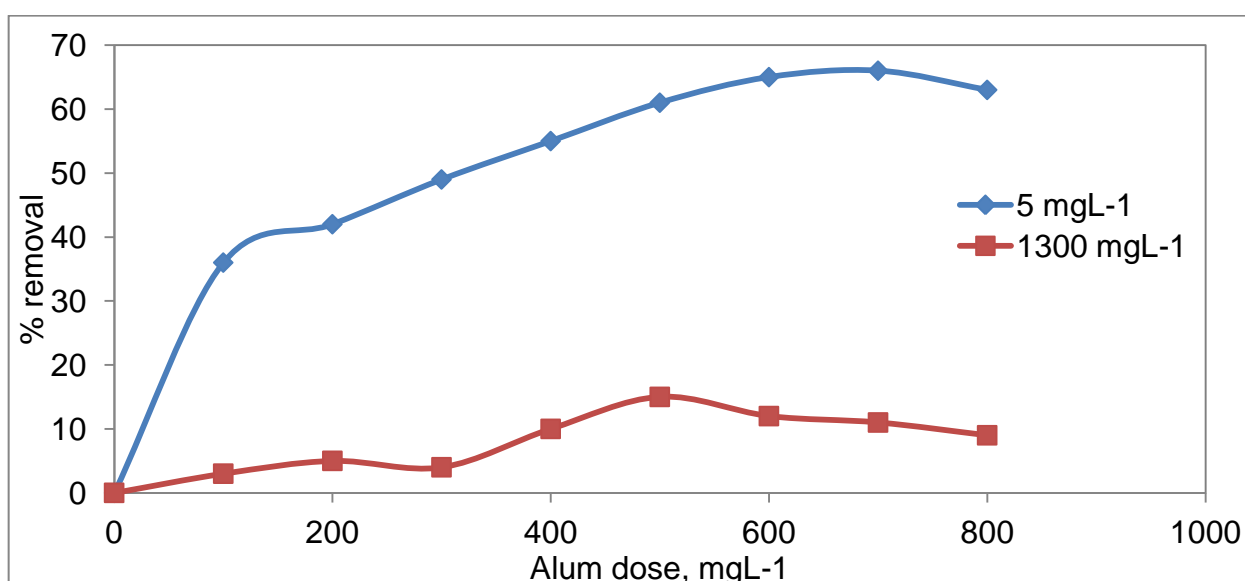


Figure 3.6 Effect of hardness on Fluoride removal.

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Vol. 6, Issue 10, October 2017

It follows from the results presented in figure 3.6 that a maximum fluoride removal of 65% was obtained for an alum dose of  $600 \text{ mgL}^{-1}$  whereas removal of hardness was only 15%. It is thus clear that presence of hardness interferes with the coagulative removal process and reduces the maximum removal of Fluorides. It may be noted that fluoride removal by alum coagulation was 80-90% for all fluoride concentrations of 2, 3 and  $5 \text{ mgL}^{-1}$  and hardness removal was 5-8%. It is clear from the experimental data that presence of hardness concentration of  $1300 \text{ mgL}^{-1}$  interferes and reduces the removal of Fluoride removal; consequently Fluoride removal reduced from 89% to 65%. However, presence of Fluoride ions has no influence and do not interfere in the removal of hardness and thus hardness removal was unaffected and was in the range of 15%. Although the presence of calcium ions enhances fluoride removal efficiency in the sense of  $\text{CaF}_2$  granules adsorbed or precipitate out, the negative impact on the fluoride removal efficiency was due to the ions like  $\text{Mg}^{2+}$ ,  $\text{Cl}_2^-$  and  $\text{SO}_4^{2-}$ .

Limited data is available on the use of iron salts as coagulants for removal of fluoride from drinking water. Sollo, et al (1978) investigated removal of fluoride from a  $5.0 \text{ mgL}^{-1}$  fluoride concentration employing 22 to  $175 \text{ mgL}^{-1}$  (as  $\text{Fe}^{+3}$ ) of ferric sulfate and pH adjusted to values in the range of 4.1 to 9.7 and found < 5.0% of the initial fluoride concentration removed from the solutions with a pH above 6.0. They observed excellent flocs that settled rapidly, but these flocs were very ineffective in the removal of fluoride. As ferric salts are ineffective for removal of Fluoride from water, no chemical coagulation experiments were conducted in this study. So also, no information is available on removal of hardness by ferric salts by chemical coagulation.

## IV. CONCLUSIONS

The present study was attempted to investigate simultaneous removal of hardness and fluoride from synthetic solutions by chemical and electrocoagulation processes. The influence of variables such as pH, reaction time and applied voltage for electrocoagulation and pH, optimum dose for chemical coagulation were investigated. Electrocoagulation was effective in simultaneous removal of hardness (65-78% for all concentrations) and fluorides (74-90% for all concentrations) for contact times 30, 60, 120, 180, 240, and 300 min at applied voltages 5, 10, and 15V. These results demonstrated that at low current values, the time needed to achieve higher efficiencies increased and the cost of the process is determined by the consumption of the sacrificial electrode and the electrical energy. Hence these results suggest 15 V as an optimal electrical potential for the treatment. Experimental results showed that hardness and fluoride removal at pH 8 are more efficient. Chemical coagulation was effective for removal of Fluorides but is ineffective to remove hardness. However, when hardness and Fluorides are present together, Fluoride removal reduced slightly (65%) due to the presence of hardness of concentration of  $1300 \text{ mgL}^{-1}$  against fluoride removal of 89%. Alum coagulation was found effective at optimum pH of 6.5. Ferric salts are ineffective for removal of Fluorides and hardness from water.

## REFERENCES

- [1] M.Arora and R.C.Maheshwari, Investigations on the Batch Performance of Fluoride Adsorption by Coconut Shell Carbon Asian Journal of Water, *Environment and Pollution*, Vol. 4, No. 2, 119-122
- [2] <http://www.fluorideandfluorosis.com/fluorosis/districts.html>
- [3] World Health Organization: Industrial Pollution Control Handbook, H.F. Lund, 1971, McGraw Hill Book Co., New York, p. 4/23-4/39 (1994).
- [4] Tripathy, S.S., Bersillon, J.-L., Gopal, K., 2006. Removal of fluoride from drinking water by adsorption onto alum-impregnated activated alumina. *Separation and Purification Technology*. 50, 310-317.
- [5] He, G.L., Cao, S.R., 1996. Assessment of fluoride removal from drinking water by calcium phosphate systems. *Fluoride* 29, 212-216.
- [6] Tahaikt, M., El Habbani, R., Ait Haddou, A., Achary, I., Amor, Z., Taky, M., Alami, A., Boughriba, A., Hafsi, M., Elmidaoui, A., 2007. Fluoride removal from groundwater by nanofiltration. *Desalination* 212, 46-53.
- [7] Maliyekkal, S.M., Sharma, A.K., Philip, L., 2006. Manganese-oxide-coated alumina: a promising sorbent for defluoridation of water. *Water Research*. 40, 3497-3506.
- [8] Wu, X., Zhang, Y., Dou, X., Yang, M., 2007. Fluoride removal performance of a novel Fe-Al-Ce trimetal oxide adsorbent. *Chemosphere* 69, 1758-1764.

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(A High Impact Factor, Monthly, Peer Reviewed Journal)

Visit: [www.ijirset.com](http://www.ijirset.com)

Vol. 6, Issue 10, October 2017

- [9] Meenakshi, S., Viswanathan, N., 2007. Identification of selective ion-exchange resin for fluoride sorption. *Journal of Colloid Interface Sciences*. 308, 438–450.
- [10] Nawlakhe WG, Kulkarni DN, Pathak BN, Bulusu KR. Defluoridation of Water by Nalgonda Technique. *Indian Journal of Environmental Health* 17 26-64, 1975.
- [11] Bulusu KR, Sundaresan BB, Pathak BN, Nawlakhe WG, Kulkarni DN, Thergaonkarg VP. Fluorides in Water. Defluoridation Methods and their Limitations. *Journal of Institution. Engineers. (India). Environmental. Engineering Division* 60 1-25 1993.
- [12] Boruff CS. Removal of Fluorides from Drinking Waters. *Industrial and Engineering Chemistry* 26 70-75 1936.
- [13] Culp RI, Stottenberg HA. Fluoride Reduction at Crosse Kansas. *Journal of American Water Works Association* 50 423-426 1958.
- [14] Scott RD, Elvolve E, Stotenberg HA. Fluoride in Ohio Water Supplies. Its Effect Occurrence and Reduction. *Journal of American Water Works Association* 29 9-15 1937.
- [15] Susheela AK. Technical Information for Training cum awareness Camp for Doctors. *Public Health Engineers and other Officers on Prevention and Control of Fluorosis*, New Delhi, India.
- [16] M. Yan, D. Wang, J. Ni, J. Qu, Y. Yan, C.W.K. Chow, Effect of polyaluminum chloride on enhanced softening for the typical organic-polluted high hardness North-China surface waters, Separation and Purification Technology. 62 (2008) 401–406
- [17] K. Suzuki, Y. Tanaka, T. Osada, M. Waki, Removal of phosphate, magnesium and Calcium from swine wastewater through crystallization enhanced by aeration, *Water Research*. 36 (2002) 2991–2998.
- [18] A. Dimirkou, M.K. Doula, Use of clinoptilolite and an Fe-over exchanged clinoptilolite in Zn<sup>2+</sup> and Mn<sup>2+</sup> removal from drinking water, *Desalination*. 224 (2008) 280–292.
- [19] R. Sheikholeslami, Composite scale formation and assessment by the theoretical Scaling Potential Index (SPI) proposed previously for a single salt, *Desalination* 278 (2011) 259–267.
- [20] L. Fu, J. Wang, Y. Su, Removal of low concentrations of hardness ions from aqueous solutions using electrodeionization process, *Separation and Purification Technology*. 68 (2009) 390–396.
- [21] J.S. Park, J.H. Song, K.H. Yeon, S.H. Moon, Removal of hardness ions from tap water using electromembrane processes, *Desalination* 202 (2007) 1–8.
- [22] J.N. Apell, T.H. Boyer, Combined ion exchange treatment for removal of dissolved organic matter and hardness, *Water Research*. 44 (2010) 2419–2430.
- [23] H. Faghilian, M.G. Maragheh, H. Kazemian, The use of clinoptilolite and its sodium form for removal of radioactive caesium, and strontium from nuclear wastewater and Pb<sup>++</sup>, Ni<sup>++</sup>, Cd<sup>++</sup>, Ba<sup>++</sup> from municipal wastewater, *Applied Radiation and Isotopes*. 4 (1999) 655–661.
- [24] H. Kazemian, H. Modarres, H.G. Mobtaker, Evaluating the performance of an Iranian natural clinoptilolite and its synthetic zeolite P for removal of Cerium and Thorium from nuclear wastewaters, *Journal of Radioanalytical and Nuclear Chemistry*. 258 (2003) 551–556.
- [25] S.J. Seo, H. Jeon, J.K. Lee, G.Y. Kim, D. Park, H. Nojima, J. Lee, S.H. Moon, Investigation on removal of hardness ions by capacitive deionization (CDI) for water softening applications, *Water Research*. 44 ( 2010 ) 2267–2275.
- [26] C.W. Li, J.C. Liao, Y.C. Lin, Integrating a membrane and a fluidized pellet reactor for removing hardness: effects of NOM and phosphate, *Desalination* 175 (2005) 279 288.
- [27] A. Torabian, H. Kazemian, L. Seifi, G.N. Bidhendi, A.A. Azimi, S.K. Ghadiri, Removal of Petroleum Aromatic Hydrocarbons by Surfactant-Modified Natural Zeolite, *Clean*. 38 (2010) 77-83.
- [28] L. Seifi, A. Torabian, H. Kazemian, G.N. Bidhendi, A.A. Azimi, S. Nazmara, M. A. M., Adsorption of BTEX on surfactant modified granulated natural zeolite nanoparticles: Parameters optimizing by applying Taguchi experimental design method, *Clean-Soil, Air, Water*, 39 (2011) 939–948.]
- [29] Edris Bazrafshan, Kamal Aldin ownagh, and Amir hossein mahvi.,2012. Application of Electrocoagulation Process Using Iron and Aluminum Electrodes for Fluoride Removal from Aqueous Environment. *E-Journal of Chemistry*, 9(4), 2297-2308.
- [30] USEPA, standard operating procedure for preparation of hard water and other diluents for antimicrobial products.
- [31] APHA, AWWA, WEF. (1995) 'Standard Methods for Examination of water & wastewater', 19th edition, APHA, AWWA, WEF, Washington, D.C.
- [32] USEPA procedure for enhanced coagulation (USEPA, 1999).
- [33] Letterman R D, Amirtharajah A and O'Melia C R, Chapter 6, Coagulation and flocculation, in, *Water quality and treatment*, 5th., AWWA, McGraw-Hill., New York, 1999.
- [34] Holt P H, Barton G W, Wark M and Mitchell A A, *Colloids Surf. A: Physicochemical and Engineering Aspects*, 2002, 211, 233.
- [35] Ranta kumar, p., Chaudhary, s., Khilar, K.C., Mahajan, S.P., (2004). Removal of arsenic from water by electro coagulation, *Chemosphere*, 55 (9):1245 – 1252.
- [36] Chen X, Chen G and Po L Y, *Separation and Purification Technology*, 2000, 9, 65.
- [37] Adhoum N, Monser L, Bellakhal N and Belgaied J E, *J. Hazardous Mater*, 2004, B112, 207.
- [38] Bayramoglu M, Kobyay M, Can O T and Sozbir M, *Separation and Purification Technology*, 2004, 37, 117.
- [39] Vik E A, Carlson D A, Eikum A S and Gjessing E T, *Water Research*, 1984, 18, 1355.
- [40] Yao Hua Ch, Lien Loa Sh, Kuan W H and Lee Y D, *Separation and Purification Technology*, 2008, 60, 1.
- [41] Kumar, P.R.; Chaudhari, S.; Khilar, K.C.; Mahajan, S.P. Removal of arsenic from water by electrocoagulation. *Chemosphere* 2004, 55, 1245-1252.
- [42] Sollo, F. W., Jr., Larson, T. E., and Mueller, H. F. (1978). Fluoride removal from potable water supplies Report No. 136, Office of Water Research and Technology, U. S. Department of the Interior, Washington, D. C.