

**REMOVAL OF FLUORIDE FROM WATER BY USING  
METAL-LOADED ORANGE WASTE**

**September 2012**

**Department of Energy and Material Science  
Graduate School of Science and Engineering  
Saga University**

**HARI PAUDYAL**

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A dissertation submitted in partial fulfillment of the requirements for the degree of  
**Doctor of Philosophy (Ph.D.)** in Chemical Engineering

by

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## Overview of Entire Thesis

Fluoride pollution in water is a result of natural leaching of fluoride from various fluoride containing mineral or induced anthropogenic activities, such as mining, metal plating, metal refining, semiconductor production and fertilizer manufacture. Fluoride ion is highly reactive ion which has high affinity with bone tissue, so that it can be accumulated easily in bone tissue once we have ingested through food, drinks or cosmetics. Fluoride ion concentration less than  $1 \text{ mg dm}^{-3}$  protects our dental caries whereas exceeding the amount of fluoride ion ( $> 1.5 \text{ mg dm}^{-3}$ ) changes the chemical constituent in our bone tissue by replacing hydroxyl ions from hydroxyapatite of our bone tissue and converts it into fluoapatite. Such a change in our bone tissue causes serious health hazards in severe case known as skeletal fluorosis. In order to remove the excessive level of fluoride from water many defluoridation method such as precipitation, ion exchange, membrane and adsorption have been reported to be successful. The adsorption of fluoride onto the adsorbent derived from biomass waste is considered to be promising technology because feed materials used for adsorbents are waste themselves, easily available, and have functional diversity; consequently, they have high potential as adsorbents. In the present investigation, 14 different types of metal loaded orange waste adsorbents were successfully prepared from wet orange juice residue just after juicing and dried orange juice residue (DOJR) marketed as cattle food in Japan after simple chemical modification. For the preparation of the adsorbents, wet orange juice residue was treated with lime water in order to saponify the methyl ester part of orange pectin and converted into saponified orange juice residue (SOJR) whereas dried orange juice residue (DOJR) was water washed prior to metal loading reaction. After loading metal ions, adsorption behavior of fluoride ion by using modeled solution and actual plating solution were systematically investigated both in batch and column mode operation.

In **Chapter 2**, adsorbent was prepared from orange juice residue (OJR) by treating with calcium hydroxide to convert OJR into SOJR by saponification reaction of methyl ester part of orange pectin in OJR. It was followed by loading of some multivalent metal ions such as Al, Fe, Ce, Sn, Ti and V to produce metal loaded orange juice residue (M-SOJR). Adsorption of fluoride ion was performed by using M-SOJR at various conditions which showed that, orange waste gels loaded with Al ion exhibited highest adsorption at around pH 6 whereas other metal

loaded adsorbents remove fluoride from acidic pH, thus Al loaded SOJR was considered to be a promising candidate to remove fluoride at neutral pH. The detail investigation of fluoride adsorption by using Al-SOJR was performed at pH 6 along with the exploration of fluoride binding and desorption mechanism onto M-SOJR.

Although adsorption behavior of Al, Fe, Sn, Ce, Ti, and Sn loaded orange waste gels were satisfactory, but maximum adsorption capacity and selectivity to fluoride ion over other anionic species were little bit poor; so that, further improvement was attempted. In **Chapter 3**, improvement of maximum adsorption capacity and selectivity to fluoride ion was conducted by loading Zr(IV) ion onto SOJR. The Zr(IV) loaded SOJR demonstrated very high adsorption capacity compared to the adsorbents investigated in the preceding chapter. Further, it was found that the selectivity towards fluoride ion was also successfully improved by loading Zr(IV) ions in the presence of high concentration of other co-existing ions. The result also showed effective adsorption of fluoride onto Zr-SOJR followed by effective elution using dilute alkali solution without destruction of active adsorption sites up to 10 repeated cycle, suggesting that Zr(IV) ions was stably immobilized onto the polymer matrix of orange juice residue.

In **Chapter 4**, the adsorption behavior of some rare earth metal ions onto orange waste gels and their application to the removal of fluoride were studied in detail. The results demonstrated that SOJR can effectively adsorb rare earth metal ions such as La(III), Sc(III), Ho(III), Sm(III) and Lu(III) from aqueous medium. In addition, for the treatment of water containing trace amount of fluoride, rare earth metal loaded SOJR, especially La-and Sm loaded SOJR, were found to be effective, indicating that these novel adsorbents can be utilized for fluoride ion removal from water.

In the adsorption of fluoride on various metal loaded adsorbents discussed in Chapters 2, 3 and 4, it was shown that adsorption capacity of fluoride ion by using SOJR loaded with tetravalent metal ion such as Zr(IV) was found to be much higher than that of trivalent metal loaded adsorbents. Hence, we thought that oxidation states of loaded metal ion in the adsorbent play some important roles for adsorption of fluoride ion. So that, in **Chapter 5**, investigation of the adsorption behavior of Ce(III) and Ce(IV) loaded SOJR for fluoride were performed to explore the effect of oxidation state of cerium ion loaded on SOJR and suitably formulate fluoride adsorption mechanism.

In the preceding Chapters, SOJR was prepared from wet orange juice residue by long chemical procedures i.e. pre-treatment, saponification and metal loading that consume some amounts of chemicals and produced large volume of waste washing water that needs further treatment before discharge. In order to overcome such a drawback, new economical method was developed to prepare effective adsorbent for fluoride ions from dried orange juice residue, i.e. DOJR, which is now commercially available as cattle food in Japan in **Chapter 6**. It was water washed and dried before metal loading. The metal loaded DOJR, especially Zr-DOJR, exhibited effective adsorption for fluoride in batch and column mode with high selectivity and high adsorption capacity. The adsorbed fluoride was successfully eluted by using dilute alkali solution suggesting reusability of adsorbent. Cycle test up to 9 repeated adsorption elution and re-adsorption cycles. The results shows the effective adsorption of fluoride onto Zr-DOJR and its successful elution by using dilute alkali solution, suggesting high stability of adsorbent with negligible destruction of active site during fluoride adsorption.

In **Chapter 7**, the adsorption behavior of two different types commercial resins (READ-F resins) containing hydrated oxides of Zr(IV) or Ce(IV) were tested and compared with that of metal loaded orange waste adsorbent investigated in this work along with other adsorbent reported in various literatures.

The Zr(IV) loaded orange gel exhibited very high selectivity towards fluoride ion and also high adsorption capacity, whereas Al(III) loaded orange waste gel remove fluoride at pH near neutral pH. The effectiveness of Zr(IV) loaded orange waste adsorbent for fluoride ion was realized from the effective adsorption of fluoride from actual plating solution both in batch and continuous system. Hence, the application of metal loaded orange waste adsorbent, especially Zr(IV)-DOJR, is expected to be a promising candidate for the economical treatment of water that contains trace amount of fluoride ion.

# TABLE OF CONTENTS

	<b>Page No.</b>
<b>Overview of entire thesis</b>	
<b>Table of contents.....</b>	<b>i</b>
<b>List of Figures.....</b>	<b>viii</b>
<b>List of Tables .....</b>	<b>xiv</b>
<b>List of Schemes.....</b>	<b>xvi</b>
<b>Acknowledgement.....</b>	<b>xvii</b>
<b>Abstract .....</b>	<b>xix</b>

## Chapter 1

### Background of the Study

1.1 General introduction.....	1
1.2 Fluorine and fluoride.....	3
1.2.1 Introduction.....	3
1.2.2 Occurrence of fluoride.....	4
1.2.3 Geochemistry and aqueous chemistry .....	4
1.2.4 Applications of fluoride.....	6
1.2.4.1 Industrial application of fluoride.....	6
1.2.4.2 Water fluoridation.....	8
1.2.5 Fluoride toxicity and its adverse effect on human health.....	9
1.3.6 Defluoridation.....	12
1.3 Orange waste, its composition and possible applications to separation science.....	18
1.4 Objectives of present study.....	20
<b>References cited.....</b>	<b>22</b>

## Chapter 2

### Orange Waste Adsorbent Loaded with Multi-valent Metal Ions

2.1 Introduction.....	31
2.2 Experimental procedure.....	32
2.2.1 Chemicals.....	32
2.2.2 Instrumental analysis.....	33
2.2.3 Preparation of metal loaded saponified orange waste gels.....	33
2.2.4 Stripping of loaded metal ions using hydrochloric acid.....	34
2.2.5 Aquaregia dissolution.....	34
2.2.6 Batch wise adsorption tests of metal ions and fluoride ion.....	35
2.2.7 Desorption of fluoride.....	36
2.3 Results and discussions.....	36
2.3.1 Characterization of adsorbents.....	36
2.3.1.1 Measurement of functional group modification.....	36
2.3.1.2 Evaluation of amount of loaded metal ions.....	37
2.3.1.3 Stability of M-SOJR in aqueous solution.....	38
2.3.2 Adsorption of metal ions onto SOJR.....	39
2.3.2.1 pH variation of metal ions adsorption on SOJR.....	39
2.3.2.2 Acid stripping of loaded metal ions from M-SOJR.....	40
2.3.3 Adsorption of fluoride onto metal loaded saponified orange gels.....	41
2.3.3.1 Time course dependency.....	41
2.3.3.2 Effect of pH.....	41
2.3.3.3 Effect of fluoride ion concentration.....	43
2.3.3.4 Effect of adsorbent dosage.....	45
2.3.3.5 Effect of co-existing ions.....	46
2.3.3.6 Mechanism of fluoride adsorption and desorption.....	46
2.3.3.7 Leakage of loaded Al(III) ion.....	47
2.3.4 Desorption of fluoride ion.....	48
2.4 Conclusion.....	49
<b>References cited.....</b>	<b>50</b>



## Chapter 3

### Improvement of Selectivity and Uptake Capacity of Adsorbent by Loading Zr(IV) Ion onto Orange Juice Residue for the Removal of Fluoride from Water

3.1 Introduction.....	51
3.2 Experimental procedure.....	52
3.2.1 Preparation of Zr-SOJR from orange waste.....	52
3.2.2 IR spectroscopy and Zr(IV) content analysis.....	53
3.2.3 Incineration behavior of orange waste adsorbents.....	53
3.2.4 Batch wise adsorption.....	54
3.2.5 Continuous adsorption test.....	54
3.3 Results and discussion.....	55
3.3.1 Analytical, spectroscopic, thermal characterization.....	55
3.3.1.1 Stripping of Zr(IV) ions from Zr-SOJR.....	55
3.3.1.2 Incineration of orange waste adsorbents.....	55
3.3.1.3 Functional group analysis.....	56
3.3.2 Results of batch wise adsorption test.....	57
3.3.2.1 Effect of contact time .....	57
3.3.2.2 Adsorption isotherm.....	58
3.3.2.3 Selectivity test.....	59
3.3.2.4 Effect of temperature.....	60
3.3.2.5 Removal of fluoride from actual plating solution.....	63
3.3.2.6 Leakage of loaded Zr(IV) from gel.....	64
3.3.2.7 Cycle test of Zr-SOJR.....	65
3.3.3 Adsorption performance in a packed column.....	66
3.4 Conclusion.....	68
<b>References cited.....</b>	<b>69</b>

## Chapter 4

### Adsorption Behavior of Orange Waste Gel for Some Rare Earth (RE) Ions and Its Application to the Removal of Fluoride from Water

4.1 Introduction.....	70
4.2 Experimental procedure.....	72

4.2.1 Rare earth metal ion adsorption on orange waste (Synthesis of Re-SOJR).....	72
4.2.2 Batch wise adsorption test.....	73
4.2.3 Leakage of RE ions.....	73
4.2.4 Energy dispersive X-ray (EDX) spectroscopy.....	74
4.3 Results and discussion.....	74
4.3.1 Spectroscopic characterization of adsorbents.....	74
4.3.2 Adsorption of RE metal ions.....	76
4.3.2 .1 Effect of pH on the adsorption of RE metal ions on SOJR.....	76
4.3.2 .2 Adsorption isotherms of RE metal ions on SOJR.....	77
4.3.3 Application of RE-SOJR for fluoride removal.....	79
4.3.3.1 Effect of contact time .....	79
4.3.3.2 Effect of solution pH.....	79
4.3.3.3 Adsorption isotherm of fluoride .....	80
4.3.3.4 Influence of adsorbent amount.....	82
4.3.3.5 Elution of loaded fluoride.....	83
4.3.3.6 Leakage of metal ions from RE-SOJR.....	84
4.4 Conclusion .....	85
<b>References cited</b> .....	86

## Chapter 5

### **Influence of Oxidation State of Cerium Ion for the Adsorption Behavior of Fluoride Ions by Using Orange Waste Loaded with Tetravalent and Trivalent Cerium Ion**

5.1 Introduction.....	87
5.2 Experimental Procedure.....	88
5.2.1 Measurement of total amount of acidic functional group in SOJR.....	88
5.2.2 Creation of active site by increasing oxidation state of cerium ion.....	89
5.2.3 Adsorption experiment.....	89
5.2.4 Elution of loaded fluoride.....	90
5.2.5 Complete dissolution of Ce-SOJR.....	90
5.3 Results and discussion.....	90
5.3.1 Characterization of adsorbent.....	90
5.3.1.1 Amount of acid functional group in SOJR.....	90
5.3.1.2 Measurement of loaded amount of Ce(III) and Ce(IV).....	90

5.3.1.3 Spectroscopic analysis by EDX.....	91
5.3.2 Influence of pH of the solution.....	91
5.3.3 Effect of equilibrium concentration.....	92
5.3.4 Effect of temperature and thermodynamic investigation.....	94
5.3.5 Desorption of fluoride from loaded Ce(III)- and Ce(IV)-SOJR .....	96
5.4 Stoichiometric calculation for the investigation of adsorption mechanism.....	97
5.5 Conclusion.....	99
<b>References cited .....</b>	<b>99</b>

## Chapter 6

### **Novel way of Using Commercially Available Dried Orange Juice Residue for the Treatment of Trace Concentration of Fluoride from Water**

6.1 Introduction.....	100
6.2 Experimental Procedure.....	101
6.2.1 Creation of active sites on dried orange juice residue.....	101
6.2.2 Analysis of surface composition and functional modification.....	102
6.2.3 Analysis of loaded metal ions.....	102
6.2.4 Batch wise studies.....	102
6.2.5 Continuous adsorption studies.....	103
6.3 Results and discussion.....	103
6.3.1 Characterization of adsorbents.....	103
6.3.1.1 Spectroscopic analysis.....	103
6.3.1.2 Analysis amount of metal ions loaded on M-DOJR.....	106
6.3.2 Batch wise adsorption of fluoride.....	106
6.3.2.1 Effect of contact time .....	106
6.3.2.2 Effect of pH.....	107
6.3.2.3 Adsorption isotherm of fluoride.....	107
6.3.2.4 Effect of foreign ions.....	109
6.3.2.5 Leaking of behavior of loaded Zr(IV).....	110
6.3.2.6 Fluoride removal from actual waste plating solution .....	111
6.3.2.7 Striping of loaded fluoride.....	112
6.3.2.8 Adsorption followed by elution and re-adsorption cycle.....	112
6.3.3 Continuous adsorption of fluoride in a packed column of Zr(IV)-DOJR.....	114

6.3.3.1 Effect of pH.....	114
6.3.3.2 Effect of feed concentration.....	115
6.3.3.3 Effect of flow rate.....	116
6.3.3.4 Influence of bed depth.....	118
6.3.3.5 Comparative study with other adsorbents.....	119
6.3.3.6 Application of Zr(IV)-DOJR in actual plating solution.....	120
6.4 Conclusion.....	122
<b>References cited</b> .....	123

## Chapter 7

### **Adsorption of Fluoride from Water by Using Porous Resins of Ethylene Vinyl Alcohol Containing Hydrated Oxide of Ce(IV) or Zr(IV) and Their Comparison with Other Adsorbents Including Metal Loaded Orange Waste Gel**

7.1 Introduction.....	125
7.2 Materials and method.....	126
7.2.1 Adsorbents.....	126
7.2.2 Batch wise adsorption test.....	126
7.2.3 Continuous adsorption and elution.....	127
7.3 Results and discussion.....	127
7.3.1 Spectral analysis of IR, XRD and EDX.....	127
7.3.2 Batch adsorption test of fluoride.....	129
7.3.2.1 Effect of pH.....	129
7.3.2.2 Adsorption isotherm .....	130
7.3.3 Dynamic adsorption followed by elution.....	131
7.3.4 Comparative study of adsorption capacities.....	133
7.4 Conclusion .....	136
<b>References cited</b> .....	137

## Chapter 8

<b>Concluding Remarks</b> .....	139
---------------------------------	-----

<b>Appendix.....</b>	<b>142</b>
<b><u>List of published papers</u>.....</b>	<b>143</b>
<b><u>Patent</u>.....</b>	<b>144</b>
<b><u>Papers prepared for publication</u>.....</b>	<b>144</b>
<b><u>Participation at different scientific forum</u>.....</b>	<b>145</b>

## List of Figures

Figures	Page No.
<b>Fig. 1.1</b> Fluoride speciation in water varies with pH, these speciation boundaries were calculated with the PHREEQC code and the WATEQ4F database	5
<b>Fig. 1.2</b> Structure of pectin	19
<b>Fig. 2.1</b> Fourier transform infrared spectra (FT-IR) of different types of orange gels	37
<b>Fig. 2.2</b> Analysis of total organic carbon leaked from the various adsorbents at temperature 30°C after 24 h shaking at different pH	39
<b>Fig. 2.3</b> Effect of pH for the adsorption of some metal ions ( $\sim 0.2 \text{ mmol dm}^{-3}$ each) from mixed solution by using saponified product of orange juice residue (volume of solution = $10 \text{ cm}^3$ , weight of gel = 10 mg, and temperature = 30°C)	40
<b>Fig. 2.4</b> Kinetics study of fluoride adsorption by using different types of M-SOJR (solid liquid ratio = $1 \text{ g dm}^{-3}$ , feed concentration = $\sim 1 \text{ mmol dm}^{-3}$ , and temperature = 30°C)	41
<b>Fig. 2.5</b> Percentage adsorption of fluoride by different types of M-SOJR as a function of equilibrium pH (volume of solution = $10 \text{ cm}^3$ , weight of gel = 10 mg, shaking time = 24 h, feed concentration = $\sim 10 \text{ mg dm}^{-3}$ , and temperature = 30°C)	42
<b>Fig. 2.6</b> Adsorption isotherm of fluoride onto metal loaded SOJR from water at their optimal pH (a) Experimental plot, (b) Langmuir isotherm, and (c) Freundlich isotherm model (volume of solution = $10 \text{ cm}^3$ , weight of gel = 10 mg, shaking time = 24 h, shaking speed = 150 rpm, and temperature = 30°C)	44
<b>Fig. 2.7</b> Removal of trace concentration of fluoride ion by using Al-SOJR at different dosage (volume of solution = $10 \text{ cm}^3$ , shaking time = 24 h, pH = 6, temperature = 30°C)	45
<b>Fig. 2.8</b> Adsorption of fluoride ion by Al-SOJR from binary mixture of various co-existing ions (volume of solution = $10 \text{ cm}^3$ , weight of gel = 10 mg, shaking time = 24 h, fluoride solution = $\sim 13.6 \text{ mg dm}^{-3}$ , and temperature = 30°C)	46

- Fig. 2.9** Leakage of loaded Al(III) from Al-SOJR at varying concentration of fluoride ions at different pH (volume of solution = 10 cm<sup>3</sup>, weight of gel = 10 mg, shaking time = 24 h, shaking speed = 150 rpm, and temperature = 30°C) **48**
- Fig. 3.1** Relationship between the weight remains percentage of H-SOJR, SOJR, and Zr-SOJR as a function of incinerating temperature **56**
- Fig. 3.2** Infrared spectra of (a) raw orange juice residue (OJR), (b) saponified orange juice residue (SOJR), and (c) zirconium loaded saponified orange juice residue (Zr-OJR) **57**
- Fig. 3.3** Time variation of fluoride adsorption by Zr-SOJR at different initial fluoride concentrations (solid/liquid ratio = 1.33 g dm<sup>-3</sup>, pH = 4, shaking time = 24 h, shaking speed = 150 rpm, and temperature = 30°C) **58**
- Fig. 3.4** Adsorption isotherm of fluoride onto Zr-SOJR at different pH (volume of solution = 15 cm<sup>3</sup>, weight of gel = 25 mg, and temperature = 30°C) **59**
- Fig. 3.5** Removal of fluoride by Zr-SOJR from co-existing system at solid/liquid ratio of 1.33 g dm<sup>-3</sup> at 30°C (a) co-existing ions at varying pH (F = 1.57 mmol dm<sup>-3</sup>), and (b) at varying concentration of co-existing ions at pH 4 (F = 1 mmol dm<sup>-3</sup>) **60**
- Fig. 3.6** Effect of temperature on fluoride adsorption onto Zr-SOJR (volume of solution = 15 cm<sup>3</sup>, weight of gel = 25 mg, pH = 4, shaking time = 24 h, shaking speed = 150 rpm) (a) adsorption isotherm, and (b) corresponding Langmuir plot **61**
- Fig. 3.7** Van't Hoff plot for the adsorption of fluoride ion onto Zr-SOJR **62**
- Fig. 3.8** Removal of fluoride from actual plating (38.2 mg dm<sup>-3</sup>) solution by using Zr-SOJR (volume of solution = 10 cm<sup>3</sup>, pH = 3, shaking time = 24 h, shaking speed = 150 rpm and temperature = 30°C) **64**
- Fig. 3.9** Leakage of loaded Zr(IV) at varying concentration of fluoride at different pH (volume of solution = 10 cm<sup>3</sup>, shaking time = 24 h, weight of gel = 10 mg, shaking speed = 150 rpm, and temperature = 30°C) **65**

**Fig. 3.10** Cycle tests of fluoride adsorption followed by elution using NaOH solution (solid/liquid ratio =  $2.5 \text{ g dm}^{-3}$ , fluoride solution =  $30 \text{ mg dm}^{-3}$ , shaking time = 24 h, eluent = 0.1 M NaOH, and temperature =  $30^\circ\text{C}$ ) **66**

**Fig. 3.11** Column performance of fluoride adsorption onto fixed bed column of Zr-SOJR ((Feed solution =  $14.82 \text{ mg dm}^{-3}$ , flow rate =  $5.7 \text{ cm}^3 \text{ h}^{-1}$ , pH = 4, weight of gel = 1.02 g, volume of the gel =  $2.11 \text{ cm}^3$ , and eluent = 0.1 M NaOH), (a) breakthrough curve, (b) breakthrough curve below  $5 \text{ mg dm}^{-3}$  (c) desorption profile **67**

**Fig. 4.1** Energy dispersive X- ray (EDX) spectra of (a) SOJR and (b) La(III)-SOJR **74**

**Fig. 4.2** Infrared spectra of (a) orange juice residue (OJR), (b) Saponified orange juice residue (SOJR), (c) Sm(III) loaded SOJR (Sm-SOJR),(d) all plot between  $2100 \text{ to } 1200 \text{ cm}^{-1}$  **75**

**Fig. 4.3** Adsorption of some rare earth (RE) metal ions from the mixed solution onto SOJR (metal solution =  $0.2 \text{ mmol dm}^{-3}$  each, volume of solution =  $15 \text{ cm}^3$ , weight of SOJR = 25 mg, shaking time = 24 h, shaking speed = 150 rpm, and temperature =  $30^\circ\text{C}$ ) **77**

**Fig. 4.4** Adsorption isotherms of some rare earth metal ions on saponified orange juice residue (a) adsorption isotherm and (b) corresponding Langmuir plot (volume of solution =  $15 \text{ cm}^3$ , weight of gel = 25 mg, shaking time = 24 h, and temperature =  $30^\circ\text{C}$ ) **78**

**Fig. 4.5** Time dependency of fluoride adsorption onto RE-SOJR from water (volume of solution =  $15 \text{ cm}^3$ , weight of RE-SOJR = 25 mg, fluoride concentration =  $\sim 0.57 \text{ mmol dm}^{-3}$ , shaking time = 24 h, shaking speed = 150 rpm, and temperature =  $30^\circ\text{C}$ ) **79**

**Fig. 4.6** Effect of pH for the adsorption of fluoride ( $\sim 10 \text{ mg dm}^{-3}$ ) by metal loaded orange gel (volume of solution =  $15 \text{ cm}^3$ , weight of gel = 25 mg, shaking time = 24 h, shaking speed = 150 rpm, and temperature =  $30^\circ\text{C}$ ) **80**

**Fig. 4.7** Adsorption isotherm of fluoride onto RE-SOJR (a) adsorption isotherm plot, (b) Langmuir plot, and (c) Freundlich plot (volume of solution =  $15 \text{ cm}^3$ , weight of gel = 25 mg, shaking time = 24 h, shaking speed = 150 rpm, and temperature =  $30^\circ\text{C}$ ) **81**

**Fig. 4.8** Influence of La(III)-SOJR and Sm(III)-SOJR amount for the adsorption of trace amount of fluoride from aqueous solution (feed solution =  $15.24 \text{ mg dm}^{-3}$ , volume of solution =  $15 \text{ cm}^3$ ,



- pH = 4 for La(III)-SOJR, pH = 5 for Sm(III)-SOJR, shaking time = 24 h, shaking speed = 150 rpm, and temperature = 30°C) **83**
- Fig. 4.9** Leakage of metal ions from RE-SOJR (a) La(III)-SOJR and (b) Sm(III)-SOJR (volume of solution = 10 cm<sup>3</sup>, weight of gel = 10 mg, shaking time = 24 h, shaking speed = 150 rpm, and temperature = 30°C) **85**
- Fig. 5.1** Analysis of SOJR before and after Ce(IV) loading by EDX spectroscopy (a) EDX spectrum of SOJR, (b) EDX spectrum of Ce(IV)-SOJR **91**
- Fig. 5.2** Influence of equilibrium pH for the adsorption of fluoride by Ce-SOJR (volume of solution = 15 cm<sup>3</sup>, weight of gel = 25 mg, fluoride concentration = ~10 mg dm<sup>-3</sup>, shaking time = 24 h, shaking speed = 150 rpm, and temperature = 30°C) **92**
- Fig. 5.3** Adsorption isotherms of fluoride on both types of Ce-SOJR from aqueous solution (volume of solution = 15 cm<sup>3</sup>, weight of gel = 25 mg, pH = 4, shaking time = 24 h, shaking speed = 150 rpm, and temperature = 30°C) **93**
- Fig. 5.4** Effect of temperature for the adsorption of fluoride using Ce(IV)-SOJR (volume of solution = 15 cm<sup>3</sup>, weight of gel = 25 mg, pH = 4) (a) adsorption isotherm, (b) Langmuir plot, and (c) Van't Hoff's plot **95**
- Fig. 5.5** Leaching of loaded fluoride by alkali solution (fluoride in Ce(IV)-SOJR = 13.6 mg g<sup>-1</sup>, fluoride in Ce(III)-SOJR = 11.56 mg g<sup>-1</sup>, fluoride loaded Ce-SOJR eluent ratio 2.5 g dm<sup>-3</sup>, shaking time = 2 h, and temperature = 30°C) **96**
- Fig. 6.1** FT-IR spectra of (a) OJR, (b) DOJR, and (c) Zr(IV)-DOJR **104**
- Fig. 6.2** Energy Dispersive X-ray spectra of (a) DOJR, (b) Ce(IV)-DOJR, (c) Zr(IV)-DOJR, and (d) Zr(IV)-DOJR after fluoride adsorption **105**
- Fig. 6.3** Adsorption kinetics of fluoride on M-DOJR from aqueous solution (volume of solution = 15 cm<sup>3</sup>, weight of gel = 25 mg, pH = 4, fluoride concentration = ~15 mg dm<sup>-3</sup>, and temperature = 30°C) **106**

- Fig. 6.4** Effect of equilibrium pH for the adsorption of fluoride on M-DOJR (volume of solution = 15 cm<sup>3</sup>, weight of gel = 25 mg, fluoride concentration = ~10 mg dm<sup>-3</sup>, shaking time = 24 h, shaking speed = 150 rpm, and temperature = 30°C) **107**
- Fig. 6.5** Adsorption isotherms of fluoride onto M-DOJR (a) adsorption isotherm, (b) Langmuir isotherm model (volume of solution = 15 cm<sup>3</sup>, weight of gel = 25 mg, pH = 4, shaking time = 24 h, speed = 150 rpm, and temperature = 30°C) **108**
- Fig. 6.6** Influence of co-existing ions during fluoride adsorption onto Zr(IV)-DOJR (volume of solution = 15 cm<sup>3</sup>, weight of gel = 25 mg, fluoride solution = ~1 mmol dm<sup>-3</sup>, shaking time = 24 h, shaking speed = 150 rpm, and temperature = 30°C) **109**
- Fig. 6.7** Leaking behavior of loaded Zr(IV) from Zr(IV)-DOJR at different pH by varying concentration of fluoride (volume of solution = 10 cm<sup>3</sup>, weight of gel = 10 mg, shaking time = 24 h, shaking speed = 150 rpm, and temperature = 30°C) **110**
- Fig. 6.8** Adsorptive removal of fluoride from actual plating solution using M-DOJR (volume of solution = 15 cm<sup>3</sup>, shaking time = 24 h, and temperature = 30°C) **112**
- Fig. 6.9** Stripping of adsorbed fluoride from fluoride loaded (0.82 mmol g<sup>-1</sup>) Zr-DOJR by using various concentration of caustic soda solution **113**
- Fig. 6.10** Cycle tests of fluoride adsorption onto Zr(IV)-DOJR and its desorption using NaOH solution (solid/liquid ratio = 2.5 g dm<sup>-3</sup>, feed solution = 18.6 mg dm<sup>-3</sup>, eluent = 0.1 M NaOH solution, shaking time = 24 h, shaking speed = 150 rpm, and temperature = 30°C) **114**
- Fig. 6.11** Effect of pH on breakthrough profile of fluoride using Zr(IV)-DOJR (feed solution = 14.3 mg dm<sup>-3</sup>, flow rate = 153.0 cm<sup>3</sup> h<sup>-1</sup>, pH = 4, bed depth = 2.4 cm, and at rt) **115**
- Fig. 6.12** Effect of influent fluoride concentration for fluoride adsorption on the bed of Zr(IV)-DOJR (flow rate = 153.0 cm<sup>3</sup> h<sup>-1</sup>, pH = 4, bed depth = 4.8 cm, and at rt) **116**
- Fig. 6.13** Adsorption behavior of fluoride at different flow rates onto Zr(IV)-DOJR (feed solution = 14.3 mg dm<sup>-3</sup>, pH = 4, bed depth = 4.8 cm, and at rt) **117**

- Fig. 6.14** Influence of bed depth ( $D$ ) for the adsorption of fluoride onto Zr(IV)-DOJR (feed solution =  $14.3 \text{ mg dm}^{-3}$ , flow rate =  $153.0 \text{ cm}^3 \text{ h}^{-1}$ , pH = 4, and at rt) **118**
- Fig. 6.15** Continuous adsorption of fluoride from plating solution in a fix bed column of Zr(IV) loaded DOJR (a) breakthrough profile (b) elution profile (feed solution =  $\sim 15.2 \text{ mg dm}^{-3}$ , flow rate =  $153.0 \text{ cm}^3 \text{ h}^{-1}$ , bed depth = 1.2 cm at rt) **121**
- Fig. 7.1** Spectroscopic characterization of READF-(PG) and READF-(HG) resins (a) EDX- (b) XRD-, and (c) FT-IR spectra **128**
- Fig. 7.2** Effect of pH for the adsorption of fluoride on READ-F resins (volume of solution =  $10 \text{ cm}^3$ , weight of gel = 25 mg, fluoride concentration =  $\sim 10 \text{ mg dm}^{-3}$ , shaking time = 24 h, shaking speed = 150 rpm, and temperature =  $30^\circ\text{C}$ ) **130**
- Fig. 7.3** Adsorption isotherm of fluoride on two different READF resins (solution =  $10 \text{ cm}^3$ , weight of gel = 25 mg, shaking time = 24 h, pH = 3, shaking speed = 150 rpm, and temperature =  $30^\circ\text{C}$ ) **131**
- Fig. 7.4** Continuous adsorption followed by elution of fluoride in a fixed bed column of READF-(PG) resin (a) breakthrough profile, and (b) elution profile (weight of gel = 500 mg, flow rate =  $5.3 \text{ cm}^3 \text{ h}^{-1}$ , pH = 3, wet volume of resin =  $0.5 \text{ cm}^3$ , feed solution =  $1.85 \text{ mmol dm}^{-3}$ , eluent = 0.1 M NaOH) **132**

## List of Tables

Tables	Page No.
<b>Table 1.1</b> Elemental composition of ethanol extract of orange (peel, pulp and seed) waste by X-ray micro analysis	<b>18</b>
<b>Table 2.1</b> Stability of fluorocomplex of some cationic species	<b>32</b>
<b>Table 2.2</b> Total amount of some metal ions loaded on SOJR	<b>38</b>
<b>Table 2.3</b> Variation of stripping percentage of metal ions from M-SOJR at different concentration of hydrochloric acid solution	<b>40</b>
<b>Table 2.4</b> Isotherm parameters for the adsorption of fluoride on metal loaded SOJR	<b>44</b>
<b>Table 2.5</b> Desorption of adsorbed fluoride ( $0.79 \text{ mmol g}^{-1}$ ) from Al-SOJR by using dilute alkali ( $0.1 \text{ M NaOH}$ ) solution	<b>49</b>
<b>Table 3.1</b> Leaching test of Zr(IV) from Zr-SOJR by hydrochloric acid solution	<b>55</b>
<b>Table 3.2</b> Thermodynamic parameters investigated for the adsorption of fluoride by using Zr(IV) loaded SOJR	<b>63</b>
<b>Table 4.1</b> Stability of fluorocomplex of some rare earth (RE) metal ions	<b>71</b>
<b>Table 4.2</b> Isotherm parameters for the adsorption of rare earth metal ions on SOJR	<b>78</b>
<b>Table 4.3</b> Langmuir and Freundlich parameters for fluoride adsorption by M-SOJR	<b>82</b>
<b>Table 4.4</b> Elution of fluoride ( $0.90 \text{ mmol g}^{-1}$ ) from La(III)-SOJR by alkali solution	<b>84</b>
<b>Table 5.1</b> Langmuir isotherm parameters for the adsorption of fluoride on Ce-SOJR	<b>94</b>
<b>Table 5.2</b> Thermodynamic parameters investigated for the adsorption of fluoride on Ce(IV)-SOJR	<b>96</b>
<b>Table 5.3</b> Stoichiometric relationships among the acidic functional group of saponified orange juice residue, loaded metal ions, and adsorbed amount of fluoride	<b>98</b>

<b>Table 6.1</b> Langmuir isotherm parameters for the adsorption of fluoride on Zr(IV) and Ce(IV) loaded DOJR and their comparison with Zr(IV) and Ce(IV) loaded SOJR	<b>109</b>
<b>Table 6.2</b> Wastewater composition ( $\text{mg dm}^{-3}$ ) of two different plating solutions	<b>112</b>
<b>Table 6.3</b> Effect of initial pH of the fluoride solution for the adsorption of fluoride by Zr(IV)-DOJR in a fixed bed system	<b>115</b>
<b>Table 6.4</b> Effect of initial fluoride concentration for the adsorption of fluoride by using Zr(IV) loaded DOJR	<b>116</b>
<b>Table 6.5</b> Influence of flow rate for the adsorptive removal of fluoride using fixed bed column of Zr(IV) loaded DOJR	<b>117</b>
<b>Table 6.6</b> Effect of bed depth for the adsorption of fluoride by using fixed bed column of Zr(IV) loaded DOJR	<b>119</b>
<b>Table 6.7</b> Comparison of column capacities of various adsorbent for fluoride	<b>119</b>
<b>Table 6.8</b> Concentration ( $\text{mg dm}^{-3}$ ) of cationic and anionic species in wastewater	<b>121</b>
<b>Table 7.1</b> Isotherm parameters for fluoride adsorption using READF resins	<b>131</b>
<b>Table 7.2</b> Comparison of adsorption capacities of fluoride by using metal loaded SOJR and DOJR together with those of some other adsorbent reported in the literature	<b>133</b>

## List of Schemes

<b>Schemes</b>	<b>Page No.</b>
<b>Scheme 2.1</b> Synthetic route of metal loaded orange waste gels where M = Sn(IV), Ti(IV), V(IV), Al(III), and Fe(III)	<b>34</b>
<b>Scheme 2.2</b> Mechanism of fluoride adsorption and desorption using alkaline solution [M = Sn(IV), Ti(IV), V(IV), Al(III), and Fe(III)]	<b>47</b>
<b>Scheme 3.1</b> Creation of active sites on SOJR by Zr(IV) loading reaction	<b>53</b>
<b>Scheme 4.1</b> Adsorption of rare earth metal ions onto SOJR gel [where, RE = La(III), Ho(III), Sm(III), Lu(III) and Sc(III)] ions	<b>72</b>
<b>Scheme 5.1</b> Development of more active site on saponified orange juice residue (SOJR) by increasing oxidation state of loaded cerium	<b>89</b>
<b>Scheme 5.2</b> Formulation of possible mechanism of metal ion complexation with SOJR and their ligand exchange mechanism for fluoride adsorption	<b>98</b>
<b>Scheme 6.1</b> Creation of active sites for fluoride ion adsorption by metal loading reaction on DOJR from aqueous solution	<b>101</b>

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Hari Paudyal

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## **ABSTRACT**

### **REMOVAL OF FLUORIDE FROM WATER BY USING METAL LOADED ORANGE WASTE**

**By Hari Paudyal**

Fluoride is the common contaminant of ground water, surface water and industrial waste water of high-tech industries. The orange juice residue has the potential to develop ligand exchange sites for fluoride ion after simple chemical modification. The carboxyl functional groups in orange juice residue were increased by saponification reaction of methyl ester part of orange pectin by lime water treatment to adsorb metal ions. The active sites were developed for fluoride ions by single step modification of saponified product of orange juice residue or commercial dried orange juice residue by loading high-valent metal ions to create novel metal loaded adsorbents. The different derivatives of metal loaded orange waste were prepared by loading Al(III), Fe(III), Ce(III), La(III), Sc(III), Ho(III), Sm(III), Ti(IV), Sn(IV), V(IV), Zr(IV), and Ce(IV) on orange waste. The obtained materials were characterized by chemical analysis, FT-IR, EDX, TOC measurement and thermal (TG-DTA) analysis. The various experimental parameters investigated for fluoride adsorption from aqueous solution were: pH, contact time, concentration, temperature and adsorbent dosage in batch mode whereas in continuous packed column system effect of flow rate, concentration, pH and bed depth were studied. It was found that maximum adsorption of fluoride by using different derivatives of metal loaded orange waste depends on the types of loaded metal ions. Among metal loaded orange waste, Al(III) loaded orange waste adsorbent possesses the maximum adsorption at around pH 6 whereas in the case of other metal loaded derivatives, it was observed in acidic pH. Adsorption kinetics of fluoride onto metal loaded orange waste gels were examined to be fast adsorption process. The isotherm data showed very good correlation with the Langmuir isotherm model than that of the Freundlich isotherm model. The maximum adsorption capacities evaluated from the Langmuir equation were higher in the case of tetravalent Zr(IV) and Ce(IV) loaded orange waste gels than other trivalent metal loaded adsorbents. The Zr(IV) loaded adsorbent exhibited higher selectivity

for fluoride even in the co-existing system whereas uptake capacity of Al(III) loaded SOJR was little bit decreased in the presence of sulphate and bicarbonate. The fluoride concentration in the actual waste plating solution could successfully removed by using small amount of Zr(IV) loaded orange waste gel both in batch and column operation. These adsorbents were successfully regenerated by using dilute alkali solution. Fluoride adsorption and desorption mechanism was inferred to be ligand exchange reaction between coordinating hydroxyl ions of loaded metal ions on metal loaded orange waste adsorbents and fluoride ions from aqueous solution. The enthalpy change ( $\Delta H$ ), entropy change ( $\Delta S$ ) and Gibbs free energy change ( $\Delta G$ ) of the system during fluoride adsorption by Zr(IV) and Ce(IV) loaded SOJR suggested the endothermic and spontaneous nature of adsorption. Fluoride concentration could be successfully lowered below the environmental standard of Japan both in batch as well as column mode operation from waste plating solution by using Zr(IV) loaded orange waste adsorbent. Thus, it is expected that metal loaded orange waste gels can be alternative candidate to remove fluoride from polluted water.

# Chapter 1

## Background of the Study

### 1.1 GENERAL INTRODUCTION

Innovation of new and advanced technologies in the different field is rapidly growing that has been directed to the elevation of living standard in our life. The uncontrolled way of industrialization and urbanization causes the depletion of natural resources in the earth surface. Among the various natural resources, water is one of the most important resources for plants, animals, and human being. The composition of freshwater is only 3% of the total water content on earth in which only a small percentage (0.01%) is available for human use [1]. However, because of rapid population growth, urbanization and unsustainable consumption of water in industry and agriculture, some portion of this freshwater is under immense stress or unsuitable for daily uses. The world population is increasing exponentially while the availability of freshwater is declining. Due to the lack of proper management and unavailability of professionals and financial constraint, the situation is more and more dangerous in developing countries [2]. Most of the health related problems appeared in our body are mainly due to the consumption of contaminated water. According to the UNESCO report, about 2.3 billion peoples are suffering from water related diseases worldwide [3]. More than 60% of the infant mortality in the world is induced by water related disease. The people in the developing countries more than 2.2 million each year die from the consumption of polluted water [4].

Our life is impossible without water. It is used for various purposes such as cooking, irrigation, drinking and other daily uses in one hand and in the other hand; it is used in various industries for production of many food, drinks and beverages. The demand of clear, pure and fresh water is increasing day by day because of the increasing population. The quality of water that we use for makings foods, beverage and other product along with drinking water is of great concern to the mankind because it is directly related to the growth and development of our

health [5]. There is the increasing trend of decreasing the quality of the drinking water by natural as well as human activities. The environmental pollution, especially water pollution, is unfavorable for living organism. The pollution of water can occur by the introduction of foreign contaminants or pollutants on to the water bodies through anthropogenic or natural process [6]. There are various substances which are considered as active water pollutants and are classified into different groups. Fluoride is one of such pollutant that directly affects the health of human being after its ingestion through food and drinks.

There are various types of industries which are established for the production of some commercial product such as HF, insecticides, pesticides, food additive, paint, plastics and semiconductors that used considerable amount of fluoride compounds. Most of these chemicals and raw material used for the production of these commercial products are potentially toxic to human being. In their production, toxic waste containing fluoride is also produced along with commercial product. In mining and refining of metal ions, production of beverage and cosmetics, manufacture of nuclear energy and weapons, plating and high-tech industries produces the waste water containing fluoride as pollutants. The water bodies such as river, lakes and ponds are also naturally polluted with fluoride by the geochemical leaching of fluoride from their ore and swept out to water bodies during the rainy season that also contribute the additional contamination of water.

The fluoride ion on the other hand possess a double edge risk for the teeth and bone tissue. It is known that the lack of fluoride as well its excess concentration in drinking water lead to adverse effects in the health of human and other animals. The optimum level of fluoride in drinking water ( $0.7 - 1.2 \text{ mg dm}^{-3}$ ) is necessary for the prevention of dental caries but above  $1.5 \text{ mg dm}^{-3}$ , it causes dental and skeletal fluorosis [7]. It is recommended that, water with low fluoride concentration should be fluoridated up to its optimum level for the prevention of our teeth whereas elevated concentration of fluoride ion in water should be lowered by available defluoridation method. In the view of these facts, present work is focused on the development of different types of low cost adsorbents from orange juice residue for effectively removing fluoride from water.

## 1.2 FLUORINE AND FLUORIDE

### 1.2.1 Introduction

Fluorine is first element in the halogen group and occurs in the form of diatomic ( $F_2$ ) gaseous molecule. It is light yellow gas and very strong oxidizing agent. It is 13<sup>th</sup> most abundant element in the earth crust. It was discovered by Moissan in 1886. At first, he prepared hydrogen fluoride by the reaction of fluorite ( $CaF_2$ ) with concentrated sulphuric acid ( $H_2SO_4$ ) which was followed by electrolysis of HF, where fluorine gas was collected at cathode and hydrogen gas was collected at anode after electrolytic dissociation. For this work, he was awarded by Nobel Prize for Chemistry in 1906 [8]. Because of very high electro negativity, small ionic radius and close to octate configuration making it the most reactive element, which results in the formation of stable complexes with all element except for lighter novel gases *i.e.* He, Ne and Ar [9]. It is capable of forming complexes with xenon and inert metals such as Au and Pt. It therefore occurs naturally only in its reduced (F<sup>-</sup>) form in combination with other elements called fluorides. It is considered as a trace element in human body because only small amount (about 2.6 g in adults) is present in side our body which is ingested through food, drinks and especially through drinking water [10]. Fluoride ion on the other hand posses a double edge risk for the teeth and bone tissue. It is known that fluoride deficiencies as well as overexposure lead to adverse effects on the health of human and other animals. There is a large variation of fluoride ion concentration in different parts of the earth. In the areas which are rich in flurorite, fluoroappatite and cryolite rich rock, fluoride concentrations are unexpectedly higher which is related to the various geochemical reactions.

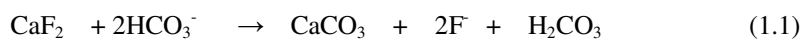
The main reason of releasing fluoride into water bodies are due to the leaching of fluoride from rocks and minerals [11, 12], industrial wastes [13], agricultural fertilizers and combustion of coal [14]. The deficiency of fluoride affects the development of teeth in children but consumption of water containing excess fluoride over a prolonged period of time led to endemic fluorosis. It is estimated that 23 countries in the world are facing skeletal or dental fluorosis due to elevated level of fluoride in ground water [15].

### 1.2.2 Occurrence of fluoride

Fluorine is one of the most common element and exist in almost all soils in the earth's surface where it exists naturally in number of different minerals. Some of the commonly known minerals of fluoride are sellaite ( $\text{MgF}_2$ ), fluorspar ( $\text{CaF}_2$ ), cryolite ( $\text{Na}_3\text{AlF}_6$ ) and fluoroapatite [ $3\text{Ca}_3(\text{PO}_4)_2 \text{CaF}_2$ ] [16]. Among them fluorospar and fluoroapatite are the main sources of fluoride minerals which are present in almost all rocks around fluoride mines. Fluorspar is common in granites, granitic gneiss and pegmatite while fluorapatite is more common in igneous and metamorphic rocks. However, fluoride is not as common in the hydrosphere, the atmosphere and the biosphere as it is in the lithosphere since most of the fluoride exists bound in different minerals. In the hydrosphere, the concentration also varies considerably. In seawater, the fluoride level is around  $1.3 \text{ mg dm}^{-3}$  [17].

### 1.2.3 Geochemistry and aqueous chemistry

In groundwater, the natural concentration of fluoride depends on the geological, chemical and physical characteristics of the aquifer, the porosity and acidity of soil and rocks, temperature, action of other chemical elements and depth of the aquifer. The mobilization of fluoride from those into groundwater is dependent on the pH and time of contact with water through the bed of minerals. The presence of high concentration of bicarbonate in percolated water accelerates the release of fluoride from fluorite minerals under favorable geophysical conditions, because of water-mineral interactions [18, 19]. The possible chemical reactions that happen when water percolates over the bed of fluoride mineral are:

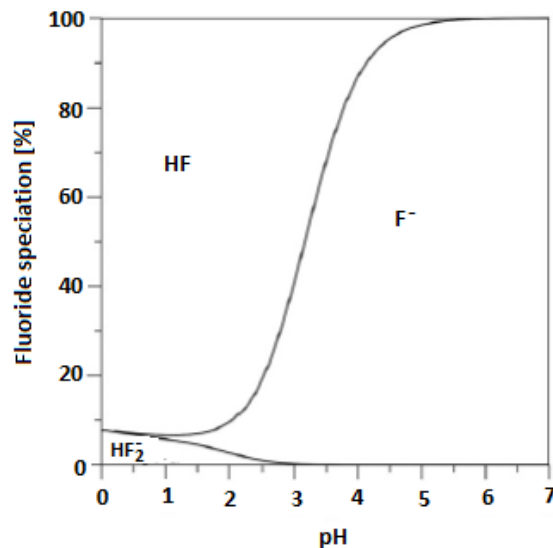


It is clear from the above mentioned geochemical reaction that fluoride ion is naturally released into the surface and ground water that leads to the increase in fluoride concentration in surface and underground water which are the main sources of drinking water in most of the countries. In some of the calcite and lime containing regions, some amount of fluoride released by geochemical reaction express by equations 1.1 and 1.2 are converted into fluorite as:



The fluorspar or fluorite ( $\text{CaF}_2$ ) formed according to the reaction express in equation (1.3) is slightly soluble in water. Due to its solubility limit ( $K_{sp} \sim 10^{-11}$ ), it leaves the residual fluoride concentration around  $8 \text{ mg dm}^{-3}$  in the surface water. In this way, excess concentrations of fluoride in surface or ground water get controlled, if no geochemical process occurs to reduce the fluoride concentration. This amount is higher compared to the maximum permissible amount of fluoride in drinking water ( $1.5 \text{ mg dm}^{-3}$ ) set by WHO [20].

Fluoride exists in the forms of different species in aqueous solution depending on pH of the solution.  $\text{HF}_2^-$ , HF and  $\text{F}^-$  are main species of fluoride in water in the absence of other ions whereas, in the present of metal ions such as Al, Ca and so on, its speciation may be changed because of its complexation with the metal ions in the aqueous solution. HF is the predominant species in water at pH less than 3 ( $pK_a$  of HF = 3.18) with a small proportion of  $\text{HF}_2^-$ , More than 90% of fluoride exists as free fluoride in aqueous solution when pH is greater than 5, which is clearly demonstrated in Fig. 1.1 [21].



**Fig. 1.1** Fluoride speciation in water varies with pH, the speciation boundaries were calculated with the PHREEQC code and the WATEQ4F database (Deng *et.al.* 2011)

### 1.2.4 Application of fluoride

Investigation of new and useful compounds and development of advance technologies and materials in several fields is increased in order to fulfill the needs of modern society. The fluoride compounds especially hydrofluoric acid is one of the widely used chemical for the production of other fluoride containing compounds, refining of metals and semiconductor production. The fluoride compounds are extensively used by the high tech industries, fertilizer manufacturing and nuclear energy production. The fluoride compounds like sodium fluoride and sodium fluorosilicate are used as a pesticides and insecticides in agriculture. In some countries fluoride compounds especially sodium fluoride (NaF) and sodium hexafluorosilicate ( $\text{Na}_2\text{SiF}_6$ ) are used as water additive for fluoridation of drinking water that also increases the application of fluoride and its compounds. The major uses or application of fluoride in the large extent can be broadly classified into two classes:

#### 1.2.4.1 Industrial application of fluoride

There are some fluoride compounds such as hydrofluoric acid (HF), sodium fluoride (NaF), cryolite  $\text{Na}_2[\text{AlF}_6]$ , fluorspar ( $\text{CaF}_2$ ), fluoroapatite [ $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ ] and so on which are widely used in industries for various purposes. Among them, hydrofluoric acid is very important and widely used as a major source of fluoride in most fluoride containing chemicals. It is either used directly in the manufacture of fluoride chemicals or in the production of intermediates for their production. Hydrogen fluoride is the industrial starting compound for organic and inorganic fluorine based chemicals such as aluminum fluoride, sodium fluoride and other fluoride salts, including chlorofluorocarbons ( $\text{CCl}_3\text{F}$ ) and their substitutes [8]. Nowadays, the uses of  $\text{CCl}_3\text{F}$  are restricted in some countries due to depletion of protective ozone layer. Teflon, one of the most useful plastics materials, also requires HF for its commercial production. HF is also used to separate uranium isotopes during the production of nuclear energy [22]. In the recent year, appreciable amount of hydrofluoric acid and ammonium fluoride have been used in the electronics and semiconductor industries as a washing and etching reagent [23].

The uses of fluoride compounds mostly HF is common in metal treatment and cleaning, laboratory analysis, etching of glass, ceramics, brick, and rust removal. Hydrofluoric acid is



used to manufacture a wide variety of products, including refrigerants, gasoline, electronic components, aluminum, and plastics [24]. It is used as a fluorinating agent in the manufacture of herbicides, pharmaceutical intermediates, inert fluorinated liquids and electronic grade etchants. The sodium fluoride and stannous fluoride are used in toothpaste for dental protections are also manufactured by using hydrofluoric acid. HF lasers have been tested for use in corneal transplants and for use in space [25]. The absolute hydrofluoric acid (anhydrous) is used in most of these industries but in some cases such as stainless steel pickling, metal coatings, chemical milling, glass etching, exotic metals extraction, and quartz purification, it is used in its diluted form [26]. HF is also used as an alkylation catalyst in the petroleum refining industry to produce gasoline blending components [27].

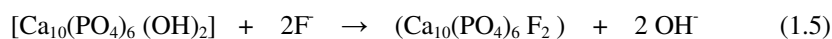
The production of fluorine becomes important for the production of some inorganic fluoride such as  $\text{AlF}_3$  and synthetic cryolite  $\text{Na}_2[\text{AlF}_6]$  which are used in the extraction of aluminium. In the recent years, the uses of fluoride are urgent for the metal refining, plating and semiconductor industries. The manufacture of phosphate in the large scale is carried out from fluoroapatite. The phosphates are later used in the production of phosphate fertilizers [28]. Due to such a widespread used of fluoride and its compounds in agricultural, medical, separation of uranium isotopes in nuclear energy plants is now in rapid with the advance in the technological development [29]. Due to heavy use of fluoride compounds in various industries, demand of fluoride compounds also increasing so that mining of fluoride ore and its production also increases. Because of these facts, fluoride compounds are extensively used in various industries, the waste water or solid material produced from these industries contains large amount of fluoride, hydrofluoric acid and other toxic fluoride compounds that adversely affect the human being and other organism. So that, innovation of suitable low cost treatment technology is required in order to remove fluoride from these waste which is one of the burning issue for the medical and environmental scientist.

### 1.2.4.2 Water fluoridation

In some countries where natural water contains insufficient amount of fluoride ions, new practice of adding fluoride compounds such as sodium fluoride (NaF), sodium hexafluorosilicate ( $\text{Na}_2\text{SiF}_6$ ) and hexafluorosilicic acid ( $\text{H}_2\text{SiF}_6$ ) into the drinking water was adopted for the purpose of preventing dental caries known as water fluoridation. There are 8 countries in the world where fluoride compounds are directly added to the public drinking water at the level of 0.5 to 1.2  $\text{mg dm}^{-3}$  for the purpose of improving dental caries [30]. It was first started in united state in 1945 then it was adopted by other countries. Very few countries have adopted this practice to any significant extent. Australia, Colombia, Ireland, Israel, Malaysia, New Zealand, Singapore, and United State are adopting this technique of adding fluoride compounds in their public drinking water and have more than 50% of their populations drinking artificially fluoridated water. Increased risk of tooth decay in human being arises due to the intake of inadequate amount of fluoride. It is investigated that effect of dental health is affected by the presence of fluoride in water and its daily consumption.

The epidemiological investigations, patterns of water consumption and the prevalence of dental caries in the different region of united state containing different amounts of fluoride in water led to the development of adequate level of fluoride in drinking water [31-33]. The people living in the regions of warm climate consumes a large amount of water compared to the people living in cold climate, thus lower concentration was recommended for warmer climates and the higher concentration was recommended for colder climate [34]. The suitable amounts of fluoride in drinking water reduce the incidence of dental caries and, under certain conditions, promote the development of strong bones [35, 36]. In bone mineral, hydroxyapatite [ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ] is one of the principle component of skeletal tissue or bone tissue. If fluoride is present in the tolerate limit, hydroxyl ions of hydroxyapatite are replaced by fluoride ions on the surface and form fluoroapatite [ $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ ] or [ $\text{Ca}_{10}(\text{PO}_4)_6\text{OH F}$ ] according to the reactions expressed in equations 1.4 and 1.5 which are more stable than hydroxyapatite resulting reduction of bone mineralization and hence especially improves our dental health [37].





The trace amount of food material attached on the tooth surface is decomposed into organic acid by some cario-genic bacteria found in dental plaque and led to the dissolution of tooth enamel. In the early stage of demineralization of tooth, fluoride ion enhances the remineralization of enamel through its interactions with hydroxyapatite [38, 39]. The deficiency of fluoride in dental caries can lead to nutritional problems and results the local infection, pain and tooth decay. The replacement of large hydroxyl ions (153 pm) by small fluoride ions (118 pm) from our bone tissue is too high after excessive intake of fluoride for long period of time [40]. Most of the hydroxyapatite of our bone tissue is converted into fluoroapatite which causes a reduction in crystal volume and finally increases the bone porosity. This will reduce the mechanical strength of our bone tissue.

It is estimated that adequate exposure of fluoride by the consumption of fluoridated water has been found to improve dental health in human [41]. In some countries such as India, China and some regions of Africa, natural fluoride level in water is, however, higher than the recommended level, thus they are suffering from the over exposure of fluoride ion [42]. The overall picture of fluoride in drinking water is complex and needs proper management and monitoring in individual areas. Water should be fluorinated in areas where fluoride concentration is very low while defluorination measures should be taken in areas with elevated fluoride concentration.

### 1.2.5 Fluoride toxicity and its adverse effect on human health

It is well known fact that fluoride compounds are toxic to health of human beings and other organisms. Some of them are well known insecticides and pesticides. For example, sodium fluoride, NaF is used to control insects in home, hospital and other public houses. Sodium fluorosilicate is used to control ectoparasites in livestock. Similarly, sodium fluoroaluminate is used as insecticides in vegetable. The acute fluoride toxicity in human being arises due to the accidental overdoses or the ingestion of fluoride pesticides, fluoride tablets and dental products. Fluoride poisoning is characterized by vomiting, hemoptysis, cramping of the arms and legs,

cardiac arrest, ventricular fibrillation, hyperkalemia, hypocalcemia, and sometimes death [43]. In some case, genetic mutations, birth defects, hypersensitivity, allergies and bone injury are developed by the over exposure of fluoride. The health related toxic effects of fluoride which are arised due to the exposure of high dosage of fluoride are briefly discussed as follows:

- (a) **Effect in dental health:** The formation of dental fluorosis are evidenced by the appearance of white horizontal striations or white patches on the tooth surface in the early stage [44, 45] whereas, in the severe case, these patches become yellow to brown or even black with the increase of tooth porosity which will finally result in the pitting or chipping. Fordyce *et. al*, (2007) investigated that more than 60 % of the population is affected by dental fluorosis if they consume drinking water containing more than  $2 \text{ mg dm}^{-3}$  of fluoride [46]. The similar study by Apambire *et al*. (1997) suggested that consumption of drinking water that contains more than  $6 \text{ mg dm}^{-3}$  would result in 100% of population affected by dental fluorosis [47].
- (b) **Skeletal fluorosis and kidney stone formation:** If the people are exposed or ingested water containing large amount of fluoride or other fluoride compounds at high dose for long time, skeletal fluorosis occur. It arises due to the increases in bone mass and density. The joint and backbone pain followed by stiffness is the first stage of skeletal fluorosis which is followed by calcification of ligament in the moderate condition whereas, at the severe case, it produces neurological defects, muscle wasting, paralysis, crippling deformities and compression of the spinal cord [48, 49]. In our body some amounts of ingested fluoride are consumed or deposited into bone tissue whereas all of non accumulated fluoride are excreted from the kidney so that kidney is continuously exposed with fluoride. The people consuming water containing high fluoride level face the problems of developing kidney stone. The study of 18700 peoples from different parts of the India by Sinha *et al*. (2001) shows that people living in the region that contains 3.5 to  $4.9 \text{ mg dm}^{-3}$  fluoride in their drinking water are mostly suffering the formation of kidney stone and bone bending [50].
- (c) **Infertility:** The reproductive power of animals is considered to be reduced with the increase of fluoride amount inside our body. Regarding the investigation on reproductive effect, most

of the research were performed for other mammals and concluded that fertility power is decreased with increasing fluoride concentration in their diet or drinking water in fluoride polluted areas. Chinoy and Narayana (1994) reported that high fluoride ingestion adversely affect the reproductive power of male than female [51]. Epidemiological study conducted in United State in 1994 observed increased rates of infertility among couples living in areas with  $3 \text{ mg dm}^{-3}$  or more fluoride in their public drinking water [52], while two studies have found reduced level of circulating testosterone in males living in high fluoride areas, and a study of fluoride-exposed workers were reported to be suffered to reproductive defect by fluoride poisoning [53, 54].

- (d) **Cancer:** As we know that main site of fluoride accumulation in our body is bone tissue so that it might have some contribution in the development of bone cancer. A number of researchers suggest the positive relationship between bone cancer formation and fluoride ingestion [55, 56]. Because of the presence of uric acid in urine, fluoride may be converted into hydrofluoric acid which is potentially toxic substance and become the cause of cancer development in urinary bladder and kidney. The higher rate of appearance of bladder and kidney cancer was observed in the workers working in the cryolite processing plants or aluminium manufacturing plants [57]. It indicates that fluoride is also one of the dangerous cancer causing agent.
- (e) **Neurotoxicity:** The ability of fluoride to damage the brain represents one of the most active areas of research on fluoride toxicity these days. The impact of fluoride on children's IQ has been documented even after controlling for children's lead exposure, iodine exposure, parental education and income status, and other known factors that might impact the results [58, 59]. In addition to IQ studies, studies have found that fluoride accumulates in the brain of fetus, causing damage to cells and neurotransmitters and study has found a correlation between exposure to fluoride during fetal development and behavioral deficits among neonates. The symptom of neurotoxicity in our body is reported to be appears when the fluoride concentration exceeds  $2 \text{ mg dm}^{-3}$  [60].

(f) *Fluoride accumulates in the body*: Healthy adult kidney excrete 50 to 60% of the fluoride they ingest each day [61]. The remainder accumulates in the body, largely in calcifying tissues such as the bones and pineal gland [62]. Infants and children excrete less fluoride from their kidneys and take up to 80% of ingested fluoride into their bones [63]. The fluoride concentration in bone steadily increases over a lifetime [64].

### 1.2.6 Defluoridation

In order to comply with the safe drinking water regulation, treatment of excess concentration of fluoride by suitable method of removing fluoride from water is necessary. The method of removing fluoride ions from water is known as defluoridation. Some defluoridation technologies based on the principle of chemical precipitation, coagulation, electrolysis, membrane and adsorption have been suggested and successfully tested for the removal of fluoride from water and industrial waste water. All the technologies have their unique approaches for fluoride removal and specific advantages over other in the particular situation. Most commonly known defluoridation technologies are briefly discussed as follows:

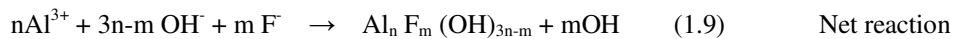
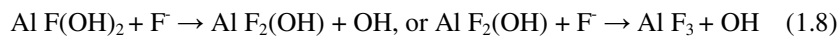
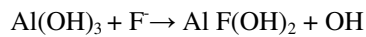
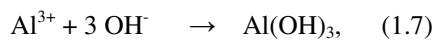
#### (a) *Precipitation-coprecipitation*

It is commonly used technique for the removal of fluoride from water. Precipitation of fluoride is generally carried out by the addition of calcium and aluminium compounds into the fluoride solution. Lime or calcium salts are widely used for the removal of excess concentration of fluoride by precipitation. After precipitation reaction with calcium ions, a fluoride ion forms fluorspar ( $\text{CaF}_2$ ) according to the reaction expressed in equation 1.6



Because of solubility product of  $\text{CaF}_2$ , although fluoride concentration can be lowered down to  $8 \text{ mg dm}^{-3}$  theoretically, this process leaves more than 10 and several  $\text{mg dm}^{-3}$  of fluoride in treated water in practical treatments [65]. In most of the countries, the maximum acceptable limit of fluoride in drinking water is  $\leq 1.5 \text{ mg dm}^{-3}$ , so that, lime precipitin method alone is unable to remove fluoride below the permissible standard, hence it is used only in the conjunction with alum treatment or other methods to ensure effective removal. In most of the

case, lime precipitation method is followed by aluminum coprecipitation. The aluminium co-precipitation occurs in two steps. At first to a fluoride containing water, aluminum salts are added and pH is increased by adding basic solution. At high pH, aluminum ions are precipitated into  $\text{Al}(\text{OH})_3$  where fluoride ions from the solution are co-precipitated as aluminium fluoride [66] according to the reaction express as:



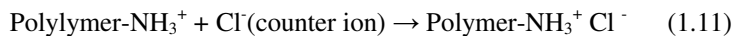
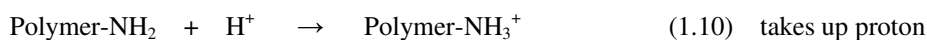
The aluminium co-precipitation is generally used for the treatment of trace concentration of fluoride from water. Although this method ensure the removal of fluoride below accepted standard, large amount of  $\text{Al}(\text{OH})_3$  sludge is generated, needing high cost for dehydration and drying. At acidic condition,  $\text{Al}^{3+}$  ions were leaked from the  $\text{Al}(\text{OH})_3$  sludge and sometimes exceed the maximum contamination level of  $\text{Al}^{3+}$  ( $0.2 \text{ mg dm}^{-3}$ ) in water [67].

### **(b) Nalgonda technique**

This technique is considered as one of the popular method of water treatment in developing countries. It is practice in Nepal, India, China and Tanzania for the removal of excess concentration of fluoride from drinking water [56, 68]. It is popularly known as the Nalgonda technique [64], named after the town in India where it was first used at water works level. The process comprises the addition of prescribed quantities of alum, lime, and bleaching powder to raw water, followed by rapid mixing, flocculation, sedimentation, filtration, and disinfection. After adding alum and lime to the raw water, insoluble aluminium hydroxide flocs are formed then sediment to the bottom and co-precipitate fluoride. The bleaching powder ensures disinfection during the process [64].

*(c) Ion exchange*

Ion exchange is the process in which solid adsorbent takes up charged ions from a solution and release equivalent amount of other ion into the solution. The driving force for the exchange of ions in the matrix is due to excessive positive or negative charge. The excessive charge is generated after the adsorbent takes up charge species which is localized in specific sites or functional group, then the overall charge is neutralized by the counter ions from a solution. This counter ion is easily replaced by other ions of same charge [69]. The whole process is termed as ion exchange process. It means that in the ion exchange process for every ion, removal of another ions having same charge occurs into the solution. In order to remove fluoride from water, a strongly basic anion exchange resin containing amine functional groups are little bit effective [64]. Mechanism of fluoride ion removal using strongly basic anion exchange resins can be express as:



Here, protonated resin attracts counter ions (for example chloride) for charge neutralization, and then it is ready for anion exchange reaction. The fluoride ions adsorbed by replacing the chloride ions of the resin. It continues until all the chloride ions on the resin are occupied by fluoride. Ion exchange type materials or resins are considered to be selective to particular ions but according to the well known Hofmeister selectivity series (*i.e.* citrate > SO<sub>4</sub><sup>2-</sup> > Oxalate > I<sup>-</sup> > NO<sub>3</sub><sup>-</sup> > CrO<sub>4</sub><sup>2-</sup> > Br<sup>-</sup> > SCN<sup>-</sup> > Cl<sup>-</sup> > formate > acetate > F<sup>-</sup>), the selectivity of fluoride is low in the presencc of usually coexisting ions such as chloride and sulphate so that presence of very high concentration of coexisting ions, the efficiency of resin is decreased which is the main draw back of ion exchange resin for the treatment of fluoride containing waste water [70].



***(d) Membrane technology***

***(i) Reverse osmosis and nanofiltration***

Nowadays, two different types of membranes namely nanofiltration membrane and reverse osmosis membrane have been reported to successfully remove fluoride and other contaminants from water. Thus, nanofiltration and reverse osmosis processes have emerged as a preferred alternative to provide safe drinking water [71]. The method is based on the process of physical separation where contaminants are removed by applying pressure on the feed water to pass it through a semi permeable membrane. It is just a reverse of the natural osmosis so called reverse osmosis. The membrane rejects the ion on the basis of size and their electrical charge [64]. The nanofiltration is low pressure process and remove large size contaminant or ions whereas reverse osmosis is generally performed in higher pressures hence rejection of most of the dissolved ions or particle is possible. Nearly quantitative removal of fluoride (> 98%) is reported to be achieved by membrane process [72]. The process also removes some essential minerals from water. Whereas single step removal and disinfection, ensure water quality or standard, no addition of chemicals and no interference by coexisting ions are the superiority of this method over other techniques [64]. However, the fouling of membrane, continuous optimization of membrane, low yield of treated water and expensive cost are some disadvantages of this method.

***(ii) Donnan dialysis and electrodialysis***

In the case of reverse osmosis and nano filtration, membrane is used to retain the solute while water passes through it. Dialysis is also types of membrane system in which electric field or donnan effect is used as a driving force to transport the solute through a membrane. The membrane pores are much less restrictive than those for nanofiltration, and the solute can be driven through by either the Donnan effect or an applied electric field [73]. In 1999, Hichour *et al.*, studied the donnan dialysis process in a counter current flow system in which the anion exchange membrane was loaded with sodium chloride and the feed was NaF (0.001 M) solution in the coexisting system [74]. He found that fluoride was migrated into the receiver as other ions

migrated into the feed and this technique was later used for the removal of fluoride from ground water ( $F > 30 \text{ mg dm}^{-3}$ ) and successfully lower down to  $1.5 \text{ mg dm}^{-3}$  [75].

**(e) Adsorption**

For the investigation of an efficient and low cost defluoridating media, a number of adsorbent materials have been tested and suggested for fluoride ion by several researchers in the past. In the adsorption process, fluoride containing water is passed through a bed of adsorbent and then adsorbent adsorb fluoride by electrostatic interaction, ion exchange and some other chemical interaction. The adsorbent gets saturated after a period of operation and requires regeneration. The literature shows that, a wide range of materials such as calcite, chitosan, magnetite, kaolinite, metal loaded adsorbents, clay, lime, metal oxides *etc.* and so on are reported to be used for fluoride removal [64, 76-81]. The general mechanism of fluoride uptake by these materials is the ion exchange, electrostatic interaction or ligand exchange reaction. The adsorption capacity of the adsorbent for fluoride can be improved by certain pre-treatments or modification. The materials such as bone char, activated alumina, activated carbon, ion exchange resins, oxides and hydroxide of some metal ions are reported to be successful for the defluoridation of water [82]. Of these, some of the adsorbents are categorically discussed as:

- i. **Natural materials as adsorbent for fluoride:** There are a number of materials found in nature which are capable of adsorbing fluoride ion. It was observed by the several researchers that coal, clay, montmorillonite, zeolite and laterite which are naturally occurred at different region of earth surface can be used to remove fluoride from water [83-88].
- ii. **Alumina based adsorbents:** Alumina, activated alumina and some modified alumina are reported to be successful for the defluoridation of water. The unmodified activated alumina and chemically modified alumina with some rare earth metal ions (La and Ce) after impregnation reaction were reported to have effective performance for fluoride ion removal from water [89-91].
- iii. **Metal and metal oxide based adsorbent:** Some metal ions such as Ca, Fe, Sn, Ti, Zr and rare earth (RE) metal ions have high affinity with the fluoride and their fluoride complex are

stable in nature. The calcium based adsorbent (lime stone, modified lime stone, quicklime), iron based adsorbent like granular ferric hydroxide, mixed oxide and hydroxide ( $\text{CeO}_2$ ,  $\text{TiO}_2/\text{SiO}_2$ , Sn-Ti bimetal oxide, Al-Ce bimetaloxide, Ce(IV) coated SIMCM-41,  $\text{MnO}_2$  coated alumina) were demonstrated to be effective adsorbents for fluoride by different researchers [92-95].

- iv. **Biosorbents for fluoride removal:** Biomass materials contain various types of polymer compound with multifunctional group in their structure. This will make them very important materials for the separation and purification research. The materials such as chitosan and modified chitosan, algal biomass, fungal biomass, colleen fibre, cellulose are the main biomaterials which are tested and suggested to be efficient adsorbents for fluoride removal from aqueous solution [96-99].
- v. **Waste materials as adsorbent for fluoride ion removal:** There are various types of waste materials derived from agricultural field, industrial processing and mining requires some suitable way of management for their disposal. Some of the industrial waste ( $\text{H}_2\text{SO}_4$  processing waste, Al industry waste, fly ash, waste of fertilizer industries, mining waste material), waste of construction process (brick powder, gas concrete, hydrated cement, aluminium cement granule) and some agricultural waste (corn, coconut, rice straw, cashew nut shell) were also tested and found to be effective for fluoride removal from water according to the earlier studies [100-108].

In addition, the mixed double layer hydroxide, hydrocalcite and some nano adsorbents such as carbon nanotubes, nano  $\text{Al}_2\text{O}_3$ , magnetic  $\text{Al}(\text{OH})_3$  nano particle, aligned carbon nanotube were also reported to successfully remove fluoride from water [109, 110]. Among all the adsorbents reported by earlier studies, adsorbents derived from biomass and agricultural biomass wastes attract the attention of researcher in this field. The agricultural waste are abundant, contains various types of functional group, high potentiality, easy to modified and low cost (as they are waste material), which make these wastes alternatives to commercially available polymeric resin which are produced by long chemical route with the consumption of large amount of chemicals.

### 1.3 ORANGEWASTE, ITS COMPOSITION AND POSSIBLE APPLICATIONS

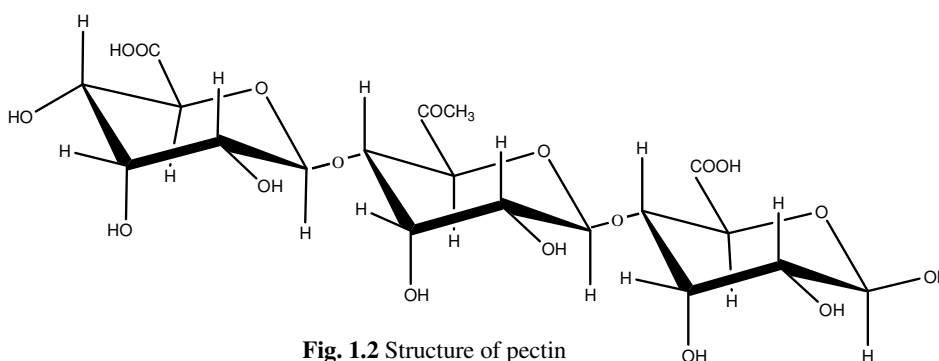
Orange is very popular fruit belongs to the genus *citrus* under Rutaceae family. There are two varieties of orange fruits *i.e.* sweet and bitter, former are most commonly consumed. The sweet variety of orange is scientifically known as *citrus sinensis* while the bitter variety is called *citrus aurantium* [111]. The fruit contain outer orange coloured thick cover called orange peel and internal segmented with juicy portion called pulp. The juice of orange fruits is rich in essential minerals and vitamins which provide necessary health benefit to our body. The antioxidant and insoluble dietary fiber presence in the juice of this fruits are considered to decrease the risk of many chronic diseases, cancers and heart diseases [112], hence, orange juice processing is one of the more important food industry in the world. It produces an enormous quantity of processing residue. This constitutes about 50% of the weight and thus provides an excellent material for the production of value added products.

The peel and other byproducts are ultimately dried and marketed as a cattle feed in some developed countries like Japan but since the selling price of the product is very low (~20 Yen per kg in Japan *i.e.* ~\$ 0.2) and the evaporation of water from these wastes consumes large amounts of heat with some chemicals, the production of dried citrus feed is valuable only as a waste disposal method with marginal economic benefits, cost effective, convenient type of modification of the natural polymer of orange juice processing by-product offer practical alternative use. Mahmood *et al.*, (1998) made the extract of orange waste (peel, pulp and seed mixed), after making its extract in mixture of NaOH and ethanol, elemental composition in filtrate and residue were analysed. The reported elements and their composition were presented here in **Table 1.1**. It shows that *Ca*, *K*, *P* and *Mg* are major elements whereas *Na*, *Si*, *Cl*, *Fe*, *Cu*, *Zn* and *Ba* are in trace amount in the extract of orange waste sample [113].

**Table 1.1** Elemental composition of orange (peel, pulp and seed) waste by X-ray micro analysis

Elements	Na	Mg	Si	P	S	Cl	K	Ca	Fe	Cu	Zn	Ba
Solid (%)	0	9.32	0	9.13	3.86	0.30	17.97	58.37	0.79	0	0.36	0
Filtrate (%)	1.18	4.72	3.65	6.34	2.82	0.38	27.37	50.33	0.82	0.38	0.42	1.59

The orange peel mostly composes of cellulose, pectin, hemicellulose, lignin, chlorophyll pigments and other low molecular weight hydrocarbons including limonene. Among them, cellulose and pectin are major components [114, 115]. Hydroxyl groups of cellulose required some difficult technique for its modification whereas carboxylic acid and ester groups of the pectin are easy to be modified. The pectin is acidic polysaccharide where pectic acid is partially esterified by methyl group (**Fig. 1.2**) and acts as intracellular cementing materials in plants. For the treatment of anionic pollutants, ion exchange resins are prepared by loading or impregnating metal ions or their oxide onto the synthetic polymers. The carboxylic acid functional groups are considered to be very important groups for metal ion binding that reflect the utilization of orange juice residue as feed material for the adsorption of metal ions. After metal loading, new active sites for anionic species are expected to be formed. Hence, in the present work ester part of orange waste, particularly pectin was chemically modified into saponified product by basic hydrolysis reaction with slaked lime that after metal loading reaction gives metal loaded orange waste that acts as effective anion exchange type materials. Here, orange waste gel, its metal binding properties, synthesis of different derivatives of metal loaded orange waste and their fluoride adsorption behavior were studied in details.



**Fig. 1.2** Structure of pectin

#### 1.4 OBJECTIVES OF THE PRESENT STUDY

It is well known fact that water is essential natural resources for sustaining life and considered as most available free gift of nature. However, due to ever growing population, urbanization, industrialization and unskilled utilization of water resources led to degradation of water quality making it unsafe for human consumption. Literature shows that number of adsorbents have been investigated to remove pollutants from water. For the adsorption of metallic pollutants carboxylic acid type cation exchange resins are effective whereas some modification should be required in order to create the active sites for anionic pollutants. In the present work, cation exchange type adsorption gel (SOJR *i.e.* saponified orange juice residue) was first prepared from orange juice residue then high valent metal ions were immobilized in order to create novel type of active adsorption sites for anionic pollutants. Adsorption media for anionic pollutant like fluoride was also prepared from cattle food of orange juice residue. The attempt has been focus to prepare metal loaded orange juice residue and their application for the effective removal of fluoride from water with the following objectives:

##### 1.4.1 Long term objectives

- (a) To develop an efficient ion exchange type material from the waste biomass of orange fruit as an alternative material to replace ion exchange resins of non or less degradable polymer of plastics materials for the removal of some cationic as well as anionic species.
- (b) To suggest the suitable way of decontamination of drinking water and industrial wastewater by using chemically modified orange waste.
- (c) To contribute an important role to the protection of environment and health of human and other living creature.

##### 1.4.2 Short term objectives

- (a) To prepare saponified orange juice residue (SOJR) for metal ion adsorption.
- (b) To synthesize metal loaded SOJR and metal loaded dried orange juice residue (DOJR) for fluoride ion removal from water.
- (d) To characterize the orange waste adsorbents by using chemical analysis, IR, EDX

and total organic carbon (TOC) measurement.

- (e) To study the feasibility of orange waste adsorbents for fluoride by varying pH, temperature, contact time, adsorbent dosage and concentration of fluoride ion in batch mode.
- (f) To interpret experimental results of adsorption isotherms of fluoride on the basis of Langmuir and Freundlich model.
- (g) To study the effect of competing ions on the removal of fluoride using metal loaded orange waste adsorbents.
- (h) To study the durability of metal loaded SOJR and DOJR during fluoride adsorption, desorption and readsorption at different cycles.
- (i) To study the role of valency of loaded cerium ion for fluoride ion removal.
- (j) To evaluate the thermodynamic parameters such as  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  for fluoride and maximum adsorption capacities of adsorbents.
- (k) To evaluate the effectiveness of zirconium loaded orange waste gel for the removal of fluoride from waste plating solution both in batch and column mode.
- (l) To perform column performance and breakthrough analysis for fluoride by using zirconium loaded dried orange juice residue (DOJR) from water.
- (m) To compare the column capacities of various adsorbents reported in the relevant literatures with Zr(IV) loaded DOJR from aqueous solution.

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## Chapter 2

### Orange Waste Adsorbent Loaded with Multi-valent Metal Ions

The present work was focused on the investigation of efficient adsorption gel for fluoride by using residual byproduct generated in orange juice factory. Adsorbents for fluoride ion were prepared by saponification followed by loading of multi-valent metal ions. Orange pectic acid creates the active adsorption sites for fluoride ion once it is loaded with multi-valent metal ions such as Sn(IV), Ti(IV), V(IV), Al(III), and Fe(III) *etc.* The equilibrium adsorption amount increases with the increase in equilibrium fluoride concentration according to the Langmuir type monolayer adsorption model. The optimum pH for fluoride removal depends on the type of loaded metal ions. Among six types of metal loaded gels tested in this chapter, Al(III) loaded gel exhibited the most favorable adsorption behavior to remove fluoride around neutral pH. Adsorptive removal of fluoride from binary solutions containing co-existing ions by Al(III)-SOJR suggested that the presence of  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  lowers the fluoride removal capacity in small extent whereas  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$  and  $\text{Na}^+$  ions have negligible effect. Application of Al(III)-SOJR for the removal of trace concentration of fluoride showed that fluoride concentration can be successfully lowered down to the acceptable environmental standard. The ligand exchange reaction of the coordinated hydroxyl group on the loaded metal ions with fluoride ions was inferred to be the dominant mechanism during fluoride adsorption onto metal loaded SOJR and also during desorption using alkali solution.

### 2.1 INTRODUCTION

The chemical modification or construction of some natural polymer on its suitable form to remove pollutants including fluoride from water is one of the most important emerging technologies in modern separation science [1-3]. The natural polymers derived from biomass of plants and animals deserve most important position because such a biomass is abundant, easy to modify, low cost and has functional diversity [4-7]. The orange waste biomass is one of the pectic acid rich biopolymers and its production increases with the increase rate of orange juice consumption throughout the world. The carboxylic acid type resins are effective for metal ions

removal but some engineering is required to remove anionic species from water. Fluoride is a widespread anionic pollutant around industrial area of metal refining, nuclear energy station and high tech industries [8-9]. The removal of fluoride directly from orange waste without any modification is difficult so that some chemical modification is required to create the active adsorption sites.

In the present investigation, an attempt has been made for the synthesis of orange waste adsorbent by simple chemical modification of carboxyl functional group of orange pectin. Here, carboxylic acid functional group of orange pectin was increased by alkaline saponification where methyl ester group of orange pectins were converted into carboxyl group with the aid of lime water then it was followed by loading of multivalent metal ions to develop active adsorption sites for fluoride anion. It is reported that, the multi valent metal ions such as Al, Fe, Ti and Sn have high stability constants with fluoride ions [10] (**Table 2.1**) and their oxides and hydroxide were reported to have very high affinity towards fluoride which are the main criteria of selecting these metal ions for loading reaction.

**Table 2.1** Stability of fluorocomplex of some cationic species

Metal ion	H	Ca	Al	Fe	Ti	Sn
Log equilibrium constant	2.95	0.82	7.01	5.16	3.81	4.0

## 2.2 EXPERIMENTAL PROCEDURE

### 2.2.1 Chemicals

In order to sapaonify orange juice residue, lime water was used. The chloride salts of some high valent metal ions such as Sn(IV), Ti(IV), Al(III), and Fe(III) were used to make Sn-SOJR, Ti-SOJR, Al-SOJR, and Fe-SOJR, respectively whereas sulphate salt of V(IV) was used to prepared V-SOJR gel. Adsorption test of fluoride was carried out by using sodium fluoride (NaF) solution where 2.10 g of NaF was dissolved in 1000 cm<sup>3</sup> of water to get 0.052 M fluoride stock solution. The stock solution was further diluted to required concentration at the time of experiment.

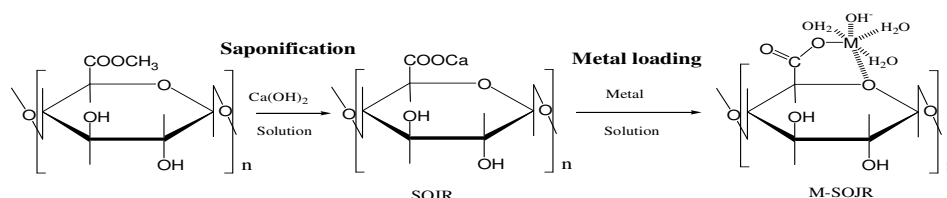
### 2.2.2 Instrumental Analysis

The total organic carbon leaked from the gel was measured by using (Shimadzu model TOC-VSH) Total Organic Carbon Analyzer. FT-IR spectra were recorded using (JASCO model FT-IR-410) Fourier Transform Infrared Spectrometer. The pH of the solution was measured by using (DKK-TOA model HM-25G) pH meter. The concentrations of fluoride in test solution was measured by (Dionex model ICS 1500) ion chromatography while that of metal ions were analyzed by using (Shimadzu model ICPS 8100) an inductively coupled plasma-atomic emission spectrometer ICP-AES.

### 2.2.3 Preparation of metal loaded saponified orange waste gel

Chemical modification of orange juice residue to prepare efficient adsorption gel for metal ions has been carried out by saponification with slaked lime. The orange waste utilized in this study was kindly donated by JA Saga Beverage Co., Ltd., Japan. The principle components of orange waste are cellulose, hemicellulose, pectin, chlorophyll pigment and other low molecular weight compounds like limonene and so on [11]. In this study, utilization of pectin portion of orange waste was performed because orange pectin contains carboxylic acid groups as well as methyl ester groups. Carboxyl group in the orange pectin can be increased by the saponification reaction of methyl ester part of orange pectin to carboxyl group by saponification reaction with lime water as follows. At first, 100 g of orange waste was washed several times with distilled water to remove water soluble organic compounds that could hinder the saponification reaction. Thus pretreated orange waste was then mixed together with 8 g of calcium hydroxide and was grounded into fine particles with the help of (HITACHI VA-10) juice mixer. The reaction mixture was shaken for 24 h at 30°C after the addition of substantial amount of water to enhance the saponification of methyl ester portion of pectin in orange waste by lime water according to the reaction described by **Scheme 2.1**. The initial pH of the reaction mixture was adjusted at around 12 by adding sodium hydroxide pellets. After the saponification, the suspension was washed several times with distilled water *via* decantation until a neutral pH was reached, which was followed by filtration, and finally the residual product was dried in a convection oven at 70°C. The white product prepared in this way

contains calcium salt of pectic acid and was termed as saponified orange juice residue, abbreviated as SOJR hereafter. In the second step, SOJR was further treated with multi-valent metal ions such as Sn(IV), Ti(IV), V(IV), Al(III) and Fe(III) ions to generate active sites for fluoride ion removal. For this, 3 g of SOJR was mixed together with 500 cm<sup>3</sup> of 0.1 M individual respective metal solutions, which were then stirred at 30°C for 24 h to complete the loading reaction of metal ion with SOJR (**Scheme 2.1**). Then, the suspensions were filtered and washed several times with de-ionized water until neutral pH. The filter cakes were dried *in vacuo* and were ground by mortar to obtain uniform particles (100-150 μm) by sieving.



**Scheme 2.1** Synthetic route of metal loaded orange gel where M = Sn(IV), Ti(IV), V(IV), Al(III), and Fe(III)

#### 2.2.4 Stripping of loaded metal ions using hydrochloric acid

To investigate the effect of hydrochloric acid concentration for the stripping or leaching behavior of metal ions from M-SOJR, stripping tests were carried out at various concentration of hydrochloric acid ranging from 0.01 to 5 M at solid-liquid ratio of 1 g dm<sup>-3</sup>. After leaching reaction for 24 h at 30°C, the metal contents in the test sample were measured by ICP-AES.

#### 2.2.5 Aquaregia dissolution

The quantity of metal ions loaded onto the adsorbents plays an important role for the development of active sites so that total amount of metal ions such as Sn(IV), Ti(IV), V(IV), Al(III), and Fe(III) in the sample of Sn-SOJR, Ti-SOJR, V-SOJR, Al-SOJR, and Fe-SOJR, respectively were analyzed by the dissolution of these metal loaded SOJR in aquaregia solution (*i.e* 3 HCl + 1 HNO<sub>3</sub>) at solid-liquid ratio of 5 g dm<sup>-3</sup>, after dissolution, metal ion concentration in the test solution were measured by ICP-AES.

### 2.2.6 Batch wise adsorption tests of metal ions and fluoride

In order to investigate the optimum condition for metal loading reaction, adsorption test of various metal ions such as Sn(IV), Ti(IV), V(IV), Ce(III), Al(III), and Fe(III) onto SOJR were carried out. For this, 10 cm<sup>3</sup> of mixed solution of above mentioned metal ions and 10 mg of SOJR at different pH were shaken in a mechanical shaker at 30°C for 24 h. Then after filtration, metal ion concentrations before and after adsorptions were measured by ICP-AES. The adsorption behavior of fluoride on different metal loaded SOJR gels was examined under the batch-mode of operation. Equilibrium adsorption tests of fluoride were performed by mixing 10 mg of the adsorbent together with 10 cm<sup>3</sup> of fluoride solution (0.52 mmol dm<sup>-3</sup>) at different pH. The mixture was shaken in a thermostated shaker at 150 rpm at constant temperature of 30°C. Kinetic tests were carried out in the similar manner using 4 different metal loaded SOJR by the variation of contact time. After the adsorption, the samples were filtered and analyzed for fluoride concentration. The percentage adsorption (%A) and amount of adsorption (q mmol g<sup>-1</sup>) were calculated according to the following equations:

$$\%A = \frac{C_i - C_e}{C_i} \times 100 \quad (2.1)$$

$$q = \frac{C_i - C_e}{W} \times V \quad (2.2)$$

where,  $C_i$  and  $C_e$  are fluoride concentration (mmol dm<sup>-3</sup>) before and after adsorption, respectively,  $W$  is the dry weight of adsorbent (g) and  $V$  is the volume of fluoride solution (dm<sup>3</sup>).

Isotherm studies were conducted by varying the initial fluoride concentration (0.5 - 8 mmol dm<sup>-3</sup>) at optimum pH. The effect of co-existing anions on fluoride adsorption was studied for Al-SOJR at varying concentration of co-existing ions (SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>) using their respective sodium salts except for calcium chloride. Treatment of fluoride solution containing trace concentration of fluoride (~15 mg dm<sup>-3</sup>) was performed by using Al-SOJR at different solid liquid ratio at pH 6.

### 2.2.7 Desorption of fluoride

Desorption of fluoride from metal loaded orange gel is necessary for its regeneration to use again and again. In the view of this fact, desorption of fluoride from fluoride loaded Al-SOJR was performed by using varying concentration of NaOH from 0.01 to 0.5 M. Desorption percentage of fluoride was calculated according to the following equation:

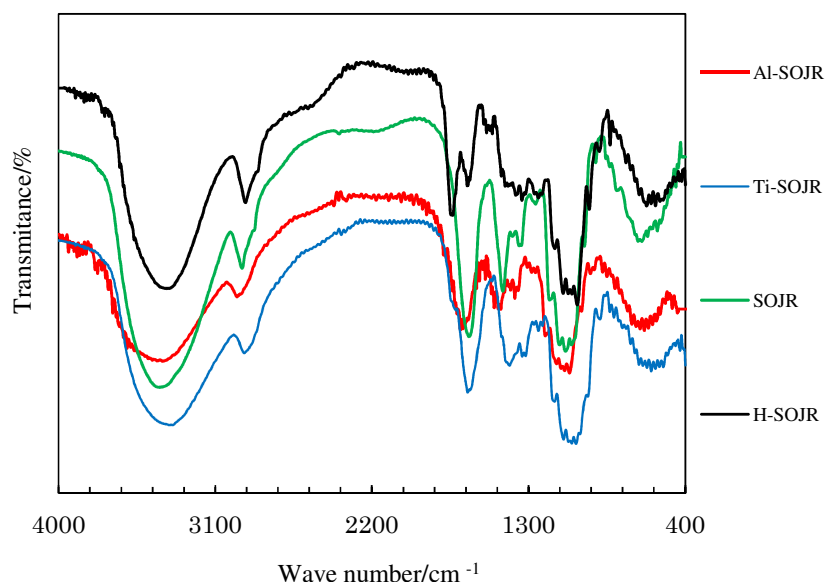
$$\% \text{ desorption of fluoride} = \frac{\text{Desorbed amount of fluoride}}{\text{Adsorbed amount of fluoride}} \times 100 \quad (2.3)$$

## 2.3 RESULTS AND DISCUSSION

### 2.3.1 Characterization of the adsorbents

#### 2.3.1.1 Measurement of functional group modification

As it is clear from the **Scheme 2.1**, SOJR is a kind of Ca(II) type pectic acid gel, comparison of IR spectra of H-type SOJR with that of SOJR and metal loaded SOJR were made in order to identify the influence of spectral shift in IR spectra due to nature of loaded ions. The IR spectra of H-type SOJR, SOJR and metal loaded SOJR are shown in **Fig. 2.1**. In the case of H-type SOJR, appearance of intense peak at  $3436 \text{ cm}^{-1}$  is due to -OH stretching vibration of polymeric compounds such as alcohol, phenol and carboxylic acid, as in pectin, cellulose and lignin. The peak at  $2888 \text{ cm}^{-1}$  is due to -CH stretching vibration. The peak at  $1714 \text{ cm}^{-1}$  is due to stretching vibration of non ionic carboxyl group. The peaks at  $1638 \text{ cm}^{-1}$  and  $1434 \text{ cm}^{-1}$  can be assigned to the symmetric and asymmetric vibration of ionic carboxyl group, respectively. In metal loaded SOJR, the peak at  $1714 \text{ cm}^{-1}$  in H-SOJR is totally disappeared and new peaks were appeared at around  $1664$  and  $1428 \text{ cm}^{-1}$  (Ti-SOJR),  $1672$  and  $1439 \text{ cm}^{-1}$  (SOJR) and  $1684$  and  $1443 \text{ cm}^{-1}$  (Al-SOJR), suggesting the existing of Ti-O, Ca-O and Al-O bonds in the metal loaded samples. Spectral shifting of stretching vibration of carboxyl functional group in Al(III) and Ti(IV) loaded SOJR and H-type SOJR compared to SOJR suggests that, carboxyl functional group is the main functional group that undergoes modification during the reaction.



**Fig. 2.1** Fourier transform infrared spectra (FT-IR) of different types of orange gels

### 2.3.1.2 Evaluation of the amount of loaded metal ions

The metal ion loaded on the gel gives very important effect on the fluoride adsorption capacity. The amounts of different metal ions loaded on SOJR at their optimum loading pH were evaluated by aquaregia dissolution method as shown in **Table 2.2**. The amount of loaded metal ions such as Sn(IV), Ti(IV), V(IV), Fe(III), and Al(III) in the sample of Sn-SOJR, Ti-SOJR, V-SOJR, Fe-SOJR, and Al-SOJR were evaluated to be 0.97, 1.20, 1.12, 0.88, and 1.16 mmol g<sup>-1</sup>, respectively. The different metal ions have different ionic size, nuclear charge density, complexation behavior, stoichiometry and stability with carboxylic acid functional group of saponified orange juice residue (SOJR) that directly effect the loading affinity of metals ion.

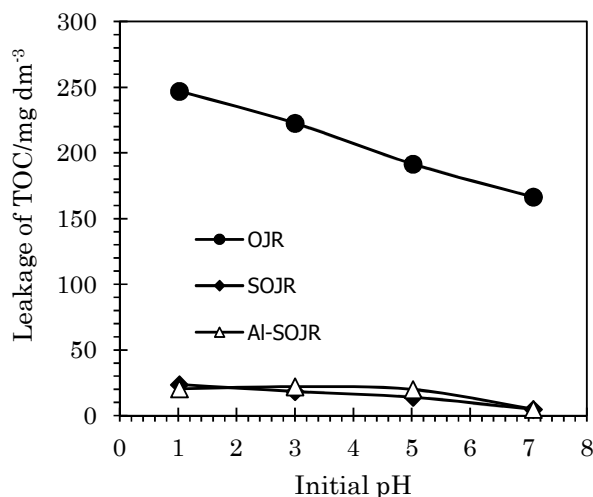
**Table 2.2** Total amount of metal ions loaded on SOJR

Adsorbents	M <sup>n+</sup> ion	pH of loading	Loaded amount/mmol g <sup>-1</sup>
Al-SOJR	Al <sup>3+</sup>	4	1.16
Fe-SOJR	Fe <sup>3+</sup>	3	0.88
Sn-SOJR	Sn <sup>4+</sup>	1	0.97
V-SOJR	V <sup>4+</sup>	3	1.12
Ti-SOJR	Ti <sup>4+</sup>	1.5	1.20

### 2.3.1.3 Stability of M-SOJR in aqueous solution

Dissolution of soluble organic compound from the adsorbent during adsorption increases the total organic carbon in the treated water. So the stability of the prepared adsorbents was studied under different conditions. The aqueous insolubility of the prepared sorbent was examined by measuring the concentration of total organic carbon (TOC) leaked from the gel at varying pH ranging from 1 up to 7. Amount of TOC leaked from raw orange juice residue (OJR), saponified orange juice residue (SOJR) and Al(III) loaded saponified orange juice residue (Al-SOJR), caused by the dissolution of water soluble organic compounds is shown in **Fig. 2.2** as a function of initial pH. The TOC from raw orange juice residue ranges from 247 mg dm<sup>-3</sup> (pH = 1) to 167 mg dm<sup>-3</sup> (pH = 7) whereas it is drastically decreased to 24 and 20 mg dm<sup>-3</sup> (pH = 1) to 4 and 5 mg dm<sup>-3</sup> (pH = 7) from SOJR and Al-SOJR, respectively. It is confirmed that great majority of water soluble organic compounds contained in raw orange juice residue was lost during the chemical modification by lime water, leaving water insoluble stable polymeric compounds in SOJR, suggesting high stability of the prepared adsorbent for practical application.



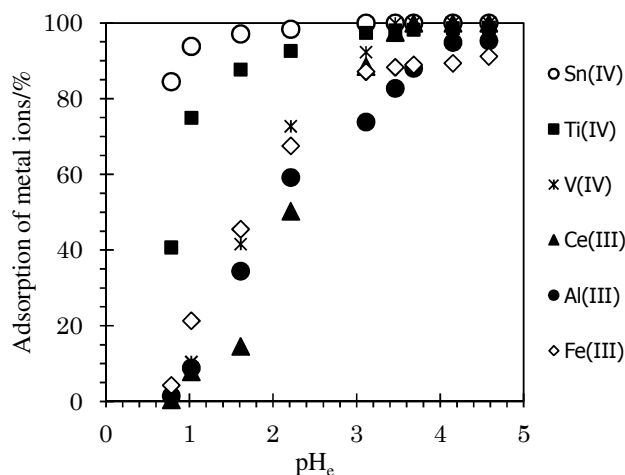


**Fig. 2.2** Analysis of total organic carbon leaked from the various adsorbents at temperature 30°C after 24 h shaking at different pH

### 2.3.2 Adsorption of metal ions onto SOJR

#### 2.3.2.1 pH variation of metal ions adsorption by SOJR

The saponified product of orange waste (SOJR) is a type of calcium salt of orange pectic acid, so that it has high possibility to adsorb some metal ions by cation exchange reaction similar to that in cation exchange resins. Adsorption behavior of some multivalent metal ions such as Sn(IV), Ti(IV), V(IV), Ce(III), Al(III), and Fe(III) from mixed solution by SOJR as a function of equilibrium pH is shown in **Fig. 2.3**. It is seen from this figure that adsorption of metal ions increases with increasing equilibrium pH of the solution, indicating that adsorption of tested metal ions onto the polymer matrix of orange pectic acid in SOJR takes place by cation exchange mechanism. The selectivity of SOJR for some metal ions tested according to **Fig. 3** is in the following order: Sn(IV) > Ti(IV) > V(IV) > Ce(III) > Al(III) > Fe(III). It shows that tetravalent metal ions shows high affinity with SOJR compared to trivalent metal ions which is attributed by the high affinity of tetravalent metal ions with orange waste adsorbent. The result obtained from this figure is very important for the metal loading reaction. Hence, on the basis of this result, optimum pHs for the adsorption of metal ions were determined for metal loading reaction.



**Fig. 2.3** Effect of pH for the adsorption of some metal ions ( $\sim 0.2 \text{ mmol dm}^{-3}$  each) from mixed solution by using saponified product of orange juice residue (SOJR) at solid liquid ratio of  $1 \text{ g dm}^{-3}$  at  $30^\circ\text{C}$

### 2.3.2.2 Acid stripping of loaded metal ions from M-SOJR

The amount of metal ions stripped from the M-SOJR at varying concentration of hydrochloric acid is shown in **Table 2.3**. The result from this table shows that the stripping behavior of metal ions was found to be increased with the increase in acid concentration. The result can be attributed to the fact that the increase in acid concentration results in the enhancement of cation exchange reaction between hydrogen ions from the acid solution and loaded metal ions from M-SOJR. Low stripping %  $\text{M}^{4+}$  compared to  $\text{M}^{3+}$  ion from metal loaded SOJR suggest the high stability of  $\text{M}^{4+}$  loaded SOJR compared to  $\text{M}^{3+}$  loaded SOJR .



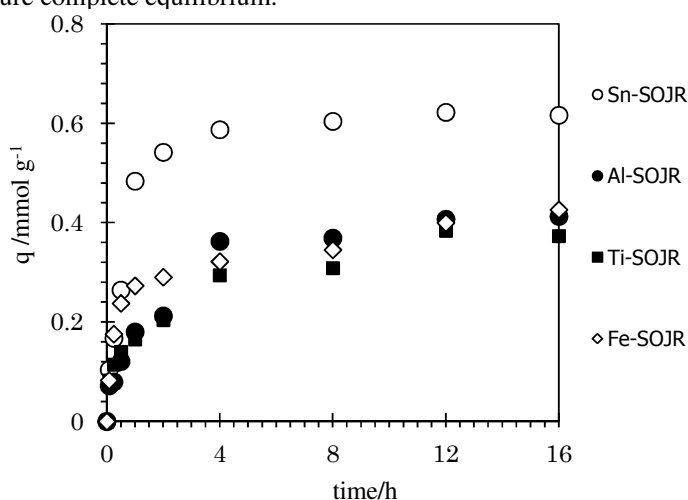
**Table 2.3** Variation of stripping percentage of metal ions from M-SOJR with HCl concentration

HCl [M]	0.01	0.05	0.1	0.5	1	2	5
<b>Al<sup>3+</sup> stripping [%]</b>	34.2	54.8	92.3	93.7	99.4	99.5	100
<b>Fe<sup>3+</sup> stripping [%]</b>	27.4	82.9	86.4	98.3	99.2	99.7	100
<b>Ti<sup>4+</sup> stripping [%]</b>	0.7	57.4	60.1	86.5	90.4	97.3	99.6
<b>Sn<sup>4+</sup> stripping [%]</b>	0	0	1.7	12.6	41.5	86.1	98.4

### 2.3.3 Adsorption of fluoride onto metal loaded orange waste gel

#### 2.3.3.1 Time course dependency

The effect of contact time on fluoride adsorption on different metal loaded SOJR, namely Al-SOJR, Fe-SOJR, Sn-SOJR and Ti-SOJR, was studied under the applied experimental conditions. **Figure 2.4** shows the fluoride adsorption on different metal loaded SOJR as a function of contact time. As can be seen from this figure, the adsorption of fluoride increases rapidly onto all of the metal loaded SOJR tested at the beginning of the contact, and then becomes slower until the attainment of equilibrium. Since the equilibrium is reached nearly within 8 h for all the adsorbents tested, subsequent adsorption experiments were performed for 24 h in order to ensure complete equilibrium.

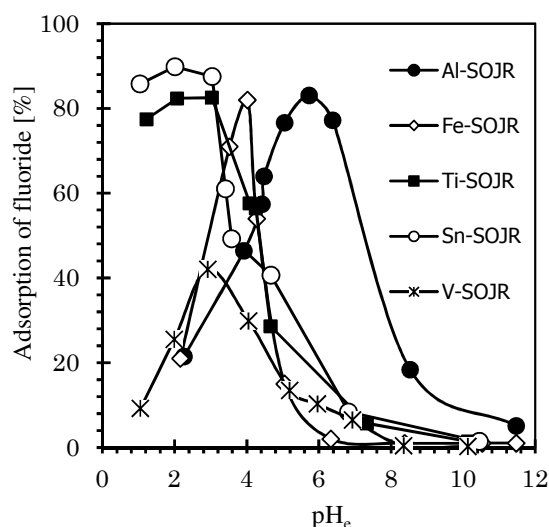


**Fig. 2.4** Kinetics study of fluoride adsorption by using different types of M-SOJR (solid liquid ratio = 1 g dm<sup>-3</sup>, fluoride concentration = ~1 mmol dm<sup>-3</sup>, and temperature = 30°C)

#### 2.3.3.2 Effect of pH

Adsorption behavior of fluoride by various metal loaded SOJR as a function of equilibrium pH (1-12) is presented in **Fig. 2.5**. As can be seen from this figure, the equilibrium uptake of fluoride increases with increasing pH of the solution and has reached maximum value, then deviated to decrease after certain pH with further increase in pH. The maximum sorption of fluoride on Sn(IV), V(IV), and Ti(IV) loaded SOJR gels were found to occur in the pH range 1-3 whereas it was found to occur at around pH = 2-4 in the cases of Fe(III) loaded SOJR gel.

However, optimum adsorption of fluoride by Al(III) loaded SOJR has taken place at pH ranging from 5.5- 6.0, suggesting that Al(III) loaded SOJR can be the most preferable candidate for the removal of fluoride from aqueous solution near neutral pH. The variation of optimum pH for the adsorption of fluoride ion from aqueous solution may be due to the physicochemical property of loaded metal ions. Similar trends in sorption behavior have been previously reported for fluoride adsorption onto bimetal oxide of Ce and Fe after doping Al(III) ions [12]. The decrease in fluoride adsorption % at high pH can be attributed to the competition of hydroxyl ions for the adsorption sites. At pH lower than 2, sparingly soluble hydrofluoric acid ( $pK_a = 3.2$ , [13]) is formed and some fraction of fluoride becomes unavailable for the adsorption, resulting in the lowering of fluoride adsorption. At low pH below 3, the equilibrium pH of the solution was found to be increased for all the metal loaded SOJR after fluoride adsorption which is attributed to the release of hydroxyl ions in the adsorption system during fluoride adsorption. However, at pH higher than 5, some complication occurred because equilibrium pH of the solution was found to be decrease after fluoride adsorption. Some of the free carboxylic acid functional group of the orange pectic acid undergoes deprotonation reaction at high pH releasing protons to the reaction system that leads to decrease of equilibrium pH of the solution.



**Fig. 2.5** Percentage adsorption of fluoride by different types of M-SOJR as a function of equilibrium pH (volume of solution = 10 cm<sup>3</sup>, weight of gel = 10 mg, fluoride concentration = ~10 mg dm<sup>-3</sup>, shaking time = 24 h, shaking speed = 150 rpm, and temperature = 30°C)

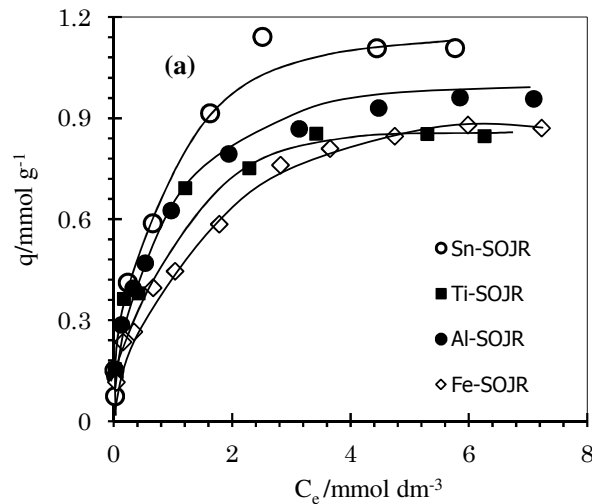
### 2.3.3.3 Effect of fluoride concentration

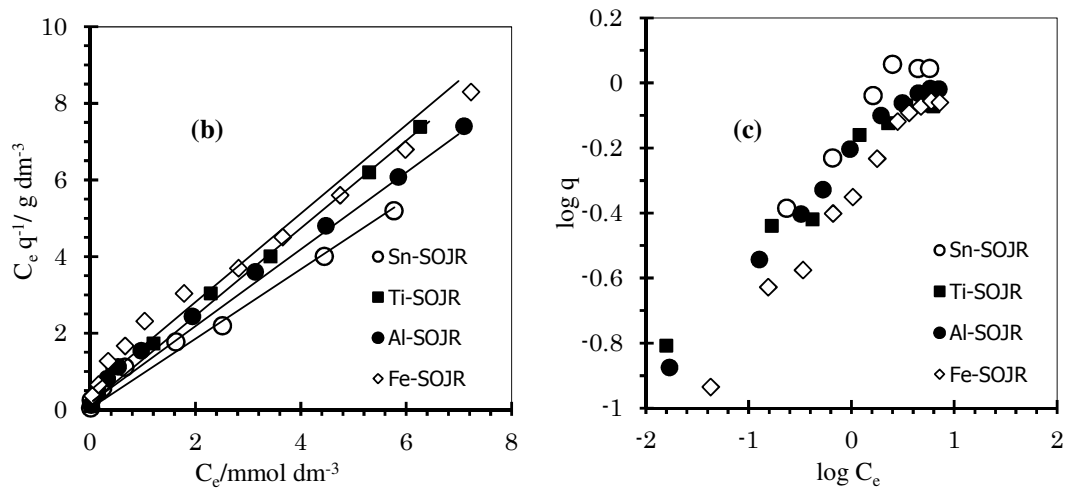
Adsorption isotherms of fluoride on various metal-loaded SOJRs are shown in **Fig. 2.6 (a)**. It is evident from this figure that the adsorption of fluoride increases with increasing concentration of fluoride in low concentration region and tends to level off in high concentration region. The equilibrium data obtained in this study were analyzed by the well known Freundlich and Langmuir isotherm models. The Langmuir isotherm that assumes monolayer adsorption with uniform energies of adsorption on the surface is expressed as:

$$\frac{C_e}{q} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \quad (2.5)$$

where,  $C_e$  ( $\text{mmol dm}^{-3}$ ) and  $q$  ( $\text{mmol g}^{-1}$ ) are equilibrium concentration and amount of adsorption, respectively, while  $q_{\max}$  is the maximum loading capacity and  $b$  ( $\text{dm}^3 \text{mmol}^{-1}$ ) is the adsorption equilibrium constant or binding constant related to the adsorption energy.

The result shows that experimental data is in good agreement with the Langmuir isotherm with high correlation regression coefficient ( $R^2$ ) as shown in **Table 2.4**. In this table, the values of  $q_{\max}$  and  $b$  were evaluated from the slope and the intercept of the straight line for the  $C_e/q$  versus  $C_e$  plot, respectively according to equation 2.5 as shown in **Fig. 2.6 (b)**.





**Fig. 2.6** Adsorption isotherm of fluoride onto metal loaded SOJR from aqueous solution at their optimal pH (a) Experimental plot, (b) Langmuir isotherm and (c) Freundlich isotherm model (volume of solution = 10 cm<sup>3</sup>, weight of gel = 10 mg, and temperature = 30°C)

**Table 2.4** Isotherm parameters for the adsorption of fluoride on metal loaded SOJR

Langmuir parameters					Freundlich parameters		
Adsorbents	pH	$q_{\max} / \text{mmol g}^{-1}$	$b / \text{dm}^3 \text{mmol}^{-1}$	$R^2$	$K_f / \text{mmol g}^{-1}$	n	$R^2$
Al-SOJR	6	1.01	2.24	0.99	0.78	2.97	0.91
Fe-SOJR	4	0.98	1.19	0.99	0.70	2.47	0.95
Ti-SOJR	3	0.91	2.53	0.99	0.77	3.40	0.93
Sn-SOJR	3	1.18	2.79	0.99	0.84	2.53	0.90

The empirical Freundlich isotherm model that is known to be satisfactory for low concentration can be expressed in the logarithmic form as:

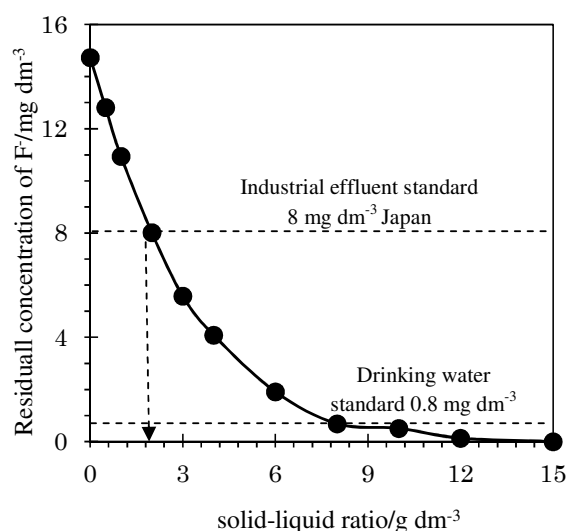
$$\log q = \log K_f + (1/n) \log C_e \quad (2.6)$$

The value of Freundlich isotherm constant  $1/n$  and  $K_f$  ( $\text{mmol g}^{-1}$ ) were calculated from the slope and the intercept of the straight line for the log-log plot of  $q$  vs  $C_e$  (Fig. 2.6 `c`) and presented also in Table 2.4. The determination coefficient value ( $R^2$ ) for the four types of

orange gels were lower than 0.93 and led to conclude that our result did not fit better to the Freundlich isotherm model.

#### 2.3.3.4 Effect of sorbent dosage

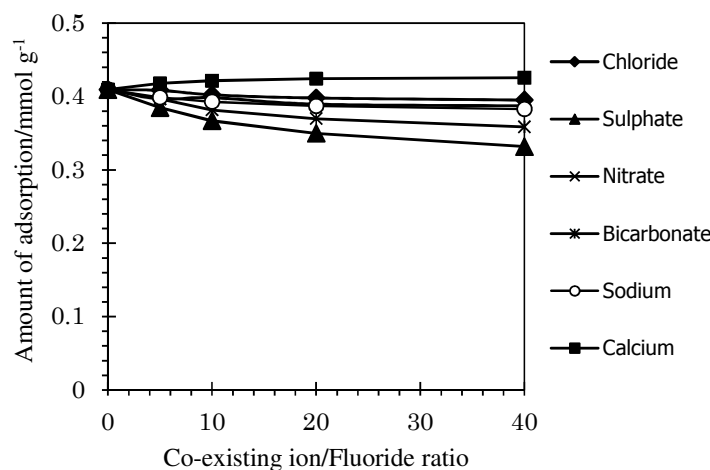
Among the adsorbents tested, optimum adsorption of fluoride has taken place at pH close to neutral pH region in the case of Al-SOJR compared to Sn-SOJR, Ti-SOJR, and Fe-SOJR, suggesting that Al-SOJR is the most suitable sorbent for the treatment of actual fluoride contaminated water. Consequently, adsorptive removal of fluoride was investigated by using Al-SOJR in the subsequent study. The influence of sorbent dosage of Al-SOJR on the fluoride removal was examined by varying the dosages from 0.5 to 15 g dm<sup>-3</sup> as shown in **Fig. 2.7**. It is clear from the result of this figure that fluoride concentration in the treated water can be lowered down to the industrial effluent standard (8 mg dm<sup>-3</sup>) in Japan by using small amount (2 g dm<sup>-3</sup>) of Al-SOJR. The result also reveals that Al-SOJR dosages of 8 g dm<sup>-3</sup> is able to lower fluoride concentration below the Japanese drinking water standard (0.8 mg dm<sup>-3</sup>), whereas complete removal of fluoride can be achieved at 15 g dm<sup>-3</sup>. Thus, it can be expected that Al-SOJR can be a suitable candidates to treat trace concentration of fluoride at neutral pH.



**Fig. 2.7** Removal of trace concentration of fluoride by using Al-SOJR at different dosage (volume of solution = 10 cm<sup>3</sup>, shaking time = 24 h, shaking speed = 150 rpm, and temperature = 30°C)

### 2.3.3.5 Effect of co-existing ions

Fluoride contaminated water contains different co-existing ions such as  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  etc. together with fluoride. **Figure 2.8** shows the amount of adsorption of fluoride on Al-SOJR in the presence of 5- 40 times higher concentration of co-existing ions from binary solutions. The result signifies that the influence of co-existing  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{Na}^+$  ions for fluoride removal from binary mixture is negligible. But, presence of  $\text{Ca}^{2+}$  ions in the fluoride solution enhanced the uptake capacity in small extent whereas  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  a little bit lower the fluoride adsorption capacity. The small increase in fluoride removal capacity with increasing calcium concentration may be attributable to the formation of calcium fluoride. The pH of the mixed solution of fluoride ( $13.6 \text{ mg dm}^{-3}$ ) with  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{Na}^+$  ( $200 \text{ mg dm}^{-3}$ ) were 8.47, 5.91, 5.95, 5.86 and 5.78, respectively. There was a considerable increase in pH of the solution (from 6.02 to 8.47) by the addition of 40 times higher concentration of  $\text{HCO}_3^-$  ion that may contribute to reduce the fluoride removal capacity.



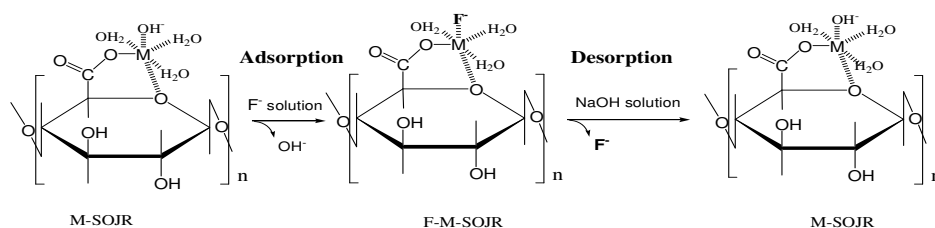
**Fig. 2.8** Adsorption of fluoride by Al-SOJR from binary mixture of various co-existing ions (volume of solution =  $10 \text{ cm}^3$ , weight of gel = 10 mg, fluoride solution =  $\sim 13.6 \text{ mg dm}^{-3}$ , shaking time = 24 h, string speed = 150 rpm, and temperature =  $30^\circ\text{C}$ )

### 2.3.3.6 General mechanism of fluoride adsorption and desorption

The loaded metal ion plays a very important role for the fluoride adsorption. It is inferred that, by loading metal ions on SOJR, carboxyl group and oxygen atom of pyranose ring of



pectic acid in SOJR form a stable five-membered chelate ring with the loaded metal ion. Since  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Sn}^{4+}$ , and  $\text{V}^{4+}$  ions tend to be extensively hydrolyzed even at very low concentration [14], a lot of hydroxyl ions as well as water molecules are available in a coordination sphere of these metal ions, that may contribute the ligand exchange reaction with fluoride. In multi-valent metal loaded SOJR, neutralization of all the positive charges of the loaded metal ions by carboxyl groups is difficult due to strong steric hindrance of pectic acid. That is, in the metal loaded SOJR, one or two positive charge of the loaded metal ion may be neutralized by carboxyl groups while other positive charges are neutralized by hydroxyl ions in aqueous medium. These hydroxyl ions are substituted by fluoride ions by ligand exchange reaction during adsorption. In desorption process, adsorbed fluoride are replaced by hydroxyl ions provided by eluent (alkali) solution. The inferred mechanism of fluoride adsorption using M-SOJR and its desorption using dilute alkali solution is depicted in **Scheme 2. 2**.

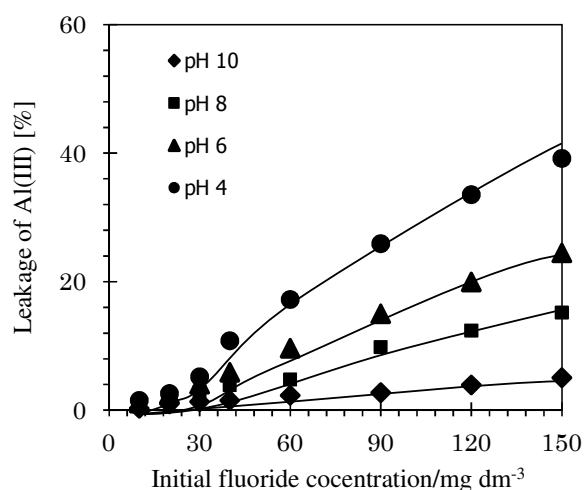


**Scheme 2.2** Mechanism of fluoride adsorption and desorption using alkaline solution [M = Sn(IV), Ti(IV), V(IV), Al(III), and Fe(III)]

### 2.3.3.7 Leakage of loaded Al(III) ions

In order to investigate the most effective condition for fluoride adsorption on Al-SOJR, leakage of  $\text{Al}^{3+}$  from Al-SOJR was measured at different pH (4-10) at varying initial fluoride concentration (10-150  $\text{mg dm}^{-3}$ ). **Figure 2.9** shows the percentage leakage of the loaded  $\text{Al}^{3+}$  from Al-SOJR as a function of initial fluoride concentration. It is clear from this figure that the leakage of  $\text{Al}^{3+}$  ion increases with increasing fluoride concentration in the high concentration range above 30  $\text{mg dm}^{-3}$  at low pH while it is negligible in the low concentration range at all pH tested, suggesting that the removal of fluoride by using Al-SOJR is limited only from dilute solution lower than 30  $\text{mg dm}^{-3}$ . On the other hand, it is insignificant at alkaline pH even at high

fluoride concentration, indicating that a use of dilute alkaline solution for elution brings about no trouble for the regeneration of the adsorbent.



**Fig. 2.9** Leakage of loaded Al(III) from Al-SOJR at varying concentration of fluoride ions at different pH (volume of solution = 10 cm<sup>3</sup>, weight of gel = 10 mg, shaking time = 24 h, string speed = 150 rpm, and temperature = 30°C)

### 2.3.3.8 Desorption of fluoride ions

Effective elution of adsorbed fluoride from the saturated gels is very important for the regeneration of adsorbents. The result shown in **Fig. 2.5** demonstrates that, fluoride is effectively adsorbed on Al-SOJR in pH range 5.5-6.05 whereas it is poorly adsorbed at alkaline pH, suggesting the possibility of desorbing adsorbed fluoride from the saturated gel using alkaline solution without accompanying the leakage of loaded Al<sup>3+</sup> ion as mentioned earlier. The desorption studies of fluoride from fluoride adsorbed gel at different concentration of NaOH is illustrated in **Table 2.5** which shows that desorption of adsorbed fluoride from Al-SOJR increases from 41% to 98% with increasing the concentration of NaOH from 0.01 to 0.1 M and remains constant with further increase in NaOH concentration. The mechanism of fluoride desorption from the saturated Al-SOJR gel can be interpreted also in terms of the ligand exchange mechanism as depicted in **Scheme 2.2**.

**Table 2.5** Desorption of adsorbed fluoride ( $0.79 \text{ mmol g}^{-1}$ ) from Al-SOJR by NaOH solution

NaOH [M]	0	0.01	0.03	0.05	0.1	0.2	0.3	0.5
Desorption [%]	0.3	41.3	71.9	93.4	98.5	99.0	98.3	99.1

## 2.4 CONCLUSIONS

The saponified orange juice residue prepared from orange waste can be easily converted into ligand exchange type material by further loading with multi-valent metal ions. Comparative study of adsorption capacities among loaded metal ions showed that Al-SOJR gel is the most promising for the treatment of fluoride contaminated water under neutral pH condition because the maximum adsorption of fluoride on Al-SOJR took place at near neutral pH whereas the maximum adsorption took place in more acidic region by other metal loaded SOJR. Adsorption tests at different solid-liquid ratios showed that fluoride concentration can be lowered to the environmentally acceptable limit by treating with Al-SOJR gel. Adsorption mechanism of fluoride on Al-SOJR gel was interpreted by ligand exchange mechanism between hydroxyl and fluoride ions. Co-existing  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{Na}^+$  ions have negligible effect on fluoride removal capacity whereas the presence of co-existing  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  retard the fluoride removal capacity in small extent. The adsorbed fluoride was successfully eluted by using alkaline solution. It can be concluded that Al-SOJR gel can be expected to be an efficient, excellent and environmentally benign adsorbent for fluoride removal.

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## Chapter 3

### **Improvement of Selectivity and Uptake Capacity of Adsorbent by Loading Zr(IV) onto Orange Juice Residue for the Removal of Fluoride**

Although adsorption behavior of the metal loaded adsorbents for fluoride (**Chapter 2**) appeared to be satisfactory by using Fe, Al, V, Ti, and Sn loaded SOJR, maximum adsorption capacity and selectivity of fluoride was little bit poor. In this Chapter, the investigation of the orange waste gel with higher adsorption capacity and selectivity towards fluoride was conducted by using Zr(IV) loaded SOJR. From the adsorption isotherm test of fluoride by this adsorbent, the maximum sorption capacity at different pH 2.5, 3, 4, 6, and 8 was improved as 1.22, 1.51, 1.74, 1.10, and 0.53 mmol g<sup>-1</sup>, respectively, compared to SOJR loaded with other metal ions (~1 mmol g<sup>-1</sup> at their optimal pH) investigated earlier. It was found that presence of co-existing anions such as Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and CO<sub>3</sub><sup>2-</sup> had negligible effect on fluoride adsorption. Application of Zr-SOJR for fluoride removal from actual waste plating solution suggested the effective removal at a solid-liquid ratio greater than 4 g dm<sup>-3</sup>. The examination of cycle test of fluoride removal showed effective adsorption as well as elution of fluoride without any significant reduction of fluoride removal efficiency, suggesting that Zr(IV) is stably immobilized onto the polymer matrix of orange waste during the consecutive repetition of adsorption followed by desorption. Adsorption test of fluoride using a packed column suggested the promising application of Zr-SOJR for fluoride removal also in continuous system.

#### **3.1 INTRODUCTION**

The safe disposal of fluoride containing waste water generated in steel production, refining of niobium and tantalum, electroplating, silicon semiconductor manufacturing, mining and fertilizer production is an increasing challenge because waste water discharge from these industries sometimes contains ten to thousand mg dm<sup>-3</sup> of fluoride which may cause serious health hazards such as neurological disorder, thyroid problems, mutation, kidney damage, mutation and fluorosis [1, 2]. The adsorption of fluoride onto the natural material can be a

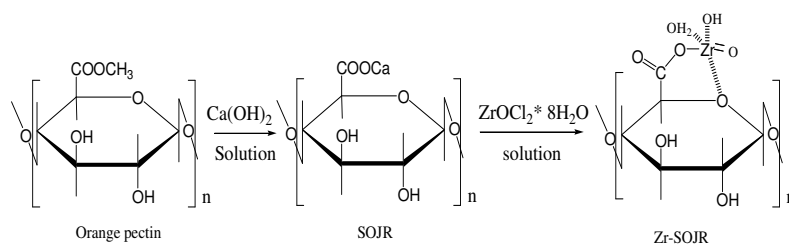
promising technology due to their available and economic reason. The utilization of various agricultural waste materials, on the other hand, attracted the attention of scientist because of the abundant, functional diversity, ease of modification, high uptake capacity and selective adsorption [3, 4]. In our previous work, we have successfully prepared adsorbents for fluoride removal by loading multivalent metal ions such as Al, Ce, Sn, V, Sn, and Ti onto orange waste. Among the different metal loaded orange waste gels, Al-loaded orange gel was found to be effective for the removal of fluoride near to neutral pH, although leakage of loaded Al at pH below 4 and at fluoride concentration higher than  $30 \text{ mg dm}^{-3}$  was considerably high. Although adsorption behavior of some of these adsorbent is satisfactory compared to the various types of adsorbents reported elsewhere in the literatures [5-7], improvement of adsorption capacity, stability and selectivity towards fluoride is further required. Hence, in the present investigation, we have developed the more effective adsorbent from orange waste by loading Zr(IV) ions by the similar method to that of other metal loaded SOJR as described in Chapter 2. The higher affinity of Zr(IV) for fluoride is resulted because of the strong complexation with fluoride, high stability of its fluorocomplex ( $k_1 = 5.88$ ) and easily hydrolyzed even at low concentration. Since Zr(IV) is characterized by high positive charge and high resistance to attack by acid or alkali, thus our attention was devoted for Zr(IV) ion to improve the stability, adsorption capacity and selectivity of adsorbent for fluoride.

## 3.2 EXPERIMENTAL PROCEDURE

### 3.2.1 Preparation of Zr-SOJR from orange waste

As in the case of preparation of Al-SOJR and other metal loaded SOJR as described in Chapter 2, Zr-SOJR was also prepared in the same manner. At first orange waste was saponified with lime water as described in Chapter 2, and then the saponified product of orange juice residue was converted into Zr-SOJR as follows. Three gram of saponified orange gel was taken in a conical flask along with  $500 \text{ cm}^3$  of  $0.1 \text{ M}$  ( $\text{M} = \text{mol dm}^{-3}$ ) zirconium oxychloride octahydrate ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ) solution maintained at pH 2.16. Then, the mixture was agitated for 24 h at  $30^\circ\text{C}$  for complete zirconium loading. After filtration, it was washed several times with

distilled water followed by hot water wash in order to remove free Zr(IV) from the gel. The Zr(IV) loaded orange gel prepared (**Scheme 3.1**) in this way is termed as Zr-SOJR hereafter.



**Scheme 3.1** Creation of active sites on SOJR by Zr(IV) loading reaction

### 3.2.2 IR spectroscopy and Zr(IV) content analysis

In order to confirm the presence of various functional groups, FT/IR spectra of OJR, SOJR and Zr-SOJR were recorded by using Fourier transform infrared spectrometer. Zirconium content analysis in a sample of Zr-SOJR was carried out by dissolving the adsorbent in aquaregia at solid-liquid ratio of  $5 \text{ g dm}^{-3}$ . After dissolution, Zr(IV) content in the test solution was analysed by ICP-AES spectrometer.

### 3.2.3 Incineration behavior of orange waste adsorbents

Incineration behavior of H-SOJR, SOJR and Zr-SOJR was conducted to investigate the effect of loaded cations on the weight remain percentage after incineration. The conversion into hydrogen ion type of SOJR, or preparation of H-SOJR was performed by mixing 100 mg of SOJR in a  $100 \text{ cm}^3$  of 0.1M HCl solution and stirred for 24 h. Then it was filtered, washed until neutral pH and finally dried in a convection oven at  $70^\circ\text{C}$ . For the thermal analysis of SOJR, 10 mg of SOJR was weighed and incinerated at temperature ranging from 40 up to  $1000^\circ\text{C}$  at increasing rate of temperature at  $10^\circ\text{C min}^{-1}$  by using (Shimadzu model simultaneous DTA-TG, DTG-60H) thermogravimetric analyzer. Similar test was carried out using H- SOJR and Zr-SOJR to compare behavior of different adsorbents loaded with cations having different molecular weights.

### 3.2.4 Batch wise adsorption tests

Equilibrium adsorption tests of fluoride on Zr-SOJR was carried out in a 50 cm<sup>3</sup> conical flask where 25 mg of the adsorbents and 15 cm<sup>3</sup> of fluoride solution at varying concentration were shaken in a thermostated shaker at 30°C for 24 h to attain equilibrium. The pH was adjusted by adding either 0.5 M NaOH or 0.5 M HCl. After 24 h of shaking, the solution was filtered and measured by using (DIONEX Model ICS 1500) ion chromatography. Influence of temperature for the adsorption of fluoride was carried out at four different temperatures by varying initial fluoride concentrations (0.5 - 10 mmol dm<sup>-3</sup>) at pH 4. The effect of co-existing anions for fluoride adsorption on Zr-SOJR was studied at varying pH as well as varying the concentration of co-existing anions (NO<sup>3-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and CO<sub>3</sub><sup>2-</sup>) using their respective sodium salts. The adsorption test of fluoride from actual waste plating solution on Zr-SOJR was carried out using a sample solution supplied from a plating company in Japan (Mitsui minini Co. Ltd., Japan) at different adsorbent dosage. The adsorption-elution cycle test was performed to investigate the repeated use of Zr-SOJR. The elution test of fluoride was carried out by 0.1 M NaOH at the same solid-liquid ratio as in the case of adsorption test. The leakage test of loaded zirconium from Zr-SOJR at varying concentration of fluoride (0.5-8 mmol dm<sup>-3</sup>) at different pH was carried at 1 g dm<sup>-3</sup>.

### 3.2.5 Continuous adsorption test

The glass column of 0.8 cm inner diameter was employed in the continuous adsorption experiment of fluoride onto Zr-SOJR. Before filling the adsorbent into the column, it was soaked in deionized water, and then the column was packed with 1.01 g of Zr-SOJR. Prior to adsorption test, column was conditioned by the fluoride free solution for 5 h at the same pH (pH = 4) as test solution. After this, fluoride solution (14.82 mg dm<sup>-3</sup>) was passed into the column at the flow rate of 5.1 cm<sup>3</sup> h<sup>-1</sup> with the help of (Iwaki model PST 100N) peristaltic pump. The effluent samples for the measurement at hourly interval were collected with the help of (Biorad Model 2110) fraction collector. The elution of loaded fluoride was performed by 0.1 M NaOH solution. Effluent samples were regularly collected and analyzed by ion chromatography.



### 3.3 RESULTS AND DISCUSSION

#### 3.3.1 Analytical, spectroscopic and thermal characterization

##### 3.3.1.1 Stripping of Zr(IV) from Zr-SOJR

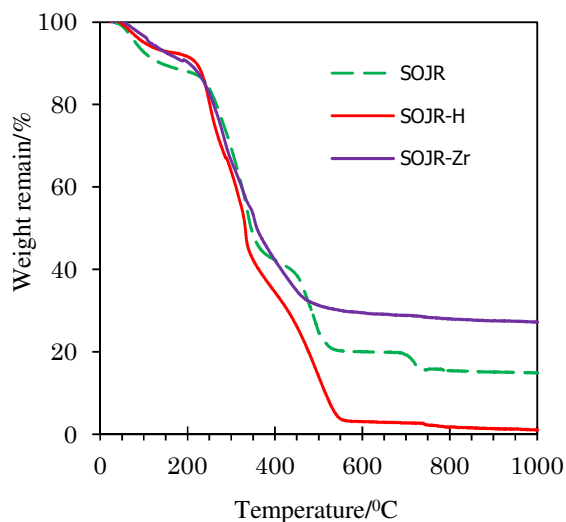
**Table 3.1** shows the result of the stripping test of Zr(IV) from Zr-SOJR at varying concentration of HCl. It shows that stripping of Zr(IV) increases with increasing HCl from 0.01 to 1M, and achieved maximum value above 1 M. However, for the evaluation of total amount of loaded Zr(IV), aquaregia dissolution of Zr-SOJR at 5 g dm<sup>-3</sup> was performed for complete dissolution. After dissolution, Zr(IV) concentration in the test solution was analyzed by ICP-AES spectrometer. The total amount of loaded Zr(IV) evaluated by this method was 1.62 mmol g<sup>-1</sup>.

**Table 3.1** Leaching test of Zr(IV) from Zr-SOJR by hydrochloric acid solution

HCl [M]	0.01	0.05	0.1	0.5	1	2	5
Stripping [%]	0	4.7	58.2	80	99.6	99.8	99.7

##### 3.3.1.2 Incineration behavior of orange waste adsorbents

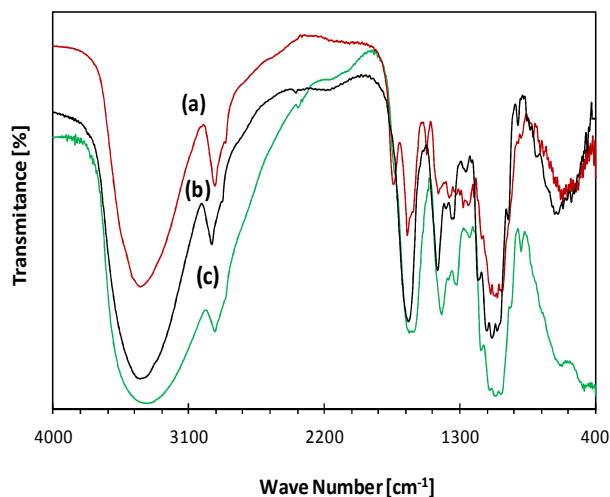
**Figure 3.1** shows the weight remain percentage of H-SOJR, SOJR and Zr-SOJR as a function of incineration temperature. It shows that, when the temperature is increased the weight loss % is gradually increases from 40°C up to 200°C for all the adsorbent whereas it is increased drastically at temperature 200°C to 500°C. The slow rate of weight loss below 200°C is due to the evaporation of moisture from the adsorbent whereas drastic loss of adsorbent weight at temperature higher than 200°C is due to the decomposition of organic part of the gel to CO<sub>2</sub> and H<sub>2</sub>O. The inorganic part of the gel including the loaded metal ions is converted into its oxide and left in the ash. After the incineration, 0.2, 1.3 and 2.8 mg of ash were remained from 10 mg H-SOJR, SOJR and Zr-SOJR, respectively, which suggests the presence of 12.3% of Zr(IV) in the tested sample Zr-SOJR. Value of ash formed after the incineration of SOJR is lower than that of Zr-SOJR, which can be reasonably attributed to the high molecular weight of oxide of loaded Zr(IV) in Zr-SOJR compared to that of Ca-O in SOJR.



**Fig. 3.1** Relationship between the weight remains percentage of H-SOJR, SOJR and Zr-SOJR as a function of incinerating temperature

### 3.3.1.3 Functional group analysis

Analysis of the main functional group on Zr-SOJR was investigated together with SOJR and its feed material, raw orange waste, with the help of infrared spectroscopic measurement. In order to show the effect of loaded metal ions, IR spectra of OJR, SOJR and Zr-SOJR were recorded and compared in **Fig. 3.2**. In OJR [**Fig. 3.2** (a)], the intense peak at  $3436\text{ cm}^{-1}$  due to hydroxyl group, peak at  $2888\text{ cm}^{-1}$  due to  $-\text{CH}_2$  stretching vibration, band at  $1742\text{ cm}^{-1}$  due to stretching vibration of  $\text{COO}^-$  group, band at  $1680\text{ cm}^{-1}$  is due to stretching vibration of  $\text{C}=\text{O}$  were observed. But, in SOJR [**Fig. 3.2** (b)], the peak at  $1742\text{ cm}^{-1}$  is completely disappeared and two new peaks appeared at around  $1672$  and  $1439\text{ cm}^{-1}$  which are due to the existence of  $-\text{O}-\text{Ca}$  bond in SOJR. Similarly in the case of Zr-SOJR [**Fig. 3.2** (c)], carboxyl peak at  $1742\text{ cm}^{-1}$  was disappeared and two new peaks at around  $1654$  and  $1434\text{ cm}^{-1}$  were observed. The bond strength of  $\text{C}=\text{O}$  bond is weakened due to the coordination of high molecular weight Zr(IV), resulting in the shifting of stretching vibration to lower frequency.

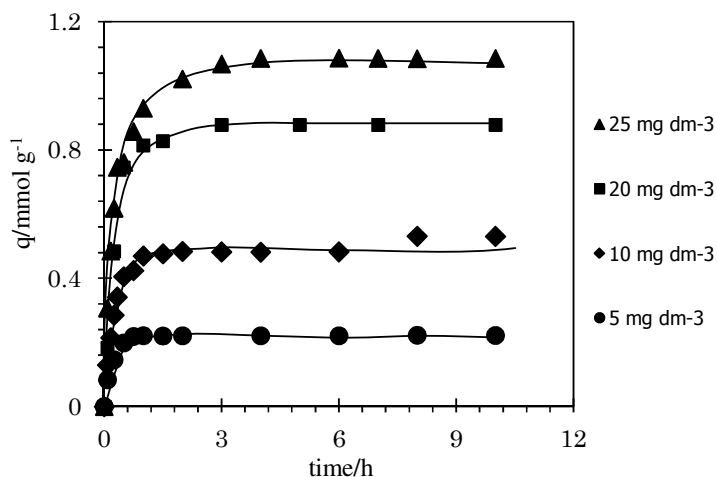


**Fig. 3.2** Infrared spectra of (a) raw orange juice residue (OJR), (b) saponified orange juice residue (SOJR), and (c) zirconium loaded saponified orange juice residue (Zr-SOJR).

### 3.3.2 Results of batch wise adsorption test

#### 3.3.2.1 Effect of contact time

Contact time plays an important role in the adsorption of fluoride on solid surface. Percentage removal is increased with increasing contact time until equilibrium is achieved. **Figure 3.3** represents the fluoride uptake on Zr-SOJR at different concentrations of fluoride as a function of shaking time. It is clear from this figure that adsorption of fluoride on Zr-SOJR sharply increases with increasing contact time at the beginning, and then it is gradually increased and the maximum removal is achieved within 4 h for all the concentration tested. The increase in adsorption of fluoride with the increase of initial concentration can be attributed to the increase of driving force for the adsorption of fluoride due to high concentration gradient. Consequently, subsequent experiments were carried out for 24 h to ensure the complete equilibrium.

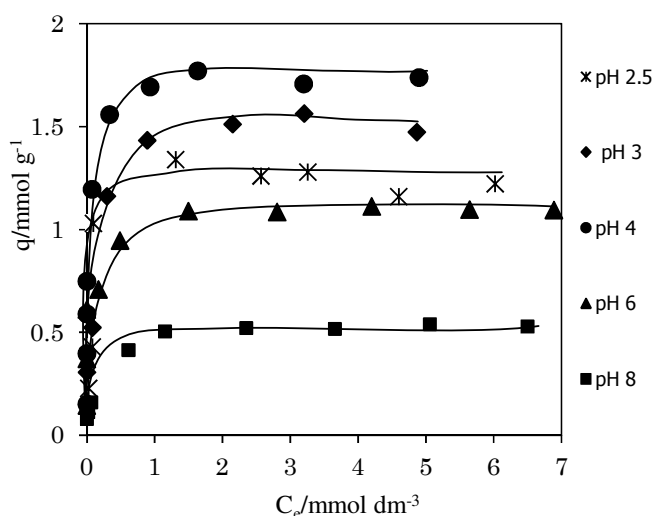


**Fig. 3.3** Time variation of fluoride adsorption by Zr-SOJR at different initial fluoride concentrations (solid liquid ratio =  $1.33 \text{ g dm}^{-3}$ , pH = 4, temperature =  $30^\circ\text{C}$ )

### 3.3.2.2 Adsorption isotherm

Equilibrium relationship between the amount of adsorbed fluoride and its residual concentration in liquid phase is the measure of adsorption potential of the adsorbent, which is known as adsorption isotherm. Adsorption isotherm of fluoride on Zr-SOJR at different pH is shown in **Fig. 3.4**. The result shows that, the pH of the aqueous solution is an important parameter that controls the adsorption of fluoride at the solution-adsorbent interface. It is apparent from this result that fluoride uptake capacity increases with increasing pH in the pH range of 2.5 to 4 and then decreased with further increase in pH. At low pH below 3, weakly ionizable HF ( $pK_a = 3.18$ ) is formed which is difficult to adsorb on the Zr-SOJR. At basic pH, fluoride adsorption capacity is decreased due to the competition with hydroxyl ion for the active sites. The maximum fluoride adsorption was found to occur at pH 4 so that pH 4 was termed as the optimum pH in further experiments. Considerable reduction in fluoride removal efficiency of Zr-SOJR was observed at pH above 6, which may be due to the competition between hydroxyl ions in solution and fluoride for the sorption site [8-11], and increased electrostatic repulsive force between the deprotonated surface of orange pectic acid and negatively charged fluoride [12]. The removal of fluoride by Zr-SOJR takes place *via* ligand exchange reaction between hydroxyl ions present in the coordination sphere of loaded Zr(IV) and fluoride in the

aqueous solution. It is clearly demonstrated from the result of Fig. 3.4 that amount of fluoride uptake by Zr-SOJR sharply increases at lower concentration of fluoride whereas it is unchanged or nearly constant at high concentration. The maximum adsorption capacities of Zr-SOJR were evaluated from the plateau value at pH 2.5, 3, 4, 6 and 8 as 1.22, 1.51, 1.74, 1.10 and 0.53 mmol g<sup>-1</sup>, respectively.

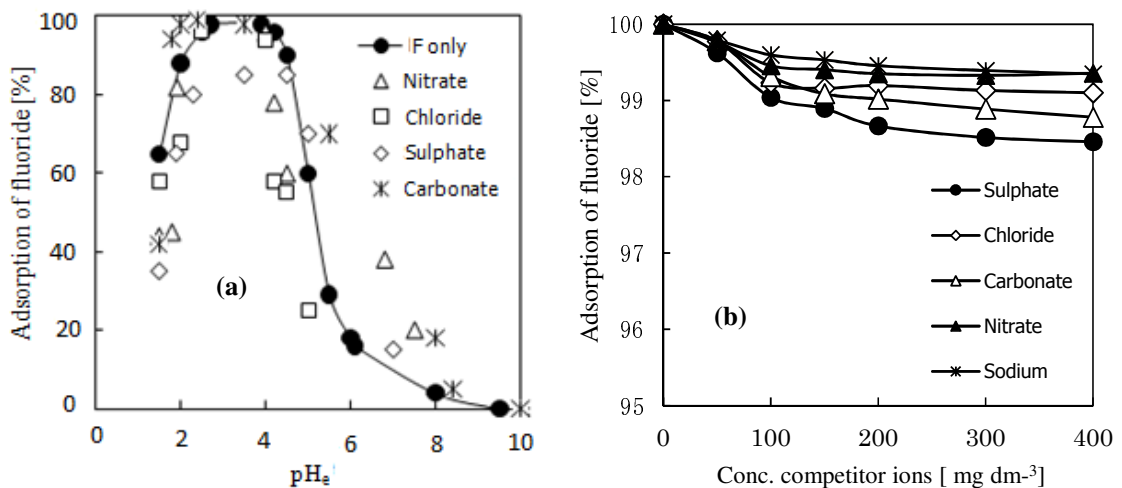


**Fig. 3.4** Adsorption isotherm of fluoride onto zirconium loaded-SOJR at different pH (volume of solution = 15 cm<sup>3</sup>, weight of gel = 25 mg, and temperature = 30°C)

### 3.3.2.3 Selectivity test

It is very important for the adsorbent to be selective to the targeted fluoride for the application in the real system because contaminated water contains some other co-existing ions like CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> together with fluoride that may compete for the adsorption sites. Hence, the adsorption behavior of fluoride on Zr-SOJR was investigated in the presence of these competing anions. Adsorption behavior of fluoride on Zr-SOJR in the presence of ten times higher concentrations of these co-existing ions at different pH is shown in Fig. 3.5 (a). It is clear from this figure that adsorption of fluoride increases with increasing equilibrium pH below 3, then it reach the maximum values at around 3-4. The adsorption of fluoride is decreased with the further increase of equilibrium pH of the solution. The result also demonstrates that adsorption behavior of fluoride is not significantly changed in the entire range of pH tested even

in the co-existing system, showing very high selectivity of present adsorbent for fluoride. It can be further proved by the selective adsorption of fluoride in the presence of varying concentration of co-existing cations ( $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ) and anions ( $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ) as shown in **Fig. 3.5 (b)**. It shows that presence of co-existing  $\text{Na}^+$  have no effect during fluoride adsorption. In the case of other co-existing anions, the interference is negligible less than 2% even in the presence of 25 times greater concentrations of interfering ions, exhibiting that Zr-SOJR investigated in this study is very much selective to targeted (fluoride) ions from water. These results suggest that Zr-SOJR investigated in this study can be one of the suitable candidates to remove fluoride from waste water.

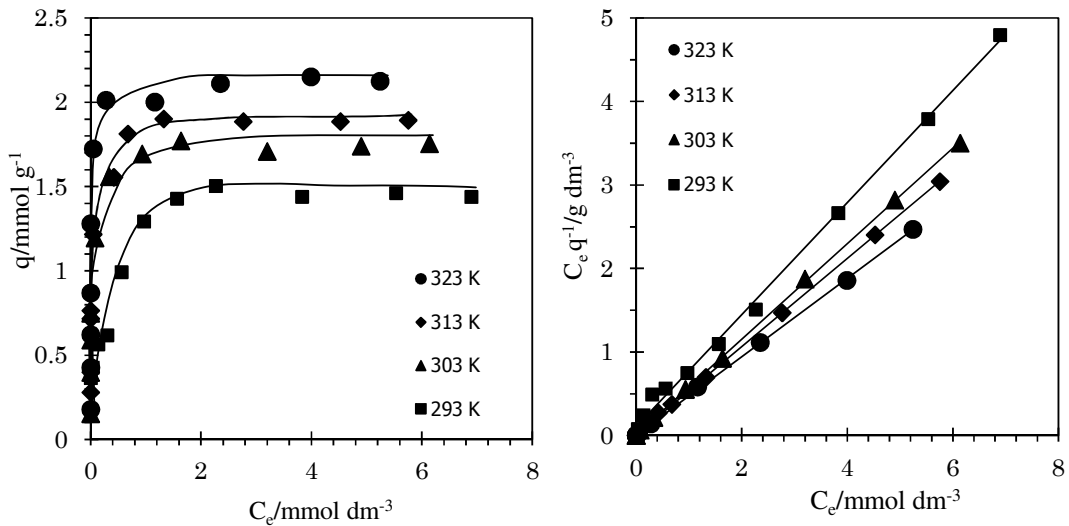


**Fig. 3.5** Removal of fluoride by Zr-SOJR from co-existing system at solid liquid ratio of  $1.33 \text{ g dm}^{-3}$  at  $30^\circ\text{C}$  (a) co-existing ions at varying pH ( $F = 1.57 \text{ mmol dm}^{-3}$ ) (b) at varying concentration of co-existing ions at pH 4 ( $F = 1 \text{ mmol dm}^{-3}$ )

### 3.3.2.4 Effect of temperature

Temperature greatly affects the adsorption of fluoride onto Zr-SOJR. Adsorption capacity of Zr-SOJR for fluoride as a function of equilibrium concentration at four different temperatures is shown in **Fig. 3.6 (a)**. It shows that adsorption of fluoride increases with increasing temperature of the reaction system which indicates the endothermic nature of reaction. The result shows that adsorption of fluoride increases with increasing concentration at lower

concentration region whereas it tends to level off at high concentration, suggesting the formation of monolayer of adsorbed fluoride on the surface of adsorbent. It is similar to that of the classical Langmuir type adsorption. Maximum adsorption capacity,  $q_{\max}$  ( $\text{mmol g}^{-1}$ ), and Langmuir equilibrium constant,  $b$  ( $\text{dm}^{-3} \text{mmol}$ ), were evaluated from the plot of  $C_e/q$  versus  $C_e$  [Fig. 3.6 (b)] which gives the straight line with high correlation coefficient ( $>0.98$ ) for all the temperature. The maximum adsorption capacity and equilibrium constants were evaluated from slope and intercept of these straight lines, respectively, which are listed in Table 3.2.



**Fig. 3.6** Effect of temperature on fluoride adsorption onto Zr-SOJR (volume of solution =  $15 \text{ cm}^3$ , weight of gel = 25 mg, pH = 4, shaking time = 24 h, and shaking speed = 150 rpm) (a) adsorption isotherm (b) corresponding Langmuir plot

The equilibrium constant calculated from Langmuir isotherm model is used for the evaluation of thermo-dynamic parameters. Investigation of temperature dependence of adsorption gives valuable information about the Gibbs free energy change ( $\Delta G$ ), enthalpy change ( $\Delta H$ ), and entropy change ( $\Delta S$ ) during the adsorption. Gibbs free energy change of the system ( $\Delta G$ ) is related to logarithm of equilibrium constant ( $\ln b$ ) by the following equation:

$$\Delta G = -RT \ln b \quad (3.1)$$

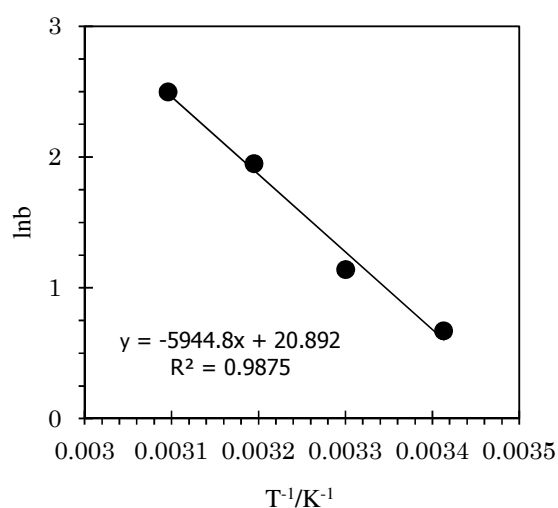
The enthalpy change and entropy change are related to Gibbs free energy change as:

$$\Delta G = \Delta H - T\Delta S \quad (3.2)$$

After the rearrangement of equation (3.1) and (3.2), it gives

$$\ln b = -\Delta H/RT + \Delta S/R \quad (3.3)$$

The relationship between the logarithm of Langmuir equilibrium constant ( $b$ ) and temperature ( $T$ ) is given in **Fig. 3.7** Gibbs free energy change evaluated using equation 3.1 and other thermodynamic parameters such as enthalpy change and entropy change were evaluated from the slope and intercept of the linear plot of  $\ln b$  versus  $1/T$  (**Eq. 3.3**), respectively. The evaluated thermodynamic parameters such as Gibbs free energy change ( $\Delta G$ ), enthalpy change ( $\Delta H$ ), and entropy change ( $\Delta S$ ) are also listed in **Table 3.2**. The negative value of  $\Delta G$  indicates that the adsorption of fluoride on Zr-SOJR is spontaneous for the temperature range tested, which is usually the case for many adsorption systems in solution. The positive value of  $\Delta H$  shows that the adsorption is endothermic, so raising temperature leads to a higher adsorption of fluoride at equilibrium. The positive value of  $\Delta S$  indicates an increase of randomness or disorderness of the system. It is attributed that some of the hydroxyl ions release during the adsorption process will increase the entropy of the system during fluoride adsorption.



**Fig. 3.7** Van't Hoff plot for the adsorption of fluoride onto Zr-SOJR

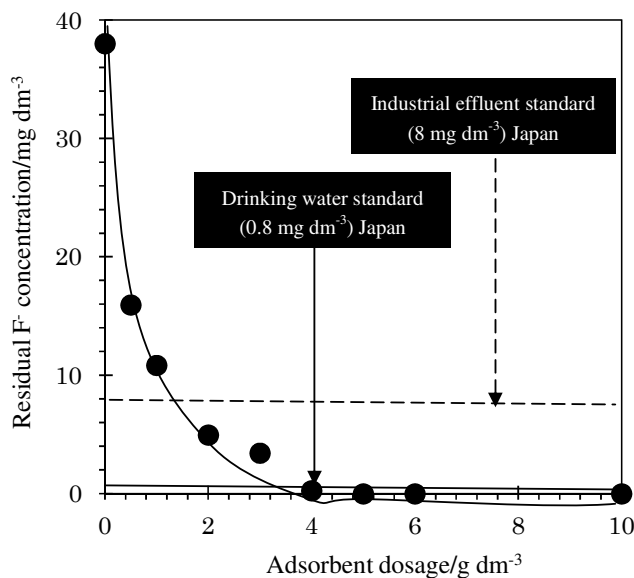


**Table 3.2** Thermodynamic parameters investigated for the adsorption of fluoride on Zr-SOJR

Temp. /K	$q_{\max}$ /mmol g <sup>-1</sup>	$b$ /dm <sup>3</sup> mmol <sup>-1</sup>	$\ln b$	$\Delta G$ /kJ mol <sup>-1</sup>	$\Delta H$ /kJ mol <sup>-1</sup>	$\Delta S$ /kJ mol <sup>-1</sup> K <sup>-1</sup>
293	1.59	1.95	0.67	-1.63	49.41	0.17
303	1.74	3.11	1.13	-2.86		
313	1.95	7.02	1.95	-5.07		
323	2.17	12.15	2.50	-6.71		

### 3.3.2.5 Removal of fluoride from actual plating solution

The relationship between the remaining concentrations of fluoride ions in actual waste plating solution at pH 3 as a function of Zr-SOJR dosage is shown in **Fig. 3.8**. It is evident from this figure that concentration of fluoride in the plating solution was found to be sharply decreased with increasing adsorbent dosage up to 3 g dm<sup>-3</sup> and at solid-liquid ratio greater than 4 g dm<sup>-3</sup>, a complete removal of fluoride was achieved. With the increase in adsorbent dosage, the number of active sites per unit volume of suspended solution increases, which leads to the increase in the removal of fluoride. In spite of the presence of other anions (Cl<sup>-</sup>: 29.2, SO<sub>4</sub><sup>2-</sup>: 24.2 and PO<sub>4</sub><sup>3-</sup>: 12.9 mg dm<sup>-3</sup>) and metal ions (Ca: 550, Si: 100, Ni: 73, Al: 55, Fe: 51, Zn: 13, Ti: 4.2 and Cu: 2.4 mg dm<sup>-3</sup>) in the actual plating solution, fluoride was found to be preferentially removed by Zr-SOJR under the stated experimental conditions without any leakage of loaded Zr(IV). This result ensures that fluoride concentration can be successfully lower down to industrial effluent standard in Japan by using 1.5 g dm<sup>-3</sup> of Zr-SOJR whereas to clear the drinking water standard of Japan (0.8 mg dm<sup>-3</sup>) can be achieved at the dosage of 4 g dm<sup>-3</sup>. Hence, it is expected that the adsorbent prepared in this study can be an alternative candidate to treat the fluoride containing wastewater produced from plating factories.

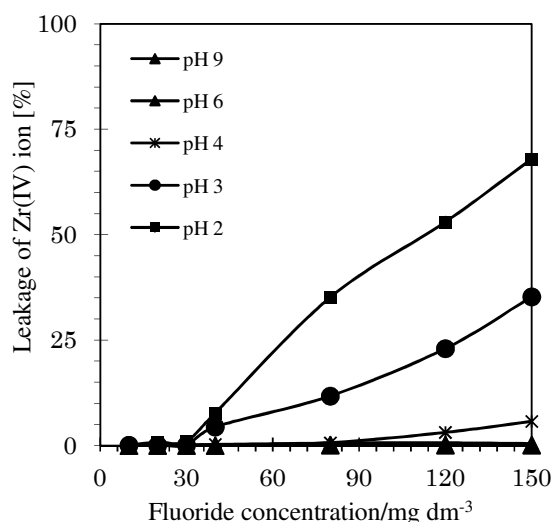


**Fig. 3.8** Removal of fluoride from actual plating ( $38.2 \text{ mg dm}^{-3}$ ) solution by using Zr-SOJR (volume of solution =  $10 \text{ cm}^3$ , pH = 3, shaking time = 24 h, and temperature =  $30^\circ\text{C}$ )

### 3.3.2.6 Leakage of loaded zirconium(IV) from the gel

No leakage of loaded Zr(IV) from the gel during adsorption and elution should be ensured for the reuse and regeneration of adsorption gel. **Fig. 3.9** shows the percentage leakage of the loaded Zr(IV) from Zr-SOJR as a function of fluoride concentration at various pH. The result shows that the leakage increases with increasing fluoride concentration above  $30 \text{ mg dm}^{-3}$  at low pH while it is negligible (less than 1%) or insignificant even at high fluoride concentration in basic pH range, suggesting that the use of dilute alkali solution for the elution of fluoride from saturated gel has no problem for regeneration purpose while the adsorption should be carried out for dilute concentration of fluoride (lower than  $30 \text{ mg dm}^{-3}$ ) at low pH. The Zr(IV) in Zr-SOJR is effectively bonded with oxygen atom of the pyranose ring of the orange pectin showing negligible leakage even at low pH (2-3) in the absence of fluoride. However, in the presence of fluoride, the strength of Zr-O bond is weakened due to the interaction of fluoride with loaded Zr(IV) which provides the additional driving force for the ion exchange reaction between loaded Zr(IV) and  $\text{H}^+$  at acidic medium. This effect is insignificant

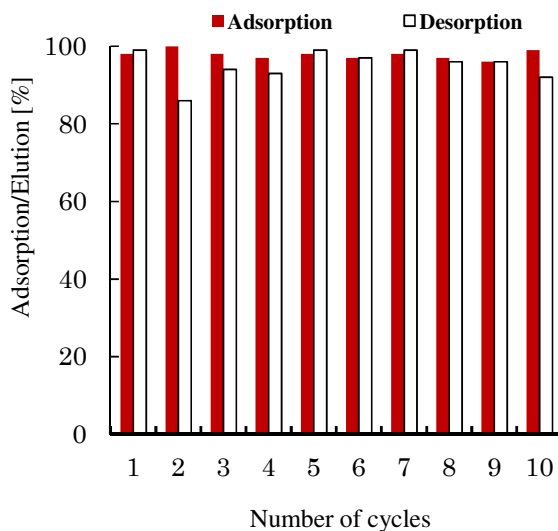
at low fluoride concentration ( $< 30 \text{ mg dm}^{-3}$ ) but it is increased with increasing concentration of fluoride.



**Fig. 3.9** Leakage of loaded Zr(IV) at varying concentration of fluoride at different pH (volume of solution =  $10 \text{ cm}^3$ , shaking time = 24 h, weight of gel = 10 mg, and temperature =  $30^\circ\text{C}$ )

### 3.3.2.7 Cycle test of Zr-SOJR

The repeated use of adsorbent is important and essential for its application to the real system. As seen from **Fig.3.5 (a)**, fluoride is effectively adsorbed onto Zr-SOJR in the pH range 2-4 while it is poorly adsorbed at pH higher than 8. From this result, adsorbed fluoride can be expected to be easily eluted by using dilute alkaline solutions like 0.1 M NaOH in order to regenerate the gel for further use. We carried out the cycle tests (adsorption-elution-adsorption) to find the reusability of the gel where 0.1 M NaOH solution was used as eluent as shown in **Fig. 3.10**. It is evident from this figure that fluoride removal efficiency of this adsorbent is not changed drastically even after ten repeated cycles, indicating that the zirconium(IV) is effectively immobilized on SOJR, suggesting that good adsorption as well as elution can be achieved without any degradation of the adsorbent.

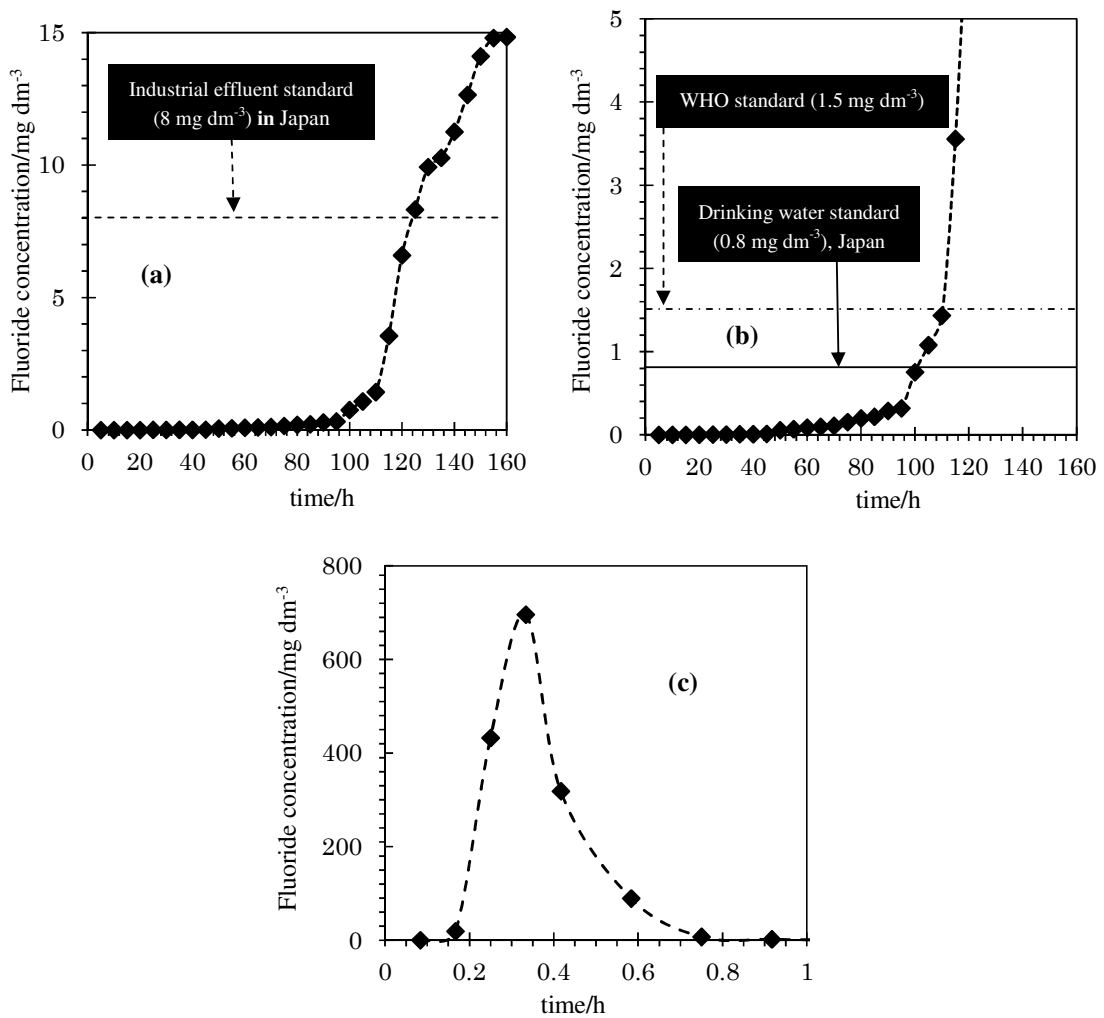


**Fig. 3.10** Cycle test of fluoride adsorption followed by elution using NaOH solution (solid liquid ratio =  $2.5 \text{ g dm}^{-3}$ , fluoride solution =  $30 \text{ mg dm}^{-3}$ , eluent =  $0.1 \text{ M NaOH}$ , and temperature =  $30^\circ\text{C}$ )

### 3.3.3 Adsorption performance in packed column

Column performance of the Zr-SOJR in continuous mode of operation was studied by percolating  $14.82 \text{ mg dm}^{-3}$  of fluoride solution at optimum pH (pH 4) as determined from batch adsorption. Breakthrough curve of fluoride using packed column of Zr-SOJR ( $1.01 \text{ g}$ ) is shown in **Fig. 3.11 (a)**. It shows that the fluoride concentration in the effluent was found to be negligibly low until 90 h, indicating that fluoride was effectively adsorbed onto the column of Zr-SOJR. After 90 h, concentration of fluoride in the effluent was gradually increased and reached near to WHO ( $1.5 \text{ mg dm}^{-3}$ ) standard [13] at 110 h, industrial effluent standard ( $8 \text{ mg dm}^{-3}$ ) at around 120 h and reached saturation at 160 h. In order to make the clear vision, the part of residual fluoride concentration below  $5 \text{ mg dm}^{-3}$  is shown in **Fig. 3.11 (b)**. The result ensures that fluoride can be successfully removed from the waste water near to the accepted standard. The effective adsorption capacity calculated from **Fig. 3.11 (a)** was  $9.48 \text{ mg fluoride g}^{-1}$  of dry Zr-SOJR, which is 28.5% compared to that of the equilibrium sorption capacity evaluated from batch wise test. The low extent of fluoride adsorption in the packed column of Zr-SOJR compared to that in the batch adsorption can be attributed to the channeling effect and

insufficient contact due to low residence time. After complete saturation of the column, elution test was carried out as shown in Fig. 3.11 (c). The elution of fluoride was found to be very efficient because adsorbed amount of fluoride onto the column of Zr-SOJR was more or less quantitatively desorbed by using 0.1 M NaOH solution. The eluted amount of fluoride calculated from Fig. 3.11 (c) was  $9.07 \text{ mg F g}^{-1}$ , which is almost 95% of the adsorbed amount of fluoride in the given experimental condition.



**Fig. 3.11** Column performance of fluoride adsorption onto fixed bed column of Zr-SOJR (a) Break through profile (Feed solution =  $14.82 \text{ mg dm}^{-3}$ , flow rate =  $5.7 \text{ cm}^3 \text{ h}^{-1}$ , pH = 4 and eluent = 0.1 M NaOH, and at rt) (b) breakthrough curve below  $5 \text{ mg dm}^{-3}$  (c) desorption profile

### 3.4 CONCLUSIONS

The results of this study have demonstrated that orange waste, an agro-industrial waste, can be used as a feed material for high-capacity adsorbent for fluoride removal from aqueous solutions. Time required to reach equilibrium was evaluated as 4 h. The optimal adsorption was observed at pH 4 while the adsorption closely followed the Langmuir adsorption isotherm, which indicated that the monolayer adsorption was involved in the process of fluoride removal. A study of fluoride adsorption at different temperature showed that the adsorption reaction of fluoride onto Zr-SOJR is endothermic and spontaneous process. The presence of  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$  had very insignificant effect on fluoride adsorption, which indicated the high selectivity of the Zr-SOJR for fluoride over the tested ions but presence of  $\text{Ca}^{2+}$  little bit enhance the fluoride removal. Adsorption of fluoride on Zr-SOJR was inferred to take place according to the ligand exchange substitution of coordinating hydroxyl ligands by fluoride. Complete removal of fluoride from actual plating solution was found to be achieved regardless of the presence of other oxo-anions as well as cations. The study on elution demonstrated that Zr-SOJR can be easily regenerated by the use of dilute NaOH solution (0.1 M). The complete removal of fluoride was found to be possible by column packed with Zr-SOJR also in continuous mode adsorption. Elution of fluoride from the column was achieved by using a small amount of 0.1 M NaOH. Thus, Zr-SOJR can be employed as an excellent and efficient adsorbent for fluoride removal.

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## Chapter 4

### Adsorption Behavior of Orange Waste Gel for Some Rare Earth Ions and Its Application to the Removal of Fluoride from Water

In this Chapter, a new type of adsorbent for rare earth metal ions was prepared from orange waste by simple method of saponification reaction with lime water. In order to evaluate the effectiveness of the prepared adsorbent, adsorption test of rare earth metal ions such as Sm(III), Ho(III), La(III), Sc(III), and Lu(III) were performed, it was found that these rare earth metal ions are effectively adsorbed on this adsorbent. Because of high stability of fluorocomplex of rare earth metal ions, their small ionic size and strong complexation with fluoride ion, rare earth metal and their oxide were extensively used for the removal of fluoride from aqueous solution so that synthesis and application of some rare earth metal loaded orange gels for fluoride ions were studied in this Chapter. It was found that fluoride ion was effectively adsorbed onto the rare earth loaded orange waste gels. The maximum adsorption capacity for fluoride was evaluated as 0.60, 0.92, 1.06 and 1.22 mmol g<sup>-1</sup> for Sc(III), Ho(III), La(III) and Sm(III) loaded SOJR, respectively. Fluoride was successfully removed below the environmental standard by the use of small amount of La(III) loaded adsorbent. Adsorbed fluoride was successfully eluted by using NaOH solution. Hence, adsorbent derived from orange waste can be a promising material for the recovery of rare earth metal ions in one hand and in the other hand rare earth metal ion loaded orange gels can be an excellent material for scavenging fluoride ions from water.

#### 4.1 INTRODUCTION

Recently, application of RE (rare earth) metal ions for the removal of some anionic species such as arsenic, antimony, phosphate and fluoride from water is increasingly growing technology. Fluoride is one of the contaminant of water which is capable of forming complex with RE elements so that application of these elements for the fabrication of new and effective adsorbent for fluoride is becoming a promising area of research. Because of high stability of fluoride complex of some RE ion (**Table 4.1**) [1], these metal ions have high affinity with



fluoride ion thus can be effectively adsorbed fluoride by using these rare earth metal loaded adsorbents and their compounds. Imai *et al.* (1987) prepared six different types hydrated oxides of RE ions namely  $Y_2O_3 \cdot 2.1 H_2O$ ,  $Nd_2O_3 \cdot 4.7 H_2O$ ,  $Gd_2O_3$ ,  $Ce_2O_3 \cdot 1.6 H_2O$ ,  $La_2O_3 \cdot 3 H_2O$  and  $Sm_2O_3 \cdot 4.1 H_2O$  by the reaction of their salts with either NaOH or ammonia solution in order to investigate the adsorption behavior of some anionic species including fluoride ion. Among the various hydrated RE oxide, oxides of La, Sm, Gd and Ce showed higher fluoride removal capacity. The study of selectivity of  $Ce_2O_3 \cdot 1.6 H_2O$  among tested anions are in the order of  $F^- > HPO_4^{2-} > SO_4^{2-} > Cl^-$ ,  $Br^-$ ,  $NO_3^-$ . The selectivity of usual anion exchange resin for fluoride is low according to Hofmeister selectivity series. However, selectivity of adsorbent for fluoride ion removal can be improved by doping RE ions [2]. Raichur and Jyoti (2001), prepared mixed RE oxide adsorbent containing 44%  $La_2O_3$ , 2%  $Ce_2O_3$ , 10.5%  $Pr_6O_{11}$ , 36.5%  $Nd_2O_3$ , 5%  $Sm_2O_3$  and 2%  $Y_2O_3$  for fluoride ion removal from aqueous solution. The results from the adsorption experiment indicated that mixed RE oxide adsorbent effectively adsorb fluoride with negligible influence of co-existing  $NO_3^-$  and  $SO_4^{2-}$  ions indicating selective nature of adsorbent [3].

**Table 4.1** Stability of fluorocomplex of some rare earth (RE) metal ions

RE element	RE ions	Log. of equilibrium constant
La	$La^{3+}$	5.1
Ce	$Ce^{4+}$	8.16
Sc	$Sc^{3+}$	6.17
Y	$Y^{3+}$	3.89

The more and more research attention has been devoted for the preparation of adsorbent to selectively remove anion like fluoride from water by loading rare earth metal ion onto the natural or synthetic polymer because of high stability of fluorocomplex of RE ions in aqueous solution. The synthesis of adsorbents from commercial polymers such as PMA, AFB, AMPA and 200CT resins loaded with La(III) ion showed effective adsorption of fluoride from water [4]. However, due to their expensive cost, direct uses of hydrated oxide of these rare earth metal

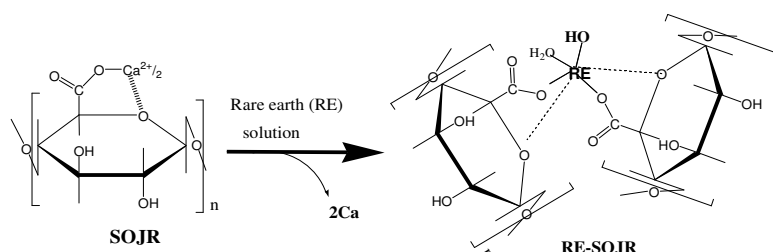
ions are not effective. Nowadays, synthetic polymer or biopolymer loaded with rare earth metal ions drawn the attention of many scientists in this field because of high stability of fluoride complex of these metal ions, high resistance to attack by acid or alkali and small ionic radii resulting very high selectivity towards fluoride ions [5- 7].

Because of these reasons, we have prepared four different types of novel adsorption gels from orange waste to effectively remove trace concentration of fluoride by loading some rare earth metal ions such as Sm(III), La(III), Ho(III) and Sc(III) onto polymer matrix of orange juice residue from aqueous solution. The adsorption behavior of orange waste gel for these rare earth metal ions and their application to fluoride removal from water were investigated.

## 4.2 EXPERIMENTAL PROCEDURES

### 4.2.1 Rare earth metal ions adsorption on orange waste (Synthesis of RE-SOJR)

To prepare RE-SOJR, at first SOJR was prepared from orange juice residue according to the method described in Chapter 2 which was subjected to load the rare earth metal ions. The SOJR (3 g) was mixed together with 200 cm<sup>3</sup> of 0.1 M metal solutions and was stirred for 24 h at 30°C for metal loading reaction. During the loading reaction, Ca<sup>2+</sup> ions present in the saponified product of orange juice residue (SOJR) undergoes cation exchange reaction with the loaded metal ions. After completion of loading reaction, it was washed several times by distilled water to remove unadsorbed metal ions until neutral pH and was dried in a convection oven at 70°C. The product obtained in this way was termed as rare earth metal loaded SOJR and abbreviated as RE-SOJR.



**Scheme 4.1** Adsorption of rare earth metal ions onto SOJR gel [where, RE = La(III), Ho(III), Sm(III), Lu(III) and Sc(III)]

#### 4.2.2 Batch wise adsorption tests

For adsorption test of La(III), Sm(III), Ho(III) and Sc(III) on SOJR, SOJR, and metal solution ( $0.2 \text{ mmol dm}^{-3}$  each) were mixed together at various pH (1-8) and shaken for 24 h at  $30^\circ\text{C}$ . Then, it was filtered and analyzed for metal ion concentration. To determine the loading capacity of these metal ions on SOJR, adsorbent (SOJR) and metal solution were shaken for 24 h by varying concentration of metal ions. Similarly, adsorption tests of fluoride ion on metal loaded SOJR were conducted as follows. In each test, 25 mg of adsorbents were mixed with  $15 \text{ cm}^{-3}$  of fluoride solution ( $\sim 10 \text{ mg dm}^{-3}$ ) at varying pH (2-12) and the mixture was shaken also at  $30^\circ\text{C}$ . After 24 h of shaking, it was filtered and filtrates were analyzed for fluoride ion concentration. The kinetics test was performed to investigate the equilibrium time required for fluoride adsorption using  $0.57 \text{ mmol dm}^{-3}$  of fluoride solution at  $1.33 \text{ g dm}^{-3}$ . Adsorption isotherm of fluoride was examined by varying the concentration of fluoride ions ( $0.5 - 12 \text{ mmol dm}^{-3}$ ) at same S/L ratio as earlier. The removal of trace amount of fluoride ( $15.24 \text{ mg dm}^{-3}$  or  $0.80 \text{ mmol dm}^{-3}$ ) was performed at different solid-liquid ratio. Desorption of loaded fluoride was performed by shaking the fluoride loaded La-SOJR and varying concentration of NaOH solution at solid-liquid ratio ( $1.33 \text{ g dm}^{-3}$ ) similar to that of adsorption test.

#### 4.2.3 Leakage of RE ions

The stability of RE loaded orange waste gels at varying concentration of fluoride ranging from  $0.5 - 8 \text{ mmol dm}^{-3}$  was tested at solid liquid ratio of  $1 \text{ g dm}^{-3}$  at different pH. The metal ion concentration in a test solution was measured by ICP-AES.

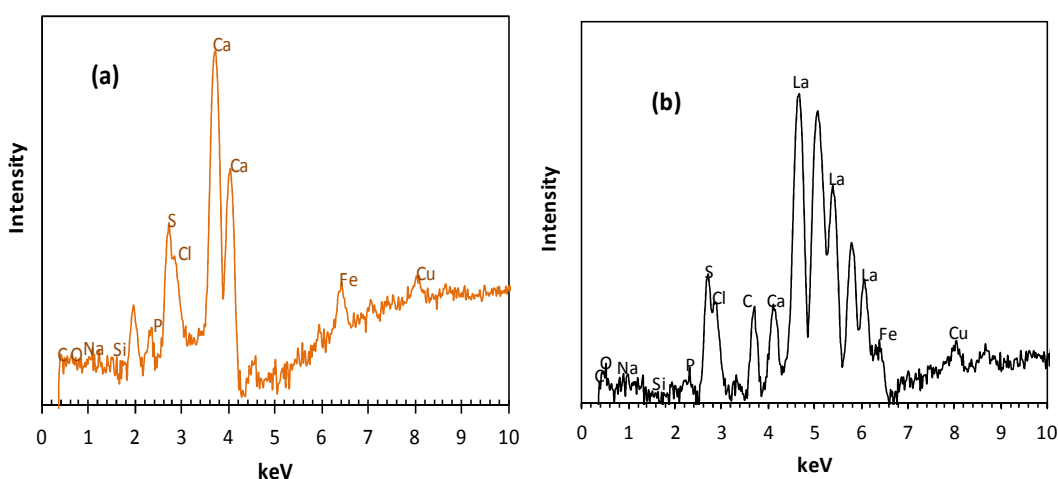
#### 4.2.4 Energy dispersive X-ray (EDX) spectroscopy

The elemental composition of the surface of SOJR before and after La(III) loading reaction was measured by using (Shimadzu model EDX 800 HS) an energy dispersive X-ray spectrometer in order to characterize the metal loading reaction and suggests the conceivable mechanism.

### 4.3 RESULTS AND DISCUSSION

#### 4.3.1 Spectroscopic characterization of adsorbents

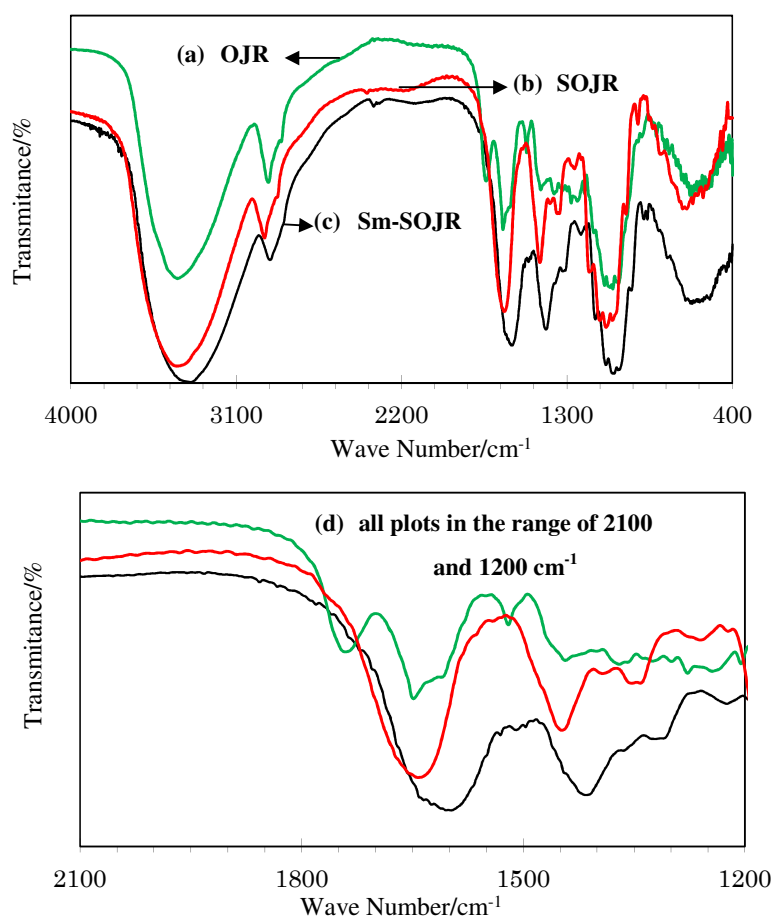
In order to confirm the effective loading of rare earth metal ions on SOJR, EDX spectra of SOJR before and after La(III) loading reaction were recorded as shown in **Figs. 4.1 (a) and (b)**, respectively. In the case of SOJR in **Fig. 4.1 (a)**, the elemental peak of C, O, Na, Si, P, S, Cl, Fe and Cu were observed at the energy values of 0.29, 0.31, 1.12, 1.79, 2.32, 2.56, 2.86, 6.40 and 8.0 keV, respectively along with the calcium ion peak at 3.68 - 4.01 keV. After La(III) loading, additional peak of lanthanum were observed at energy values 4.66 to 6.06 keV along with the peaks of these elements as shown in **Fig. 4.1 (b)**, which is the direct evidence of the La(III) loading reaction. In addition, the intensity of the peak corresponding to calcium in SOJR was drastically decreased after La(III) loading, indicating that there was the calcium substitution reaction by La(III) ions during the loading showing cation exchange reaction. The intensity of the peaks corresponding to iron and copper ions in SOJR was also reduced after La(III) loading.



**Fig. 4.1** Energy dispersive X- ray (EDX) spectra of (a) SOJR and (b) La(III)-SOJR

In order to investigate the functional group of orange juice residue that take part in the metal loading reaction, FT/IR spectra of raw orange juice residue (OJR), SOJR and Sm-SOJR were compared. FT/IR spectra of OJR in **[Fig. 4.2 (a)]** shows intense peak observed at around 3381, 2913, 1742 and 1683  $\text{cm}^{-1}$  are the stretching vibration of OH,  $\text{CH}_2$ , COO and C=O groups,

respectively. The peak observed at around  $1742\text{ cm}^{-1}$  disappeared [Fig. 4.2 (b)] in SOJR, a calcium type orange pectic acid, and two new peaks appeared at around  $1672$  and  $1439\text{ cm}^{-1}$  which suggest the existing of  $\text{O-Ca}^{2+}$  in saponified product. Similarly, in Sm-SOJR, disappearance of peak around  $1742\text{ cm}^{-1}$  and appearance of two additional new peak at  $1681$  and  $1434\text{ cm}^{-1}$  [Fig. 4.2 (c)] suggest the existence of  $\text{O-Sm}$  bond, which is due to the formation of samarium salt of pectic acid after loading reaction. These results confirm that carboxyl functional group is the main functional group that undergoes chemical modification. In order to make clear vision, the part of spectra from  $1200$  to  $2100\text{ cm}^{-1}$  are replotted and presented as shown in Fig. 4.2 (d).

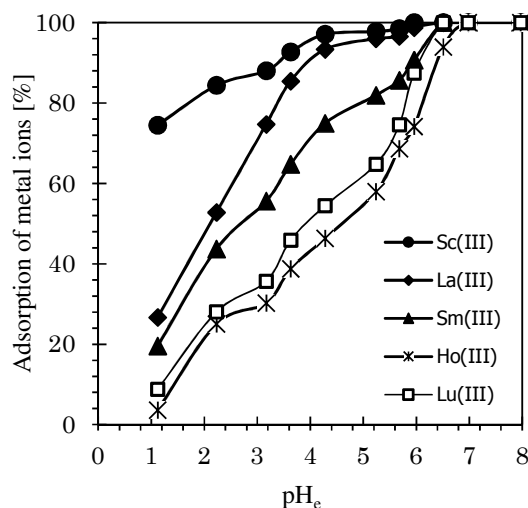


**Fig. 4.2** Infrared spectra of (a) orange juice residue (OJR), (b) Saponified orange juice residue (SOJR), (c) Samarium(III) loaded SOJR (Sm-SOJR), (d) all plots between  $2100$  to  $1200\text{ cm}^{-1}$

### 4.3.2 Adsorption of rare earth metal ions

#### 4.3.2.1 Effect of pH on the adsorption of rare earth metal ions on SOJR

**Figure 4.3** shows the % adsorption of some rare earth metal ions such as Sc(III), La(III), Sm(III), Ho(III) and Lu(III) ( $0.2 \text{ mmol dm}^{-3}$  each) on SOJR at different pHs ranging from 1-8 from their mixing solution. As seen from this figure, adsorption of rare earth metal ions increases with increasing equilibrium pH, suggesting that these metal ions are absorbed by cation exchange mechanism. The selectivity order of the tested metal ion is as follows: Sc(III)>La(III)> Sm(III)>Lu(III) >Ho(III). The pH values of the solution at which 50% of the La(III), Sm(III), Ho(III) and Lu(III) are adsorbed on SOJR from aqueous solution were found to be 2.3, 2.7, 4.6 and 4.0, respectively. On the other hand, the corresponding values in the case of solvent extraction with 0.5 M Versatic 10, a carboxylic acid commercially employed as a solvent extraction reagent, in xylene from 1 M sodium nitrate solution for these rare earth metal ions were reported to be 5.8, 5.3, 5.2 and 5.1 [8], suggesting that the order of the selectivity in this case is Lu(III) > Ho(III) > Sm(III) > La(III), which is reverse with the case of SOJR. This result also suggests that SOJR more strongly interacts with these rare earth metal ions than Versatic 10, which is attributable to the formation of stable five membered chelate with SOJR. That is, it is inferred that oxygen atom of pyranose ring of orange pectic acid and carboxyl group reasonably forms a stable five membered ring chelate with cationic rare earth metal ions as shown in **Scheme 1**. The result shows all metal ions are quantitatively adsorbed on SOJR at pH higher than 7, suggesting the high affinity of SOJR towards tested rare earth (RE) metal ions. The different amount of RE metal ions loading onto SOJR is due to their different physicochemical behavior. The different affinity of SOJR for different types of rare earth metal ion is due to the fact that the tested rare earth metal ions have different physical and chemical properties such as ionic size, nuclear charge, stability, complexation properties and stoichiometry with the functional group of orange waste adsorbent thus showing different binding affinities.

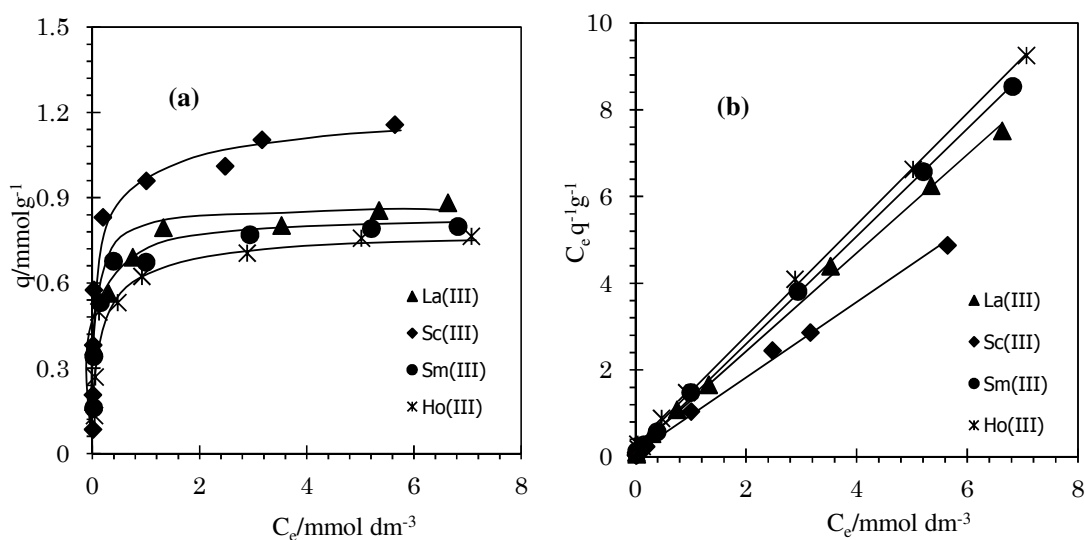


**Fig. 4.3** Adsorption of some rare earth (RE) metal ions from the mixed solution onto SOJR (metal solution =  $0.2 \text{ mmol dm}^{-3}$  each, volume of solution =  $15 \text{ cm}^3$ , weight of SOJR = 25 mg, and temperature =  $30^\circ\text{C}$ )

#### 4.3.2.2 Adsorption isotherms of rare earth metal ions on SOJR

Influence of equilibrium concentration of some rare earth metal ions such as La(III), Sm(III), Ho(III) and Sc(III) on their amount of adsorption onto SOJR is presented in **Fig. 4.4 (a)**, which shows that adsorption of these metal ions increases with increasing equilibrium concentration in the low concentration range and reaches plateau value at higher concentration. The experimental data were modeled by using the well known Langmuir and Freundlich isotherm equations. **Figure 4.4 (b)** shows the data replotted by Langmuir isotherm ( $C_e/q$  versus  $C_e$ ), which shows that experimental data are in good agreement with the Langmuir isotherm with high correlation coefficient. The values of maximum adsorption capacities ( $q_{\text{max}}$ ) and binding constant ( $b$ ) were evaluated from the slope and intercept of the straight lines in this figure, respectively, and are listed in **Table 4.1**. The values of Freundlich isotherm constants,  $n$  and  $K_f$ , calculated from the slope and the intercept of the straight line for the plot of  $\log q_e$  vs.  $\log C_e$ , respectively, are also tabulated in **Table 4.2**. The lower value of the correlation coefficient evaluated according to the Freundlich isotherm model shows that the Freundlich isotherm model can not well described the experiment results for all the

metal ions investigated in this study. It was found that loading capacities of some rare earth metal ions such as La(III), Ho(III), and Sm(III) onto SOJR were 0.91, 0.77, and 0.80 mmol g<sup>-1</sup>, respectively, which correspond to 12.5, 12.6 and 12.0 weight % of La(III), Ho(III) and Sm(III) of RE-SOJR, respectively.



**Fig. 4.4** Adsorption isotherms of some rare earth metal ions on saponified orange juice residue (a) Adsorption isotherm and (b) corresponding Langmuir plot (volume of solution = 15 cm<sup>3</sup>, weight of gel = 25 mg, shaking time = 24 h, and temperature = 30°C)

**Table 4.2** Isotherm parameters for the adsorption of rare earth metal ion on SOJR

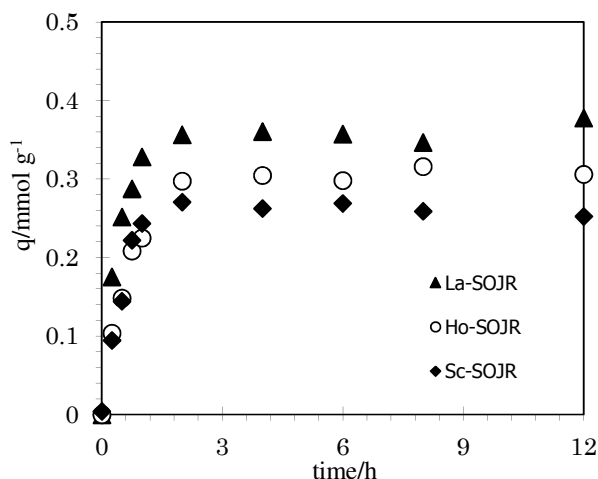
Langmuir Parameters					Freundlich Parameters		
Metal ions	pH	q <sub>max./mmol g<sup>-1</sup></sub>	b/dm <sup>3</sup> mmol <sup>-1</sup>	R <sup>2</sup>	K <sub>f</sub> /mmol g <sup>-1</sup>	n	R <sup>2</sup>
Sc(III)	4	1.15	10.02	0.98	0.96	6.23	0.91
Sm(III)	6	0.80	6.67	0.99	0.83	7.08	0.90
La(III)	4	0.91	8.96	0.99	0.84	6.71	0.97
Ho(III)	6	0.77	5.80	0.99	0.81	8.66	0.96



### 4.3.3 Application of RE-SOJR for fluoride removal

#### 4.3.3.1 Effect of contact time

Adsorption kinetics of fluoride on some rare earth metals loaded SOJR namely Sc-SOJR, La-SOJR, Ho-SOJR were measured to investigate the minimum time required to reach equilibrium. **Figure 4.5** shows the time variation of fluoride adsorption on the metal loaded SOJR at their respective optimal pH. As seen from this figure, the adsorption of fluoride is rapidly increases with increasing the contact time at the beginning and then it slowed down and reached equilibrium for all adsorbents tested. The equilibrium is reached nearly within 3 h for all the RE-SOJR tested. Consequently, subsequent adsorption experiments were performed for 24 h in order to ensure complete equilibrium.

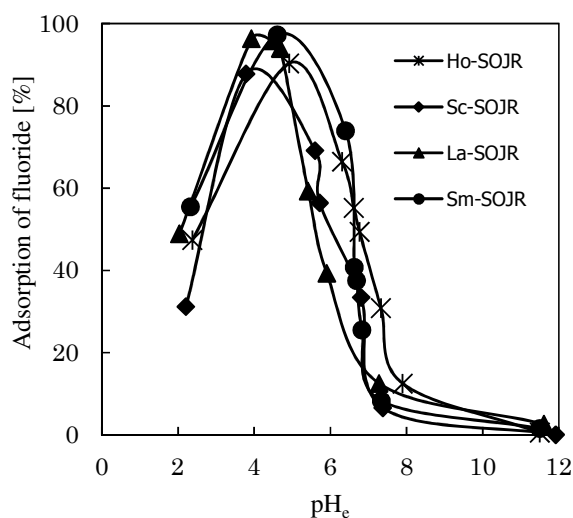


**Fig. 4.5** Time dependency of fluoride adsorption on RE-SOJR from water (volume of solution = 15 cm<sup>3</sup>, weight of RE-SOJR = 25 mg, fluoride concentration = ~0.57 mmol dm<sup>-3</sup>, and temperature = 30°C)

#### 4.3.3.2 Effect of solution pH

The % adsorption of fluoride on different metal loaded SOJR gels at various pH is shown in **Fig. 4.6**. As seen from this figure, the adsorption of fluoride increases with increasing pH of the solution up to pH around 3, then reached maximum value, after that it started to decrease with further increase of pH. The maximum adsorption was found to occur at pH around 3-5 for all the rare earth metal loaded SOJR gels. The pH of the solution was found to be increased in lower pH

region after fluoride adsorption in all the metal loaded SOJR tested which can be reasonably attributed to the replacement of hydroxyl ligand by fluoride during adsorption reaction. However, in high pH region, the behavior was just opposite, *i.e.* the equilibrium pH of the solution was found to be decreased after the adsorption. At neutral to basic pH, carboxylic groups of the orange pectic acid undergo deprotonation reaction and released proton in the aqueous solution, which leads to the decrease in pH of the solution. The result clearly indicates that there is the reduction of fluoride adsorption at pH lower than 4 and also at pH higher than 5. The decrease in fluoride adsorption at pH above 5 can be attributed to the competition of hydroxyl ions for the adsorption sites whereas the decrease at pH below 4 is due to the formation of hydrogen fluoride, which may be hardly adsorbed.

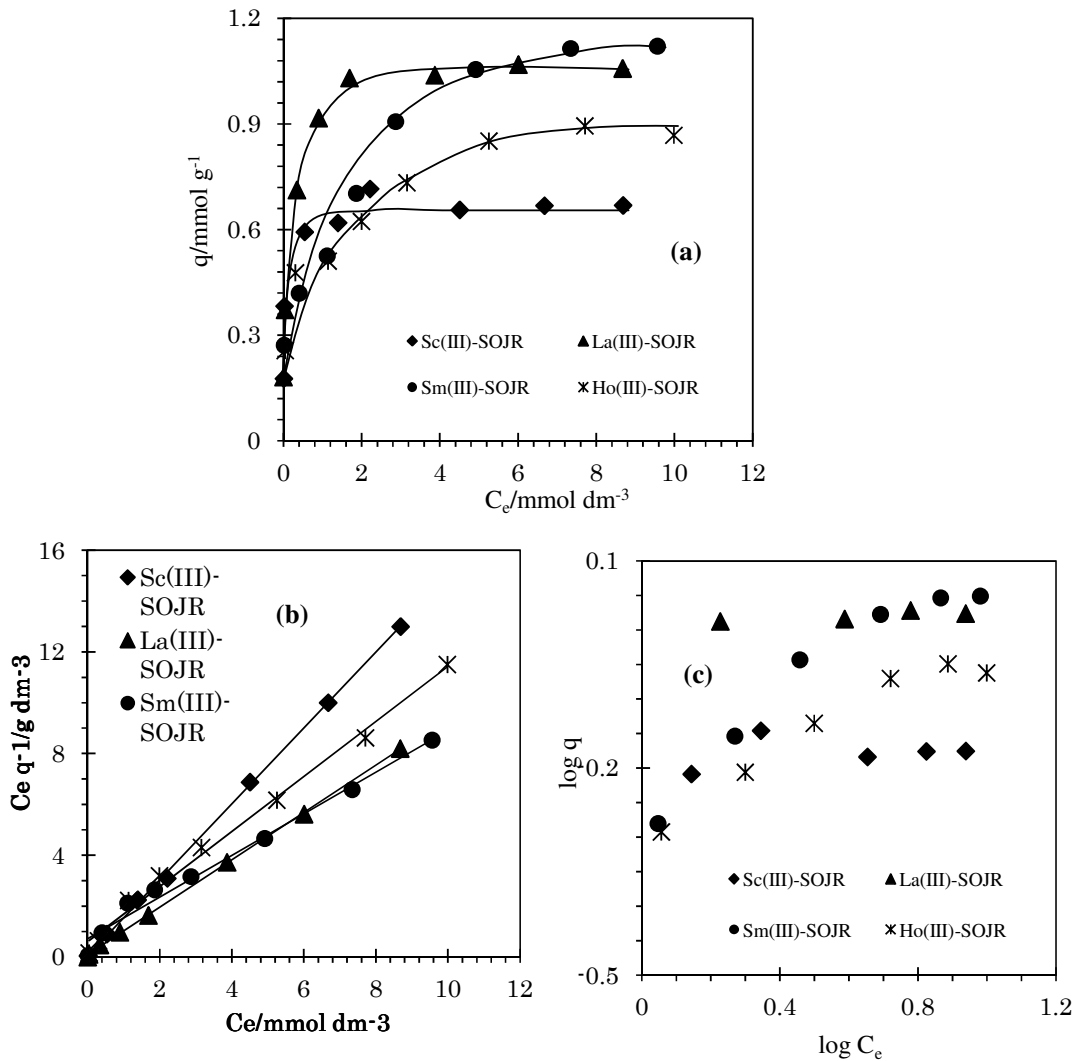


**Fig. 4.6** Effect of pH for the adsorption of fluoride ( $10 \text{ mg dm}^{-3}$ ) by metal loaded orange gel (volume of solution =  $15 \text{ cm}^3$ , weight of gel = 25 mg, shaking time = 24 h, and temperature =  $30^\circ\text{C}$ )

#### 4.3.3.3 Adsorption isotherms of fluoride

Adsorption isotherms of fluoride on SOJR loaded with some rare earth metal ions such as La-SOJR, Sm-SOJR, Ho-SOJR and Sc-SOJR were examined under the determined optimal pH. The results are presented in **Fig. 4.7**. The adsorption of fluoride on La-SOJR, Sm-SOJR, Ho-SOJR and Sc-SOJR was firstly increased with increasing the equilibrium concentration of fluoride and

then tended to approach constant values, which may be consistent with the formation of monolayer of fluoride ions on the surface of adsorbent. The linear relationship on the basis of Langmuir and Freundlich equations (expressed by equations 2.3 and 2.4) was observed for all metal ion loaded SOJR tested. Adsorption constants evaluated by the Langmuir and Freundlich equations for SOJR loaded with four kinds of rare earth metal ions are listed in Table 4.3 together with their correlation regression coefficient. From the comparison of correlation regression coefficient, adsorption process is better fitted by Langmuir than by Freundlich equation also in these cases.



**Fig. 4.7** Adsorption isotherm of fluoride on RE-SOJR (a) adsorption isotherm (b) Langmuir plot and (c) Freundlich plot (volume of solution = 15 cm<sup>3</sup>, weight of gel = 25 mg, and temperature = 30°C)

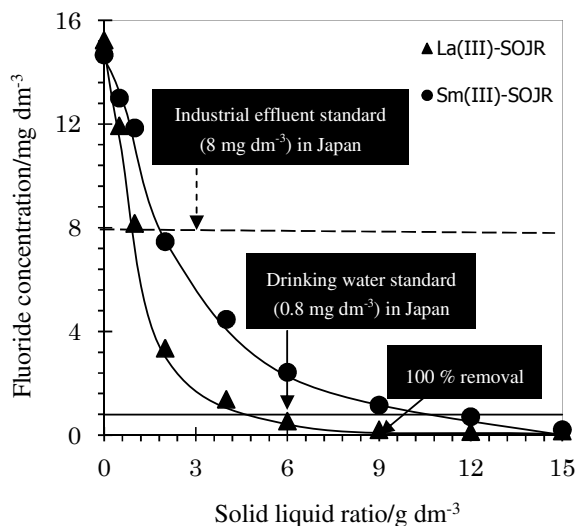
Because of the presence of different metal ions on various metal loaded SOJR, the fluoride binding properties of RE-SOJR also varies depending on their stoichiometry, complexation affinity with fluoride ions and their stability constant so that different amounts of fluoride were found to be adsorbed by using different types of rare earth metal loaded SOJR.

**Table 4.3** Langmuir and Freundlich parameters for fluoride adsorption by RE-SOJR

Langmuir parameters					Freundlich parameters		
Adsorbents	pH	$q_{\max}/\text{mmol g}^{-1}$	$b/\text{dm}^3 \text{mmol}^{-1}$	$R^2$	$K_f/\text{mmol g}^{-1}$	n	$R^2$
Sc-SOJR	4	0.60	9.65	0.99	0.78	10.82	0.83
Ho-SOJR	5	0.92	1.80	0.99	0.77	4.45	0.92
La-SOJR	4	1.06	10.92	0.98	0.91	5.16	0.89
Sm-SOJR	5	1.22	1.03	0.99	0.82	4.13	0.93

#### 4.3.3.4 Influence of adsorbent amount

In order to optimize the dosage of adsorbent to lower the fluoride concentration below the accepted environmental standard, fluoride removal experiment was conducted at different dosages of La(III)-SOJR and Sm(III)-SOJR. **Figure 4.8** shows the plot of residual fluoride concentrations as a function of solid (weight of added adsorbent)/liquid (volume of fluoride solution) ratio ranging from 0.5 to 15 g dm<sup>-3</sup>. The result shows that residual concentration of fluoride decrease with increasing adsorbent amount and lowers down to the industrial effluent standard in Japan (8 mg dm<sup>-3</sup>) by using small amount ( 1 g dm<sup>-3</sup> La(III)-SOJR and 2 g dm<sup>-3</sup> Sm-SOJR) of adsorbents. As **Fig. 4.8** clearly suggests, fluoride concentration can be effectively lowered so as to clear the environmental standard of Japan (0.8 mg dm<sup>-3</sup>) at 6 g dm<sup>-3</sup> in the case of La(III)-SOJR while it is 12 g dm<sup>-3</sup> in the case of Sm(III)-SOJR, whereas 100% removal of fluoride from aqueous solution can be achieved at the dosage higher than 9 g dm<sup>-3</sup> by using La(III)-loaded SOJR. Thus, La(III)-SOJR investigated in this study can be a promising sorbent for the treatment of large amount of waste water containing trace amount of fluoride.



**Fig. 4.8** Influence of La(III)-SOJR and Sm(III)-SOJR amount for the adsorption of trace amount of fluoride from aqueous solution (feed solution =  $15.24 \text{ mg dm}^{-3}$ , volume of solution =  $15 \text{ cm}^3$ , pH = 4 for La(III)-SOJR, pH = 5 for Sm(III)-SOJR, and temperature =  $30^\circ\text{C}$ )

### 3.3.3.5 Elution of loaded fluoride

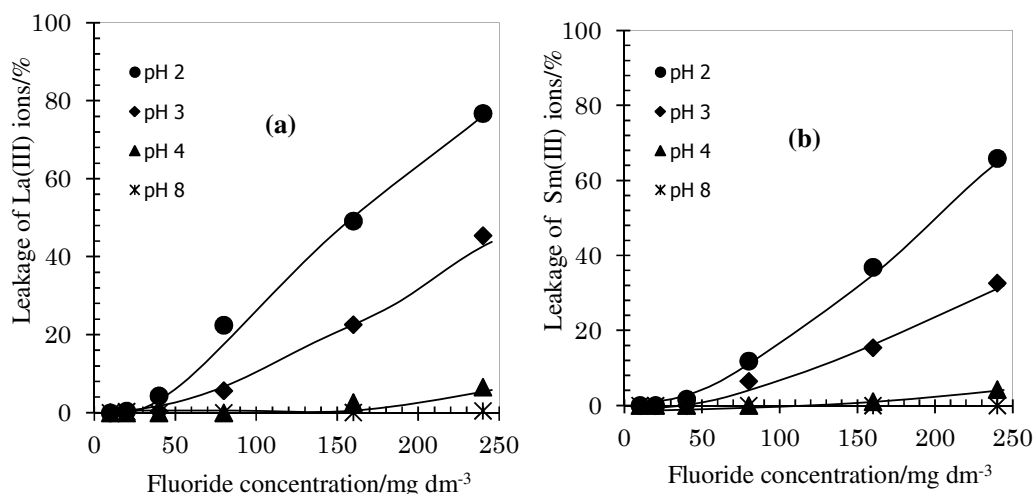
As shown in **Fig. 4.6**, fluoride is effectively adsorbed at pH range 3-5 on all the metal loaded SOJR whereas it is poorly adsorbed at basic pH, suggesting that basic solution can be used for the elution of adsorbed fluoride from RE-SOJR. **Table 4.4** shows % elution of adsorbed fluoride ( $0.90 \text{ mmol g}^{-1}$ ) from La(III)-SOJR at different concentration of NaOH ranging from 0.005 to 0.4 M at solid-liquid ratio  $1.33 \text{ g dm}^{-3}$ , which demonstrates that desorption from La(III)-SOJR increases from 31.1 to 98.1 % by increasing NaOH concentration from 0.005 to 0.1 M and the elution is not so drastically changed with further increasing NaOH concentration. The trace amount (1.5%) of fluoride was found to be eluted without using NaOH solution which can be attributed to the washing of un-adsorbed fluoride from the gel surface. The leakage of rare earth metal ions during elution was found to be insignificant or negligible. Hence, 0.1 M NaOH solutions can be concluded to be a suitable eluting agent for the regeneration of the adsorbent.

**Table 4.4** Elution of fluoride ( $0.90 \text{ mmol g}^{-1}$ ) from La(III)-SOJR by dilute alkali solution

<b>NaOH [M]</b>	0	0.005	0.01	0.05	0.1	0.2	0.4
<b>Desorption [%]</b>	1.5	31.1	60.4	84.6	98.1	98.8	98.5

#### 4.3.3.6 Leakage of metal ions from RE-SOJR

The leakage test of metal ions loaded on SOJR was carried out for La(III) and Sm(III) loaded SOJR at different pH at varying fluoride concentration. The % leakage of these metal ions is shown as a function of initial fluoride concentration from 10 up to  $240 \text{ mg dm}^{-3}$  in **Figs. 4.9 (a)** and **(b)**, respectively. The result shows that the leakage of metal ions increases with increasing fluoride concentration at pH below 3 whereas it is insignificant at pH higher than 4. The leakage of loaded metal ions from La(III) and Sm(III) loaded SOJR at acidic pH can be reasonably attributed to the ion exchange reaction between proton from acidic solution and loaded metal ions from rare earth loaded SOJR *i.e.* RE-SOJR. In the case of La-SOJR, the strength of La-O bond in La-SOJR is weakened by the strong interaction between fluoride ion in aqueous solution and loaded La(III) in La(III) loaded SOJR resulting in the increase in leakage with the increase of fluoride concentration. This effect is insignificant, however, at high pH due to the stronger interaction between the La(III) ion and hydroxyl ions. This phenomenon is same also with the case of Sm-SOJR. There is negligible leakage of loaded metal ions from the gel below  $40 \text{ mg dm}^{-3}$  even at pH below 3, suggesting that La(III)- and Sm(III)-SOJR investigated in this study can be used only for the treatment of solutions containing trace concentration of fluoride ion.



**Fig. 4.9** Leakage of metal ions from RE-SOJR (a) La(III)-SOJR and (b) Sm(III)-SOJR (volume of solution = 10 cm<sup>3</sup>, weight of gel = 10 mg, and temperature = 30°C)

#### 4.4 CONCLUSIONS

The techniques such as energy dispersive X-ray (EDX) spectroscopy, infrared spectroscopy (IR) used for the characterization confirmed that rare earth metal ions were successfully adsorbed on SOJR. The equilibrium adsorption data for Sm(III), Ho(III), La(III), Sc(III) and Lu(III) from their mixture solution revealed the effective adsorption of these metal ions on orange waste gel. Adsorption of fluoride on RE-SOJR was influenced by initial concentration of fluoride, solid to liquid ratio and pH of the solution. The Langmuir isotherm model precisely described the equilibrium data for the adsorption of fluoride onto RE-SOJR. The La(III)- and Sm(III)-SOJR successfully lower the residual fluoride concentration down to environmental standard in Japan, which confirmed the possible application of La(III)- and Sm(III)-SOJR for the treatment of fluoride polluted water. Fluoride loaded La(III)-SOJR was easily regenerated by washing with alkali (NaOH) solution. The La(III)- and Sm(III)-SOJR showed stronger interaction with fluoride ion even at trace concentration, suggesting that these materials can be employed as an effective adsorbents for the treatment of industrial effluents containing trace concentration of fluoride ion.

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## Chapter 5

### **Influence of Oxidation State of Cerium Ions for Adsorption Behavior of Fluoride by Using Tetravalent and Trivalent Cerium Loaded Orange Waste**

In the adsorption of fluoride on various metals loaded adsorbents in Chapters 2, 3 and 4, show that adsorption capacity of fluoride by orange waste gel loaded with tetravalent metal ions such as Zr was found to be much higher than that of trivalent metal loaded orange waste. Hence, we thought that oxidation states of the loaded metal ions in the adsorbent should have some role for adsorption affinity for fluoride. So that, investigation of effect of oxidation state of particular metal ions (cerium) loaded SOJR was performed in order to elucidate the clear mechanism for fluoride adsorption. Chemically modified orange juice residue *i.e.* SOJR was prepared according to the method described in preceding Chapters and then SOJR was treated with Ce (IV) and Ce(III) solution to convert SOJR into Ce(IV)-SOJR and Ce(III)-SOJR, respectively. It was characterized by metal content analysis and EDX spectroscopy. The SOJR loaded with tetravalent cerium ions exhibits higher adsorption potential for fluoride than trivalent cerium loaded SOJR. Factors affecting fluoride adsorption such as pH, concentration, and temperature were investigated. Investigation of thermodynamic parameters such as enthalpy change ( $\Delta H$ ), entropy change ( $\Delta S$ ) and Gibbs free energy change ( $\Delta G$ ) during fluoride adsorption onto Ce(IV)-SOJR were also performed.

#### **5.1 INTRODUCTION**

In the previous Chapters, the metal loaded orange waste gels were synthesized and tested for fluoride removal from synthetic as well as real waste plating solution. It was found that metal loaded orange waste effectively remove fluoride from water. However, comparison of fluoride removal ability of various metal loaded orange gels suggests that, tetravalent Zr(IV) loaded orange waste gel exhibits higher removal efficiency than other trivalent metal loaded orange waste gels. Hence, it was concluded that valency of metal ions should have some important role for the generation of active sites for fluoride removal. There are some works

published elsewhere for the synthesis and application of adsorbent loaded with high valent metal ions but in our knowledge no or negligible research has been conducted to evaluate the effect of oxidation states of loaded metal ions for the performance in adsorption process [1-4]. From such point of view, we have synthesized the metal loaded adsorbent by loading particular metal ions (cerium) having different oxidation state in order to evaluate the influence of oxidation state of loaded metal ions onto the adsorbents for fluoride removal. The different metal ions have different physical and chemical properties such as ionic size, nuclear charge, complexation constant, stoichiometry and stability so that comparison becomes more complicated. Thus we have choosed cerium metal which stably exists in trivalent and tetravalent oxidation state for comparisons. With increasing the oxidation state of loaded metal ions, more active sites are expected to be created because higher numbers of hydroxyl ions are necessary to neutralize the positive charge of high valent metal ions. These hydroxyl ions are expected to be the main active site for ligand exchange reaction with fluoride. The overall arching objective of this work was to examine whether different oxidation states of loaded cerium ions on saponified orange juice residue (SOJR) have some influence on fluoride adsorption or not. For that, tetravalent and trivalent cerium loaded SOJR were prepared according to the method described in previous Chapters and their adsorption behavior towards fluoride were examined by batch wise adsorption test.

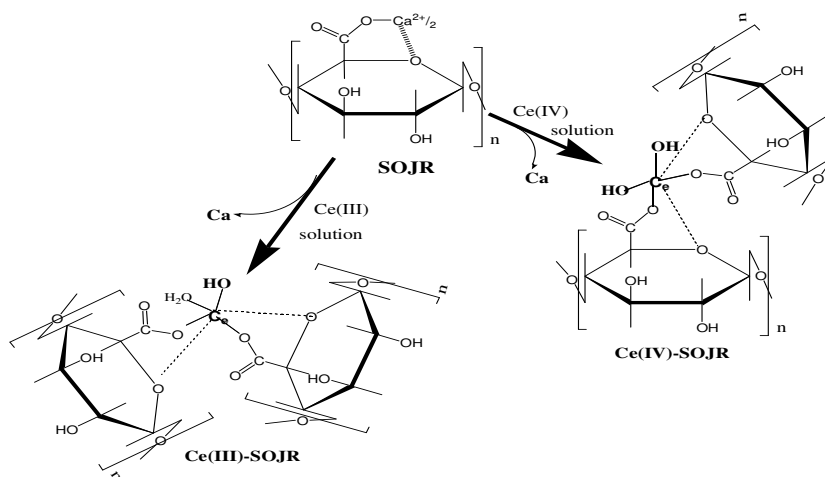
## 5.2 EXPERIMENTAL PROCEDURE

### 5.2.1 Measurement of total amount of acidic functional groups in SOJR

For the analysis of total amount of acidic functional group, SOJR (500 mg) was treated with 100 cm<sup>3</sup> of 0.1 M HCl for 24 h to convert SOJR into H-SOJR. Then it was filtered, wash until neutral pH by using deionized water and finally dried in a convection oven for at 70°C temperature. The H-SOJR (100 mg) was treated with 20 cm<sup>3</sup> of standardized 0.01M NaOH solution for 24 h at 30°C then it was filtered. The consumption of alkali amount by H-SOJR was estimated by volumetric titration of filtrate with 0.01 M HCl solution by using phenolphthalein as indicator.

### 5.2.2 Creation of more active sites by increasing oxidation state of cerium ion

The tetravalent or trivalent cerium loaded orange waste gels were prepared by loading cerium ions onto SOJR as follows. 3 g of SOJR and 500 cm<sup>3</sup> of 0.1 M Ce(III) solution was mixed together at its optimum pH in order to make Ce(III)-SOJR whereas in the case of Ce(IV)-SOJR, it was treated with 2.5% Ce(IV) solution for 24 h at 30°C for metal loading reaction. After the completion of loading reaction, it was filtered washed until neutral pH and dried in a vacuum drier for 8 h as shown in **Scheme 5.1**. The evidence of this mechanism was obtained from the stoichiometric calculation which will be described in details in section 5.4.



**Scheme 5.1** Development of more active site on SOJR by increasing oxidation state of loaded cerium

### 5.2.3 Adsorption experiment

Similar to the previous chapter, batch adsorption experiments were performed to evaluate the adsorption behavior of tetravalent and trivalent cerium loaded orange gel by contacting 25 mg of the selected Ce-SOJR samples with 15 cm<sup>3</sup> of the fluoride solution (~10 mg dm<sup>-3</sup>) at different pHs (2-12). The samples were shaken in thermostatic shaker at controlled temperature (30°C) for a period of 24 h at 150rpm. The remaining concentration of fluoride in each sample after adsorption was determined by ion chromatography. Adsorption isotherms of both the adsorbents for fluoride were investigated by employing the adsorption of fluoride at different concentrations. For these experiments, the fluoride solutions together with adsorbent at solid liquid ratio of 1.33 g dm<sup>-3</sup> were shaken, keeping the pH (4) and shaking speed (150 rpm)

constant. Removal tests of trace concentration of fluoride were carried out at different dosage of Ce(III)- and Ce(IV)-SOJR at pH 4. Thermodynamic investigation of Ce(IV)-SOJR was also performed in same condition as in isotherm study at different temperatures.

#### **5.2.4 Elution of loaded fluoride**

For the elution experiment, both types of fluoride loaded Ce-SOJR were prepared by contacting Ce-SOJR with fluoride solution at pH 4, then elution test of loaded fluoride was carried out by varying concentration of NaOH solution at  $1.33 \text{ g dm}^{-3}$ .

#### **5.2.5 Complete dissolution of Ce-SOJR**

The amount of loaded cerium ions in the sample of Ce(III)-SOJR and Ce(IV)-SOJR is directly related to the adsorption capacity of the prepared adsorbent. So that total amount of Ce(III) and Ce(IV) loaded in the samples of Ce-SOJR were determined. At first 50 mg of Ce(III)-SOJR and Ce(IV)-SOJR were separately weighed in a  $50 \text{ cm}^3$  reagent bottle then  $10 \text{ cm}^3$  of aquaregia solution were added and shaken for 24 h at  $30^\circ\text{C}$  for complete dissolution. After 24 h, sample were filtered and analyzed for cerium ions by ICP-AES.

### **5.3 RESULTS AND DISCUSSION**

#### **5.3.1 Characterization of adsorbent**

##### **5.3.1.1 Amount of acidic functional groups in SOJR**

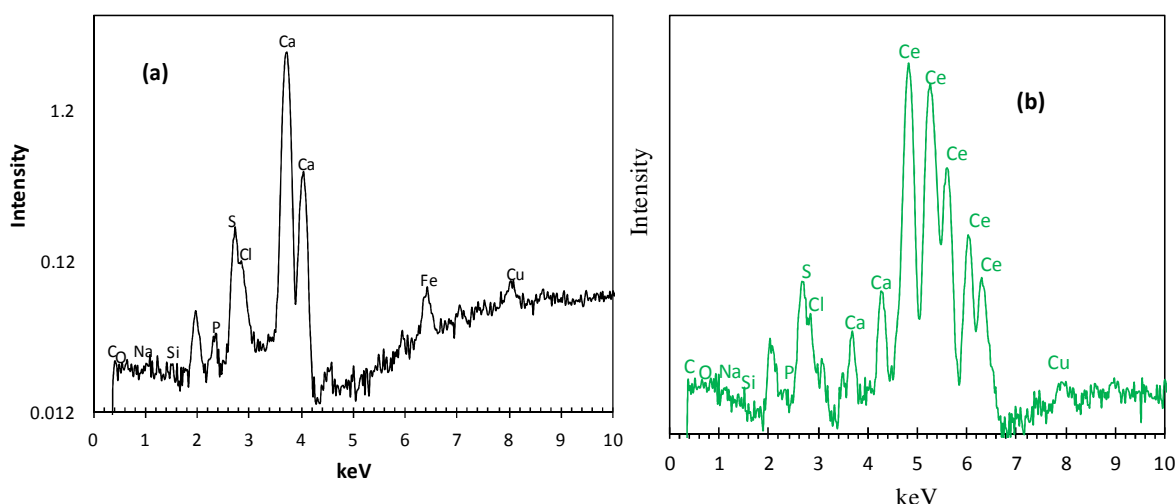
Acidic functional groups of SOJR are directly involved in the metal loading reaction. Amount of acidic functional groups in SOJR by titration method was found to be  $2.04 \text{ mmol g}^{-1}$ .

##### **5.3.1.2 Measurement of loaded amount of Ce(III) and Ce(IV)**

The total amount of Ce(III) and Ce(IV) in the sample of Ce(III)-SOJR and Ce(IV)-SOJR were found to be  $0.91$  and  $0.89 \text{ mmol g}^{-1}$ , respectively. The result shows that loaded cerium ions in both the samples were approximately the same amount, indicating that the difference in the adsorption behavior of fluoride ions by using these two kinds of cerium loaded SOJR are influenced by other factors.

### 5.3.1.3 Spectroscopic analysis by EDX

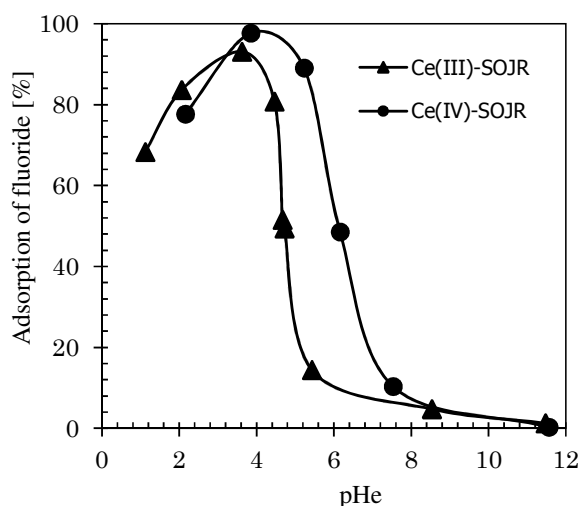
Energy dispersive spectroscopic analysis is one of the very important tools to investigate and analyzed the different types of elements present on the tested sample. Here, for the confirmation of the presence of exchangeable  $\text{Ca}^{2+}$  ions in saponified product of orange juice residue and mechanism of cerium loading reaction, EDX spectra of SOJR and Ce(IV)-SOJR were recorded and presented in **Fig. 5.1**. As can be seen from the EDX spectra [**Fig. 5.1** (a)] of SOJR, there is the presence of intense peaks at around 0.29, 0.31, 1.12, 1.79, 2.32, 2.56, 2.86, 6.40 and 8.0 keV which are the elemental peak of C, O, Na, Si, P, S, Cl, Fe and Cu, respectively. The result also shows that there appears an intense peak of calcium at 3.68 - 4.01 keV, suggesting that exchangeable calcium ions are present in the tested sample of SOJR. In EDX spectrum of Ce(IV)-SOJR [**Fig. 5.1** (b)], new peaks of cerium were observed at energy values 4.28, 4.82, 5.24, 5.60, 6.04, and 6.30 keV. This result confirms the effective loading of Ce(IV) onto SOJR. The intensity of calcium ion peak at 3.86 and 4.01 keV was drastically decreased in Ce(IV)-SOJR, suggesting that Ce(IV) loading reaction took place by the replacement of calcium ions of SOJR by Ce(IV) ions. Almost similar types of spectra was observed in the case of Ce(III)-SOJR. Hence, the mechanism of Ce(IV) loading reaction is inferred to be cation exchange reaction between the calcium and cerium ions as depicted in **Scheme 1**.



**Fig. 5.1** Analysis of SOJR before and after Ce(IV) loading by EDX spectroscopy (a) EDX spectrum of SOJR (b) EDX spectrum of Ce(IV)-SOJR

### 5.3.2 Influence of pH of the solution for fluoride adsorption

Adsorption of fluoride on Ce(III)-SOJR and Ce(IV)-SOJR at different pH (1-12) were shown in **Fig. 5.2**. It was suggested that the fluoride removal increased with an increase of pH of the solution below 4 and then decreased sharply when solution pH was further increased. This behavior is similar as that in the case of other metal loaded SOJR except Al-SOJR in earlier Chapters.

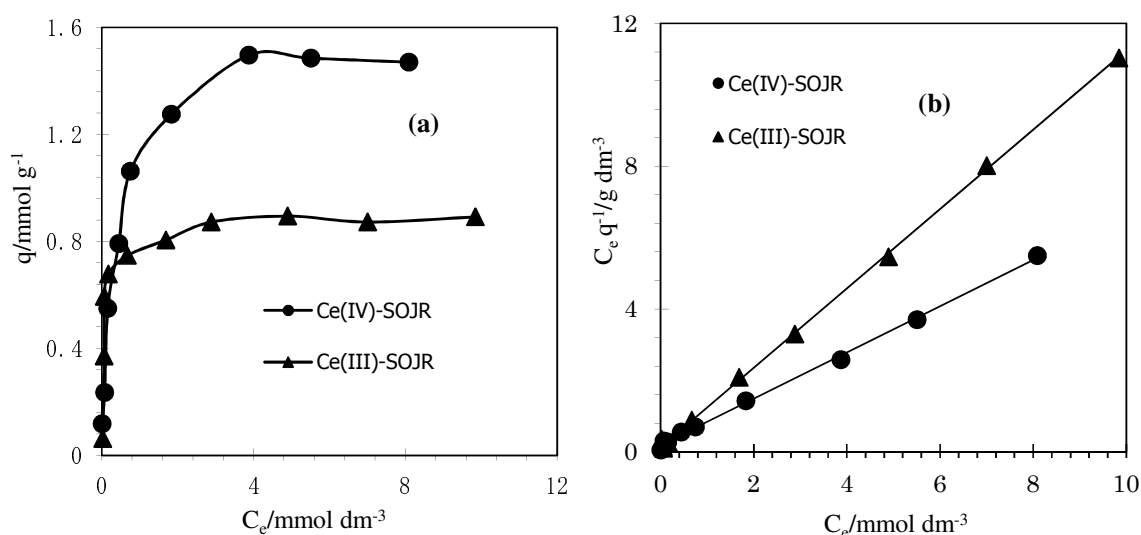


**Fig. 5.2** Influence of equilibrium pH for the adsorption of fluoride by Ce-SOJR (volume of solution = 15 cm<sup>3</sup>, weight of gel = 25 mg, fluoride concentration = ~10 mg dm<sup>-3</sup>, and temperature = 30°C)

### 5.3.3 Effect of equilibrium concentration

The adsorption isotherms of fluoride onto both types of cerium loaded SOJR is shown in **Fig. 5.3 (a)**. In general, uptake capacity of cerium loaded SOJR increases with an increase in equilibrium concentration. However, the fluoride sorption capacities onto the Ce(III)-SOJR is low compared to the Ce(IV)-SOJR. Sorption performance of fluoride on Ce(IV)-SOJR is more favorable than that on Ce(III)-SOJR, indicating successful improvement in the uptake of fluoride as a result of increasing oxidation state of cerium ion in the sample. Increasing trend of adsorption capacity at low concentration was observed to be nearly constant at higher concentration of fluoride. It is one of the indications of the formation of monolayer surface coverage of fluoride on the surface of adsorbent as described by Langmuir model [5]. The

maximum adsorption capacity  $q_{\max}$  ( $\text{mmol g}^{-1}$ ) and Langmuir constant  $b$  ( $\text{dm}^3 \text{mmol}^{-1}$ ) related to the affinity between the adsorbent and the fluoride were evaluated from the slope and intercept of  $C_e/q$  vs  $C_e$  [Fig. 5.3 (b)], respectively, by the Langmuir equation (equation 2.3). The fitted results and the equilibrium constants with correlation regression coefficient are presented in Table 5.1. The results show that Langmuir isotherms can well described the adsorption with high correlation regression coefficient ( $R^2$ ). The high value of maximum adsorption capacity of Ce(IV)-SOJR is due to the increase of active sites due to high oxidation state of tetravalent cerium ion. The values of Langmuir constant  $b$  is small in the case of Ce(IV)-SOJR suggesting that adsorbent have low affinity to remove trace concentration of fluoride compared to Ce(III)-SOJR. The creation of possible active sites for fluoride depends upon the charge neutralization reaction of loaded metal ion on metal loaded SOJR. The neutralization of positive charge of high valent metal ions requires large number of hydroxyl ions which are replaced by fluoride during adsorption. Hence, in metal loaded SOJR, with the increase of oxidation state, more active sites are created according to the reaction Scheme 5.1 that leads to the increase of adsorption capacity for fluoride by using Ce(IV)-SOJR.



**Fig. 5.3** Adsorption isotherm of fluoride (pH= 4) on both types of Ce-SOJR from aqueous solution (a) adsorption isotherm, and (b) corresponding Langmuir plot (volume of solution = 15 cm<sup>3</sup>, weight of gel = 25 mg, pH = 4, and temperature = 30°C)

**Table 5.1** Langmuir isotherm parameters for the adsorption of fluoride on Ce-SOJR

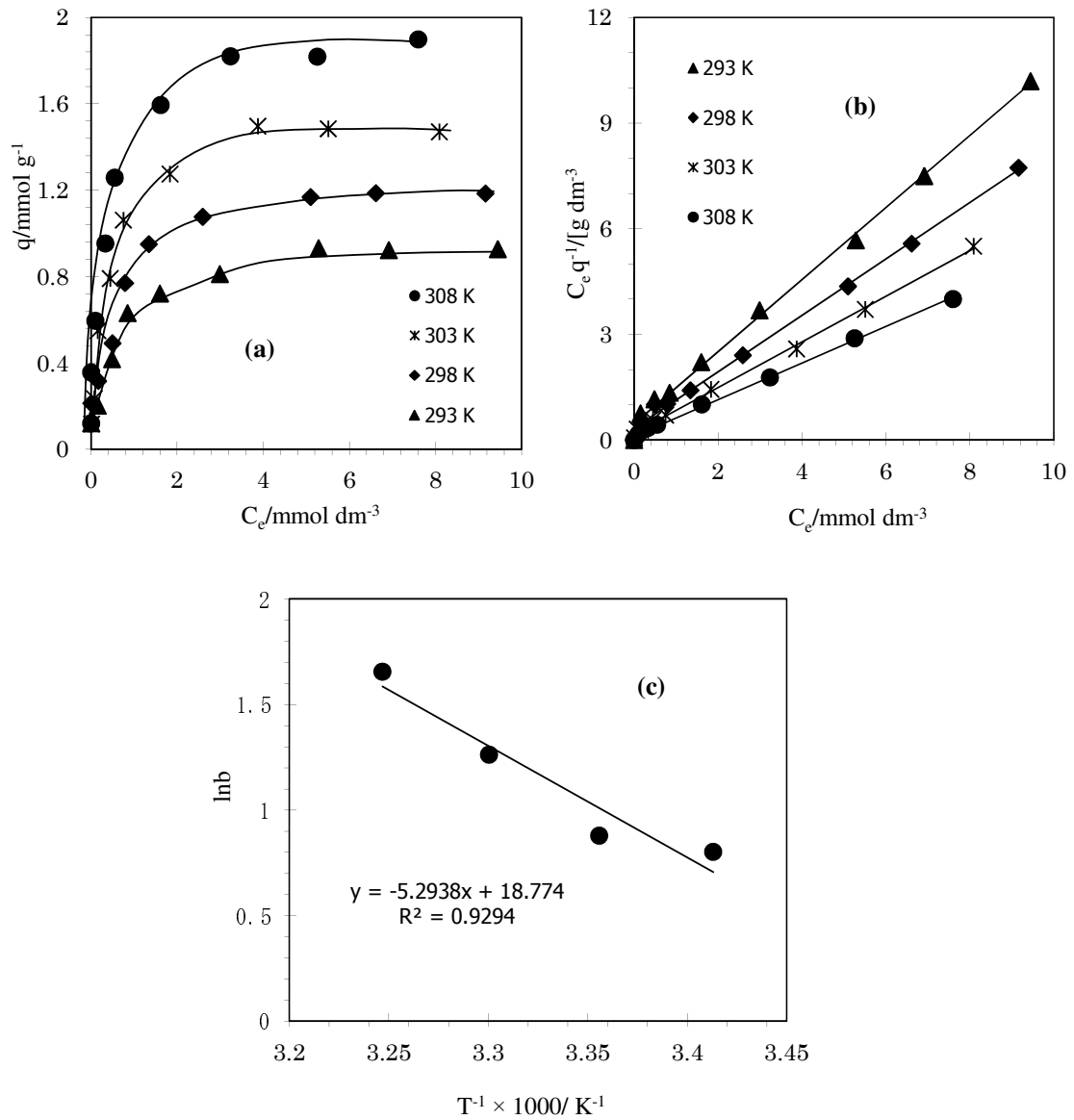
Adsorbents	pH	$q_{\max}/\text{mmol g}^{-1}$	$b/\text{dm}^3 \text{mmol}^{-1}$	$R^2$
Ce(III)-SOJR	4	0.91	7.86	0.98
Ce(IV)-SOJR	4	1.53	3.59	0.99

### 5.3.4 Effect of temperature and thermodynamic investigation

Adsorption isotherms of fluoride at four different temperatures namely, 20, 25, 30, and 35°C that corresponds to 293, 298, 303 and 308 K are presented in **Fig. 5.4 (a)**. The result shows that increasing temperature enhanced the adsorption capacity of Ce(IV)-SOJR at all the concentration tested which is one of the indication of endothermic nature of the reaction. The endothermic nature of adsorption process is further confirmed by the investigation of thermodynamic parameter such as enthalpy change. The maximum adsorption capacities and equilibrium constant for all the temperature were determined from the slope and intercept of the straight lines according to the Langmuir equation as the plot of  $C_e/q$  versus  $C_e$  [**Fig. 5.4 (b)**], respectively. These values are listed in the **Table 5.2**.

The thermodynamic parameters such as enthalpy change ( $\Delta H$ ), entropy change ( $\Delta S$ ), and free energy ( $\Delta G$ ) change were evaluated from the Van't Hoff plot [**Fig. 5.4 (c)**] and values are also listed in **Table 5.2**. It shows negative value of Gibbs free energy change for all the temperature tested suggesting spontaneous nature of adsorption. The positive value of enthalpy change ( $44.01 \text{ kJ mol}^{-1}$ ) and entropy change ( $0.15 \text{ kJ mol}^{-1}\text{K}^{-1}$ ) of a system indicates the endothermic nature of adsorption and increase randomness at solid solution interface during adsorption process. Similar types of result (natures of thermodynamic parameters) were reported for the adsorption of fluoride by metal loaded ion exchanger and Fe(III)-Sn(IV) bi-metal oxide from aqueous solution [6, 7].





**Fig. 5.4** Effect of temperature for the adsorption of fluoride using Ce(IV)-SOJR at different temperatures (volume of solution = 15  $cm^3$ , weight of gel = 25 mg, pH = 4, and temperature = 30°C)

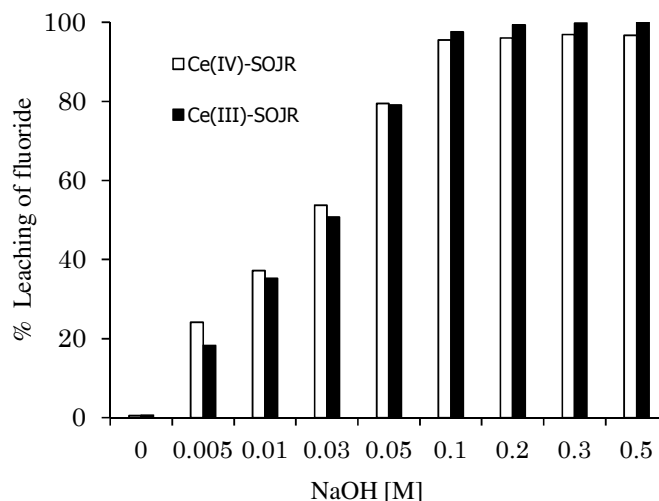
(a) adsorption isotherm (b) Langmuir plot and (c) Van't Hoff plot

**Table 5.2** Thermodynamic parameters investigated for the adsorption of fluoride on Ce(IV)-SOJR

Temperatures /°C	$q_{\max}$ /mmol g <sup>-1</sup>	$b$ /dm <sup>3</sup> mmol <sup>-1</sup>	$\ln b$	$\Delta G$ /kJ mol <sup>-1</sup>	$\Delta H$ /kJ mol <sup>-1</sup>	$\Delta S$ /kJ mol <sup>-1</sup> K <sup>-1</sup>
20	0.97	2.23	0.80	-1.95	44.01	0.15
25	1.24	2.41	0.88	-2.18		
30	1.53	3.53	1.26	-3.18		
35	1.91	5.24	1.65	-4.24		

### 5.3.5 Desorption of fluoride from loaded Ce(III)- and Ce(IV)-SOJR

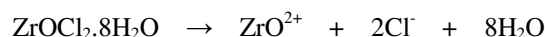
Desorption of fluoride from the loaded adsorbent is very important for the reduction of its cost by its repeated usage. The results of desorption studies of fluoride from loaded adsorbents are shown in **Fig. 5.5**. It shows that loaded fluoride was able to be desorbed with increasing leachate (NaOH) concentration. The leaching of fluoride increased from 21% to 94% in the case of Ce(III)-SOJR and 18 % to 96% in the case of fluoride loaded Ce(IV)-SOJR by increasing NaOH concentration from 0.01 to 0.1 M. But it is nearly the constant with further increase of alkali concentration in both the case, suggesting that 0.1 M NaOH can be a suitable leaching agent for loaded fluoride from cerium loaded orange waste gels.



**Fig. 5.5** Leaching of loaded fluoride from cerium loaded SOJR by using dilute alkali solution (fluoride in Ce(IV)-SOJR = 13.6 mg g<sup>-1</sup>, fluoride in Ce(III)-SOJR = 11.56 mg g<sup>-1</sup>, fluoride loaded Ce-SOJR eluent ratio = 2.5 g dm<sup>-3</sup>, and temperature = 30°C)

#### 5.4 Stoichiometric calculation for the investigation of adsorption mechanism

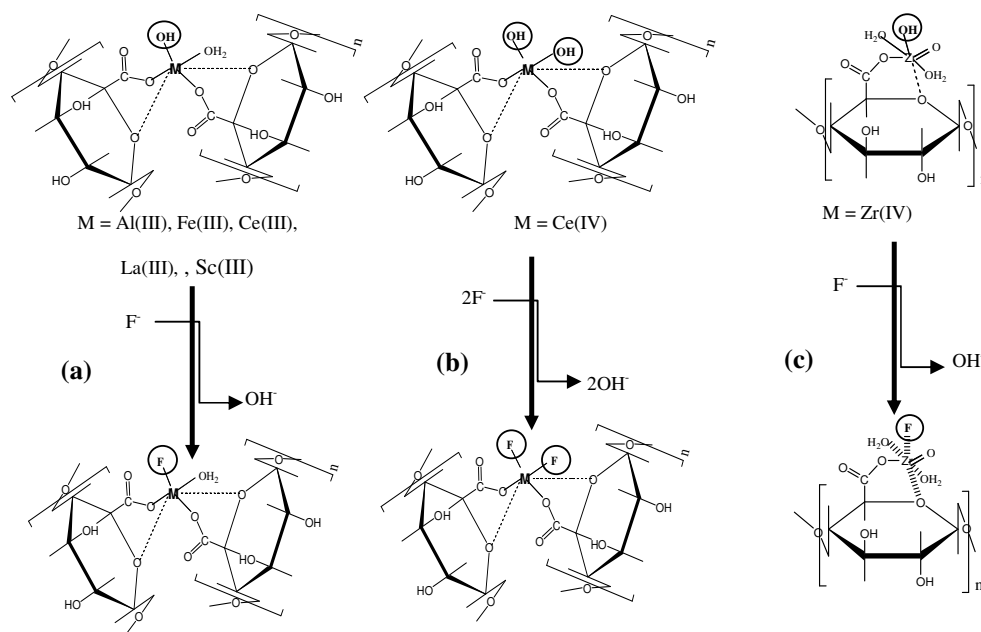
The stoichiometry of metal ions with carboxylic acid functional groups of orange pectic acid is very important for the creation of active adsorption sites on the coordination sphere of loaded metal ions in metal loaded SOJR. **Table 5.3** summarizes the complexation ratios of total amount of acidic functional groups of SOJR and loaded metal ions together with complexation ratios of adsorbed amount of fluoride and loaded metal ions. As can be seen from **Table 5.3**, the trivalent metal ions such as Al(III), Fe(III), La(III), Ce(III), Sc(III) forms 2:1 complex with the acidic functional group of orange waste. The results suggest that two positive charges of these trivalent metal ions are neutralized by acidic functional groups of SOJR where as rest one is neutralized by hydroxyl ion which undergoes ligand exchange reaction with fluoride during fluoride adsorption. Such a reaction is well explained by the formation of 1:1 complex of fluoride with these metal loaded SOJR by the reaction expressed by **Scheme 5.2 (a)**. This ratio was little bit low in the case of Sc-SOJR which is attributed to the high leakage of loaded Sc(III) from Sc-SOJR. However, in case of tetravalent cerium Ce(IV), complexation ratio with acidic functional group of SOJR is around 2:1 leaving two positive charge for neutralization with hydroxyl ions in aqueous solution. Hence, exchangeable hydroxyl ions in the coordination sphere of loaded Ce(IV) increase that leads to the increase of fluoride adsorption capacity thus it form 2:1 complex with fluoride as shown in **Scheme 5.2 (b)**. However, in case of Zr(IV) loaded SOJR, ratio of acidic functional group of SOJR to the loaded Zr(IV) ions was 1:1 so that it was expected to form 3:1 complex with fluoride with Zr-SOJR during adsorption. But, complexation ratio of fluoride and Zr-SOJR was evaluated to be 1:1 (**Table 5.3**). In the loading of Zr(IV) on SOJR, SOJR was treated with 0.1 M  $ZrOCl_2 \cdot 8H_2O$  solution. Thus, zirconium oxychloride possibly dissociate into zirconium oxide and chloride as:



In stead of Zr(IV) ions,  $ZrO^{2+}$  was loaded onto SOJR at the complexation ratio of 1:1 leaving single positive charge for neutralization by hydroxyl ion in aqueous solution. This hydroxide ions from the coordination sphere of loaded  $ZrO^{2+}$  in Zr-SOJR reasonably adsorbed fluoride ion in 1:1 stoichiometric ratio as shown in the reaction **Scheme 5.2 (c)**.

**Table 5.3** Stoichiometric relationships among the acidic functional group of saponified orange juice residue, loaded metal ions and adsorbed amount of fluoride

Metal ions	Al(III)	Fe(III)	Ce(III)	La(III)	Sc(III)	Zr(IV)	Ce(IV)
Acidic group in SOJR	2.04	2.04	2.04	2.04	2.04	2.04	2.04
M <sup>n+</sup> uptake by SOJR	1.16	0.88	0.93	0.95	1.15	1.62	0.89
A.G/M <sup>n+</sup> ratio	1.75	2.31	2.19	2.14	1.77	1.25	2.29
	2:1					1:1	2:1
F uptake by M-SOJR	1.01	0.98	0.91	1.07	0.60	1.74	1.53
F/M <sup>n+</sup> ratio	0.87	1.11	0.97	1.12	0.52	1.07	1.71
	1:1						2:1



**Scheme 5.2** Formulation of possible mechanism of metal ions complexation with SOJR and their ligand exchange mechanism for fluoride from aqueous solution

## 5.5 CONCLUSIONS

In this study, trivalent and tetravalent cerium loaded orange waste gel was prepared from basic hydrolysis of orange waste with lime water followed by loading of cerium ions. Adsorption of fluoride is strongly depends on solution pH and maximum adsorption took place at pH 4 for both the adsorbents. Maximum adsorption capacity of Ce(III)-SOJR and Ce(IV)-SOJR were found to be 0.91 and 1.53 mmol g<sup>-1</sup>, respectively. Compared with Ce(III)-SOJR, the adsorption capacity of Ce(IV)-SOJR increased nearly 2 times for fluoride. This is due to the increase in coordinating hydroxyl ligand in high valent cerium ions. The adsorption process follows the Langmuir adsorption isotherm model. Mechanism of fluoride adsorption and elution using metal loaded SOJR is inferred to be ligand exchange reaction between coordinating hydroxyl group of M-SOJR and fluoride. Adsorbed fluoride was successfully leached out by using dilute alkali solution.

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## Chapter 6

### **Novel Way of Using Commercially Available Dried Orange Juice Residue for the Treatment of Trace Concentration of Fluoride in Water**

In the previous Chapters, metal loaded SOJR for fluoride were investigated. The production route of metal loaded SOJR is little bit tedious, long synthetic procedure and produces large amount of waste water which needs further treatment thus increase the production cost. In order to avoid this disadvantage, adsorbents for fluoride were synthesized from dried orange juice residue marketed as additives of cattle food at cheap price after single step of metal loading reaction and which was found to be effective for fluoride removal. The effectiveness for fluoride removal by metal loaded dried orange juice residue from actual waste water was investigated in both batch and column mode. The energy dispersive X-ray spectroscopy (EDX) and infrared (IR) spectroscopic analysis indicated that effective adsorption of metal ion on dried orange juice residue and also fluoride on metal-loaded dried orange juice residue. Application of Zr(IV) loaded dried orange juice residue for real plating solution suggested effective removal of trace concentration of fluoride down to the accepted standard. Thus, this work shed light on the potential application of metal loaded dried orange juice residue to remediate the toxic fluoride from contaminated water.

#### **6.1 INTRODUCTION**

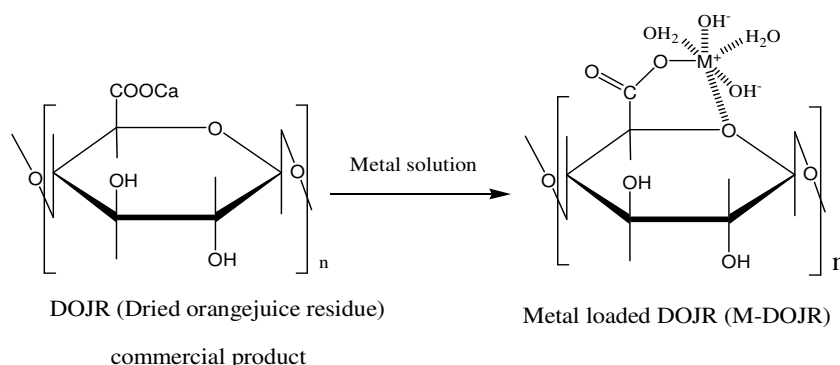
In the commercial production of dried orange juice residue, orange juice residue just after juicing mixed with 1% calcium hydroxide and dried to give dried orange juice residue, abbreviated DOJR hereafter, it is inferred that some part of orange juice residue is converted into SOJR by the aid of calcium hydroxide. In the present work, we attempted to employ commercially available dried orange juice residue marketed as additives for cattle foods for the fluoride removal. It also acts as cation exchanger and effectively adsorbed some high valent metal ions such as Zr(IV), Ce(IV) and Al(III) from aqueous solution. The Zr, Ce, La, Fe and Al

loaded adsorbents so far investigated elsewhere were reported to effectively adsorb fluoride from water [1, 2], so that, the new types of adsorbents investigated in this chapter are also expected to effectively remove fluoride from water.

## 6.2 EXPERIMENTAL PROCEDURE

### 6.2.1 Creation of active sites on dried orange juice residue

Because DOJR contains large amounts of calcium and water soluble organic compounds like citric acid and sugar, it was water washed several times to remove these components in advance. Here, the removal of water soluble organic acids, citric acid in particular, is indispensable because they desorb the loaded high valent metal ions like Zr(IV). In typical runs of the present experiment, at first, 50 g of DOJR was washed several times by decantation and, finally, it was filtered. The filter cake was dried in a convection oven for 24 h at 70°C, which was further loaded with some high valent metal ions such as Zr(IV), Ce(IV) and Al(III) according to the reaction shown in **Scheme 6.1** as follows. Three grams of the dried filter cake was mixed together with 0.5 dm<sup>3</sup> of 0.1 M Zr(IV) and Al(III) solution at their optimal loading pH. However, Ce(IV) loading was performed by using 2.5% Ce(IV) solution at pH 2.78. The mixture was shaken for 24 h at 30°C in order to complete the metal loading reaction and, then, it was filtered and washed until neutral pH and vacuum dried at temperature -20°C. The material obtained in this way is termed as metal loaded DOJR (M-DOJR), hereafter.



**Scheme 6.1** Creation of active sites for fluoride ion adsorption by metal loading reaction on DOJR

### 6.2.2 Analysis of composition and functional modification

Functional modification of DOJR was analyzed by using (JASCO FT-IR 410) Fourier transform infrared spectrometer. To determine the chemical composition of the dried orange juice residue (DOJR), Zr(IV)-loaded DOJR, and Zr(IV)- loaded DOJR after fluoride adsorption (Shimadzu model EDX 800 HS) an energy dispersive X-ray spectrometer was used.

### 6.2.3 Analysis of loaded metal ions

The amount of Zr(IV), Ce(IV) and Al(III) ions loaded on DOJR were quantitatively evaluated by dissolving 50 mg of M- DOJR in 10 cm<sup>3</sup> of aquaregia solution and shaken for 24 h in order to ensure complete dissolution. After filtration, metal ion concentration was measured by using (Shimadzu model ICPS 8100) an inductively coupled plasma atomic emission spectrometer ICP-AES.

### 6.2.4 Batch wise studies

The experiments were performed in 50 cm<sup>3</sup> glass bottle containing 15 cm<sup>3</sup> fluoride solution and 25 mg Zr(IV)-DOJR at 30°C. To study the effect of pH on fluoride uptake by Zr(IV)-DOJR, it was varied from 1 up to 12 by adding 0.5 M HNO<sub>3</sub> or 0.5 M NaOH solution. Influence of sorbents amount was studied by using different doses of Zr(IV)- and Al(III)-DOJR by using two different waste plating solutions. In the similar way, maximum uptake capacity of Ce(IV)- and Zr(IV)-DOJR for fluoride were determined by changing the concentration of fluoride in the range of 0.5 to 12 mmol dm<sup>-3</sup> at pH 4. After each experiment, filtrates were analyzed for fluoride by using (Dionex model ICS 1500) ion chromatography. Adsorption tests in co-existing system were carried out in a binary solution at sorbent-solution ratio of 1.33 g dm<sup>-3</sup> at constant pH (pH = 4) and temperature (30°C). In order to evaluate the most suitable condition for adsorption of fluoride on Zr(IV)-DOJR, leakage test of loaded Zr(IV) from the sorbent was performed at varying concentrations of fluoride (0.5 - 6 mmol dm<sup>-3</sup>) at different pHs. The Zr(IV) solution leaked at different concentrations of fluoride was measured by ICP-AES. Similarly, desorption test of fluoride was carried out by NaOH solution.



### 6.2.5 Continuous adsorption studies

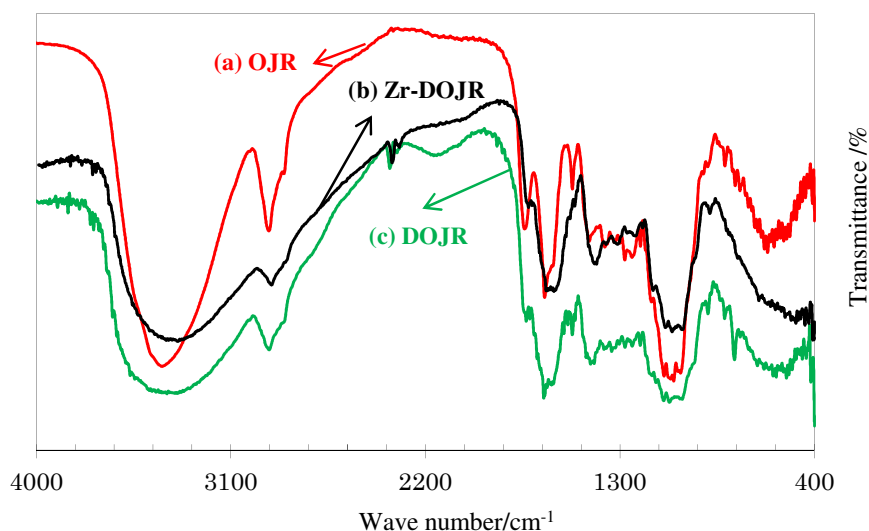
The adsorption test of fluoride from water was also carried out by using a column packed with Zr(IV)-DOJR. The column used in this study was a glass column of 0.8 cm diameter. For the breakthrough test, the column was washed overnight by fluoride free solution *i.e.* de-ionized water at the same pH as test solution. The effect of various parameters such as pH, influent fluoride concentration, adsorbent amount, and flow rates were investigated. Feed solution were percolated into the bed of Zr(IV)-DOJR at required flow rate by using (Iwaki model PST 100N) peristaltic pump. Effluent samples were collected by using (Biorad model 2110) fraction collector. The concentrations of fluoride in the effluent sample were measured by ion chromatography.

## 6.3 RESULTS AND DISCUSSION

### 6.3.1 Characterization of adsorbents

#### 6.3.1.1 Spectroscopic analysis for the functional groups in the adsorbent

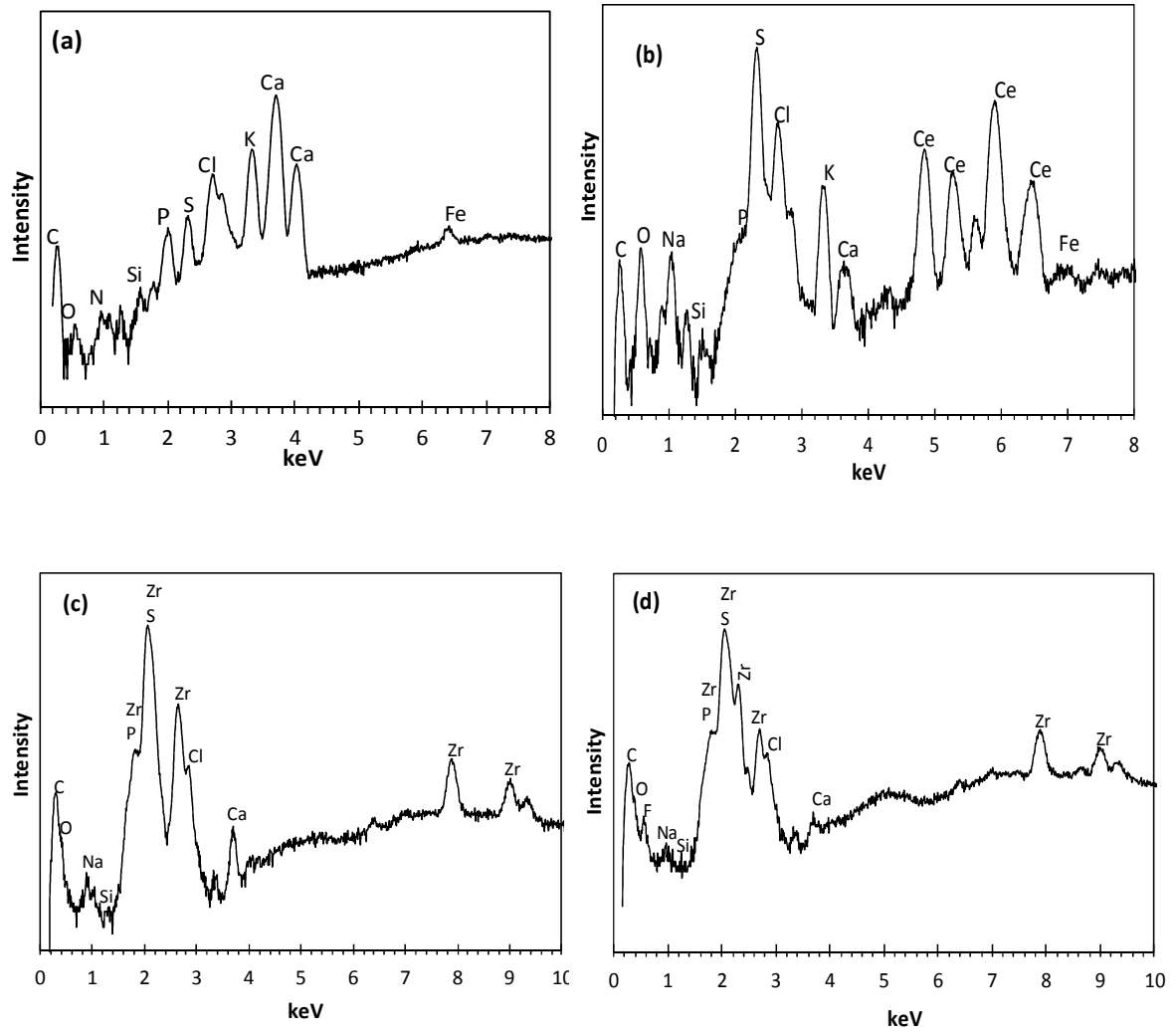
**Figure 6.1** illustrates the FT-IR spectra of OJR, the feed material of DOJR, water washed DOJR before and after the loading of Zr(IV). In the case of raw OJR, the peaks pointed at around 3381, 2913, 1742 and 1683  $\text{cm}^{-1}$  are assigned to the stretching vibration of OH,  $\text{CH}_2$ , COO and C=O groups, respectively. In case of dried orange juice residue (DOJR), there are no significant changes in the stretching vibration of OH and  $\text{CH}_2$  groups. The main and detectable changes occurs in carboxyl functional groups. The result from the spectral data shows that the peak around 1742  $\text{cm}^{-1}$  which was appears in raw orange juice residue (OJR) due to carboxylic acid (COO) functional group was disappeared and two additional new peaks appeared at around 1662 and 1439  $\text{cm}^{-1}$ , which is due to the formation of calcium salt of carboxylic acid *i.e.* calcium salt of orange pectic acid. Moreover, the peak at around 1662 and 1439  $\text{cm}^{-1}$  in DOJR were shifted at around 1651 and 1429  $\text{cm}^{-1}$  after Zr(IV) loading. Hence, comparison of FT-IR spectra confirms that carboxylic acid functional group of DOJR is the main functional group that takes part in the metal loading reaction.



**Fig. 6.1** FT-IR spectra of (a) OJR, (b) DOJR, and (c) Zr(IV)-DOJR

The expected loading reaction of metal ions on DOJR can be further confirmed by the measurement of energy dispersive x-ray spectra. The EDX spectra of DOJR, Ce(IV)-DOJR and Zr(IV)-DOJR after fluoride adsorption are shown in **Fig. 6.2**. As seen from **Fig. 6.2 (a)**, the elemental peak of C, O, Na, Si, P, S, Cl, K and Fe were observed in a DOJR at energy values of 0.25, 0.31, 1.02, 1.76, 1.96, 2.28, 2.62, 3.28 and 6.38 keV, respectively, in addition to calcium ion peak at 3.68 - 4.01 keV. After loading cerium ion as shown in **Fig. 6.2 (b)**, the calcium ion peak appeared at around 4.01 keV was completely disappeared and new peak of cerium element were appeared at energy values 4.84, 5.24, 5.97, and 6.32 keV, suggesting that Ce(IV) ions were effectively loaded onto the DOJR.

The calcium ion peak appears at around 4.01 keV was disappeared also after Zr(IV) loading reaction as shown in **Fig. 6.2 (c)** suggesting that calcium substitution reaction by cation exchange mechanism is inferred to occur during loading reaction also in the case of Zr(IV)-DOJR as depicted by the reaction expressed in **Scheme 6.1**. In addition, disappearance of elemental peak of calcium after loading reaction is one of the evidence that Ce(IV) or Zr(IV) loading reaction takes place by the substitution of calcium ions. After fluoride adsorption, another new peak of fluoride in the EDX spectra [**Fig. 6.2 (d)**] at 0.68 keV was observed which suggest the strong affinity of present adsorbent for fluoride ion.



**Fig. 6.2** Energy dispersive X-ray spectra of (a) DOJR (b) Ce(IV)-DOJR, (c) Zr(IV)-DOJR, and (d) Zr(IV)-DOJR after fluoride adsorption

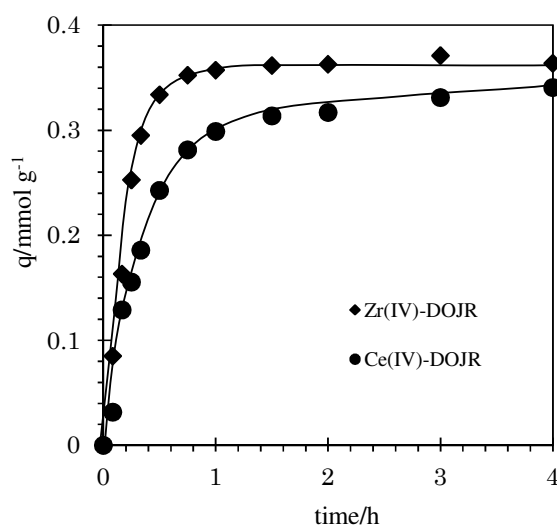
### 6.3.1.2 Analysis of metal ions loaded on M-DOJR

Amount of loaded Zr(IV), Ce(IV), and Al(III) in the sample of Zr(IV)-DOJR, Ce(IV)-DOJR, and Al(III)-DOJR evaluated by ICP-AES measurement after aquaregia dissolution at  $5 \text{ g dm}^{-3}$  and were found to be 0.90, 0.85 and  $0.97 \text{ mmol g}^{-1}$ , respectively.

## 6.3.2 Batch wise adsorption of fluoride

### 6.3.2.1 Effect of contact time

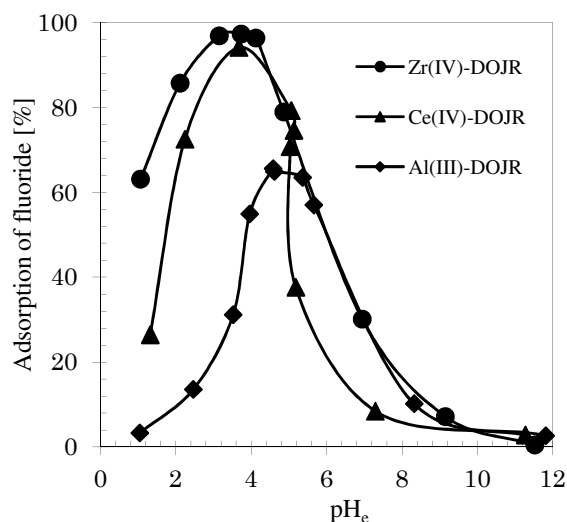
The effect of contact time was studied using  $15 \text{ mg dm}^{-3}$  of fluoride solution at  $30^\circ\text{C}$  temperature. The adsorption of fluoride was examined on Zr(IV)-DOJR and Ce(IV)-DOJR as a function of time in the range of 5 – 240 min. The removal of fluoride as a function of contact time is shown in **Fig. 6.3**. The result in the figure indicates that initially the adsorption of fluoride on both adsorbents increased rapidly and the equilibrium was attained at within 2 h. Consequently, for further experimental work, it was shaken for 24 h to ensure the complete equilibrium. Adsorption kinetics of these metal loaded adsorbents investigated in this study is similar to that of zirconium loaded leather fiber and similar other metal loaded adsorbents [3, 4].



**Fig. 6.3** Adsorption kinetics of fluoride on M-DOJR from aqueous solution (volume of solution =  $15 \text{ cm}^3$ , weight of gel = 25 mg, pH = 4, fluoride concentration =  $\sim 15 \text{ mg dm}^{-3}$ , and temperature =  $30^\circ\text{C}$ )

### 6.3.2.2 Effect of pH

To recognize the effect of pH, adsorption studies were carried out at different pH (1-12). The influence of pH plays a key role on the separation sciences, as in this study the adsorption of fluoride onto three different kinds of metal loaded DOJR namely Zr(IV)-, Ce(IV)- and Al(III)-DOJR were explored at fixed concentration ( $\sim 10 \text{ mg dm}^{-3}$ ) of fluoride ion. The results obtained are shown in **Fig. 6.4**. The adsorption efficiencies increases by increasing the pH of the solution in the pH range 1-3 and attains maximum values at around 4 in the case of Zr(IV)- and Ce(IV)- DOJR, in the case of Al(III)-DOJR, it was found to occur at around 6. The less uptake of fluoride by using trivalent aluminium loaded DOJR is due to low affinity of loaded Al(III) with fluoride ions compared to Zr(IV) or Ce(IV) ions. The phenomenon is similar to that in M-SOJR as described in the previous Chapter.



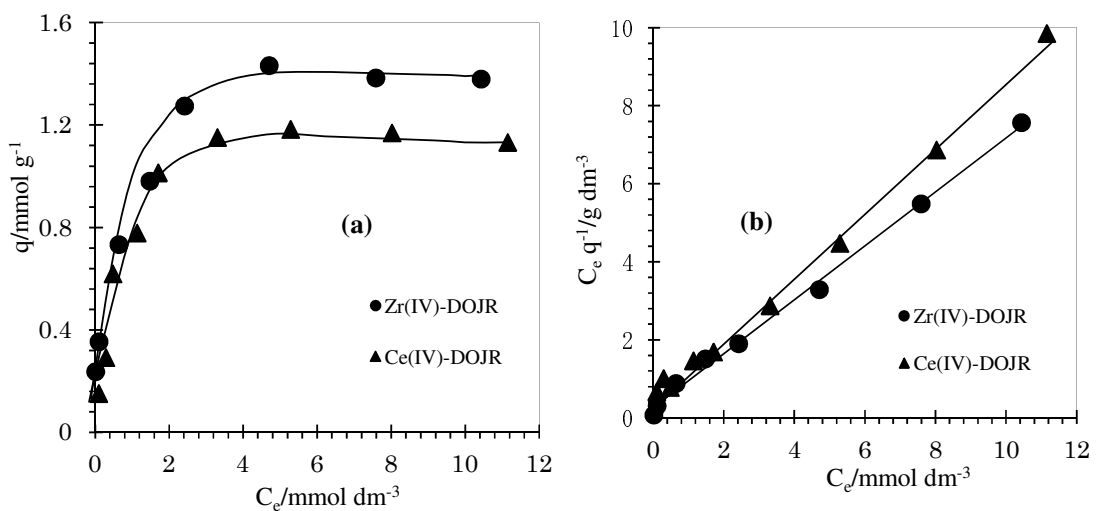
**Fig. 6.4** Effect of equilibrium pH for the adsorption of fluoride on M-DOJR (volume of solution =  $15 \text{ cm}^3$ , weight of gel = 25 mg, fluoride concentration =  $\sim 10 \text{ mg dm}^{-3}$ , and temperature =  $30^\circ\text{C}$ )

### 6.3.2.3 Adsorption isotherms of fluoride

The adsorption capacity of M-DOJR for fluoride as a function of equilibrium concentration of fluoride is shown in **Fig. 6.5 (a)**. Langmuir parameters for fluoride adsorption on both the M-DOJR evaluated from the linear plots of equation 2.3 (Chapter 2) are presented in

**Table 6.1.** The plot of  $C_e/q$  vs  $C_e$  for both the M-DOJR tested [Fig. 6.5 (b)] were found to be linear with high correlation regression coefficient suggesting that classical Langmuir model is good selections to explain the ongoing phenomenon. The maximum adsorption capacity of Zr(IV)- and Ce(IV)-DOJR for fluoride was found to be 1.43 and 1.22 mmol g<sup>-1</sup>, respectively.

The comparative study of maximum adsorption capacities of Zr(IV) and Ce(IV) loaded DOJR with that of Zr(IV) and Ce(IV) loaded SOJR is also presented in Table 6.2. The result shows that metal loaded dried orange juice residue possesses little bit low adsorption capacities than metal loaded SOJR. However, production of SOJR required long chemical treatment and released a large amount of waste water that needs further treatment before wasting that ultimately increases the production cost of the adsorbent. The commercially available DOJR can be used after water washing and behaves similar behavior to that of SOJR. In addition, wet orange juice residue which is required for the preparation of SOJR is difficult to store compared to storage of dried product (DOJR). Hence, the utilization of inexpensive (\$ 0.1 kg<sup>-1</sup>) commercial DOJR for the preparation of metal loaded orange waste adsorbents for fluoride removal from water looks promising.



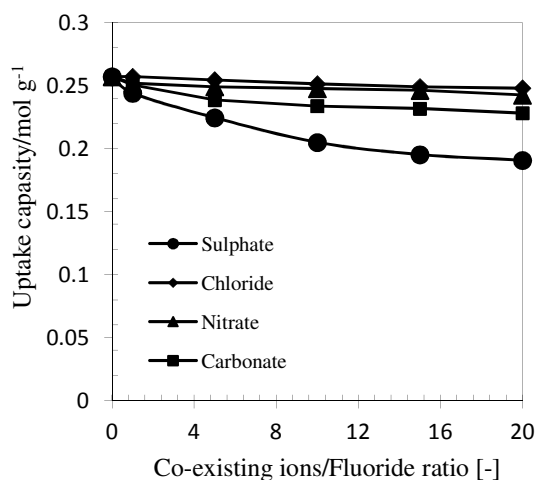
**Fig. 6.5** Adsorption isotherms of fluoride on M-DOJR (a) adsorption isotherm, (b) Langmuir isotherm model (volume of solution = 15 cm<sup>3</sup>, weight of gel = 25 mg, shaking time = 24 h, shaking speed = 150 rpm, pH = 4, and temperature = 30°C)

**Table 6.1** Langmuir isotherm parameters for the adsorption of fluoride on Zr(IV)- and Ce(IV) loaded DOJR and their comparison with Zr(IV)- and Ce(IV) loaded SOJR

M-DOJR					M-SOJR			
Adsorbents	pH	$q_{\max}$ /mmol g <sup>-1</sup>	$b$ /dm <sup>3</sup> mmol <sup>-1</sup>	$R^2$	Adsorbents	$q_{\max}$ /mmol g <sup>-1</sup>	$b$ /dm <sup>3</sup> mmol <sup>-1</sup>	$R^2$
Zr(IV)-DOJR	4	1.43	2.91	0.99	Zr(IV)-SOJR	1.74	3.11	0.99
Ce(IV)-DOJR	4	1.22	1.86	0.99	Ce(IV)-SOJR	1.53	3.59	0.99

#### 6.3.2.4 Effect of foreign anions

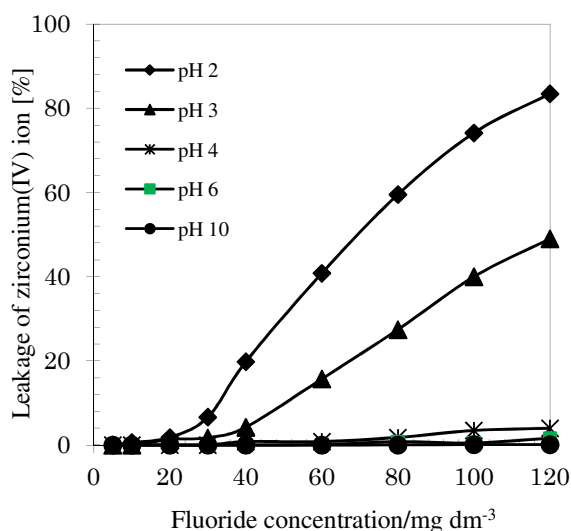
Selectivity test of Zr(IV)-DOJR for fluoride in the binary co-existing systems of some ions such as, nitrate, chloride, sulphate, and carbonate that usually exist in the fluoride containing waste water was investigated. The ratio of the concentrations of these co-existing ions and fluoride were varied from 1 to 20 to evaluate their relative interference on fluoride adsorption. The influence of co-existing ion/fluoride ratio on fluoride uptake capacity of Zr(IV)-DOJR is shown in **Fig. 6.6**. It shows that the presence of some anions such as chloride, nitrate, and carbonate show negligible influence on the fluoride adsorption capacity whereas sulphate exerts little bit interference. Such a behavior of Zr(IV) loaded DOJR towards fluoride is similar to the metal loaded SOJR and other previously reported literature [3, 5, 6].



**Fig. 6.6** Influence of co-existing ions during fluoride adsorption onto Zr(IV)-DOJR (volume of solution = 15 cm<sup>3</sup>, weight of gel = 25 mg, feed solution = ~1 mmol dm<sup>-3</sup>, and temperature = 30°C)

### 6.3.2.5 Leaking behavior of loaded Zr(IV)

For the purpose of ensuring the leakage of the loaded metal ions, the leakage test from the adsorbent by fluoride was carried out under different conditions for Zr(IV)-DOJR. **Fig. 6.7** shows % leakage of Zr(IV) from loaded DOJR at varying concentration of fluoride (0.5- 6 mmol dm<sup>-3</sup>) at different pH ranging from 2 - 8. It is evident from this figure that the leakage of loaded Zr(IV) increases with increasing fluoride concentration above 30 mg dm<sup>-3</sup> at low pH while it is negligible at high pH. The leakage of Zr(IV) was found to be insignificant at basic pH even at high concentration of fluoride, which clearly suggests that there is no or negligible leakage of Zr(IV) even at acidic pH in the case of the removal of low concentration of fluoride below 30 mg dm<sup>-3</sup>. Hence, it is concluded that Zr(IV) loaded DOJR investigated in this study can be a promising adsorbent for the treatment of large volume of waste water containing trace concentration of fluoride ion. These phenomena are same as in the case of metal loaded saponified orange juice residue (M-SOJR).



**Fig. 6.7** Leaking behavior of loaded Zr(IV) from Zr(IV)-DOJR at different pH by varying concentration of fluoride (volume of solution = 10 cm<sup>3</sup>, weight of gel = 10 mg, shaking time = 24 h, shaking speed = 150 rpm, and temperature = 30°C)



### ***6.3.2.6 Fluoride removal from actual waste plating solution***

Two samples of actual waste plating solutions were provided from different plating companies in Japan for the removal test of fluoride using M-DOJR. One sample (**Sample 1**) contained trace concentration of fluoride while another sample (**Sample 2**) contained high concentration of fluoride. For these actual solutions, the tests of adsorptive removal of fluoride were carried out batch wise using Zr(IV)- and Al(III)-DOJR at varying dosage of the adsorbents. **Table 6.2** shows the components of these sample solutions.

#### ***6.3.2.6.1 Treatment of waste plating solution containing trace amount of fluoride***

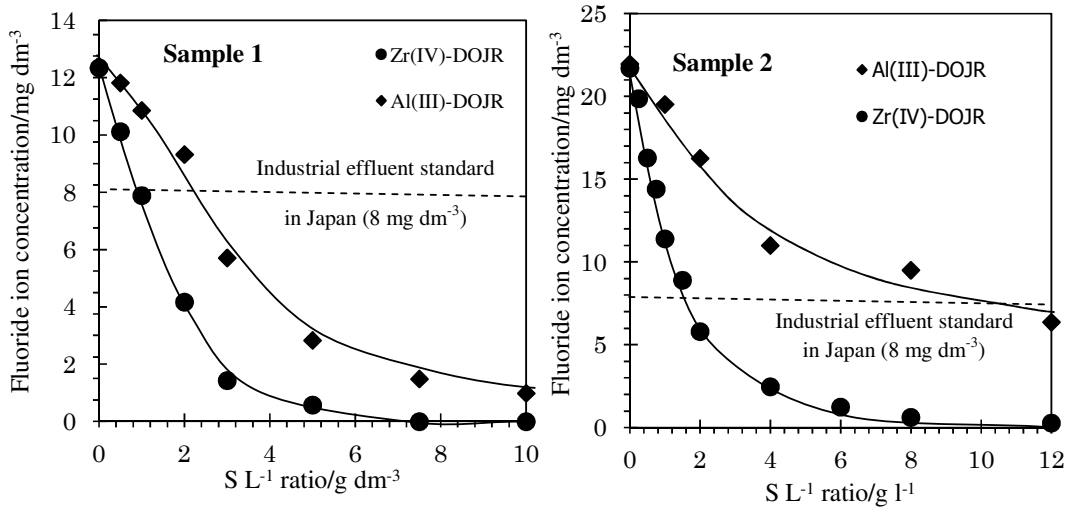
The effects of dosage of M-DOJR on the concentration of fluoride remained in the solution after the adsorption is shown in **Fig. 6.8 (Sample 1)**. It is apparent that the residual concentration of fluoride in the solution decreases with increasing amount of M-DOJR added. However, although, in the case of Zr(IV)-DOJR, the residual fluoride concentration can be effectively lowered below  $8 \text{ mg dm}^{-3}$ , the effluent standard in Japan, by adding 1 g of the adsorbent per unit volume ( $1 \text{ dm}^3$ ) of the sample solution, around 3 g of the adsorbent is necessary to be added in the case of Al(III)-DOJR.

#### ***6.3.2.6.2 Treatment of waste plating solution containing high concentration of fluoride***

As mentioned earlier, M-DOJR adsorbents can be employed only for dilute concentration of fluoride (lower than  $30 \text{ mg dm}^{-3}$ ) at low pH, it is difficult to apply M-DOJR directly to Sample 2 solution which contains high concentration of fluoride ( $520.4 \text{ mg dm}^{-3}$ ). Consequently, after the fluoride concentration was lowered to  $21.14 \text{ mg dm}^{-3}$  by conventional calcium precipitation method by adding 0.6 g of  $\text{CaCl}_2$  to  $100 \text{ cm}^3$  of Sample 2 solution in advance, the residual concentration of fluoride from waste water was then removed by using Zr(IV)- and Al(III)-DOJR.

The relationship between the residual concentration of fluoride and adsorbent dosage ( $0.5$  to  $12 \text{ g dm}^{-3}$ ) is shown in **Fig. 6.8 (Sample 2)**. It is clear from this figure that fluoride concentration can be effectively lowered down to effluent standard in Japan by adding  $12 \text{ g dm}^{-3}$  of Al(III)-DOJR while it is only  $1.5 \text{ g dm}^{-3}$  in the case of Zr(IV)-DOJR. In this case, the concentration of interfering sulphate ion was also decreased from  $1461.5 \text{ mg dm}^{-3}$  to  $134.7 \text{ mg}$

$\text{dm}^{-3}$  after calcium precipitation, suggesting that the competition for fluoride by sulphate was also decreased, making easy removal of fluoride from the sample solution.



**Fig. 6.8** Adsorptive removal of fluoride from actual plating solution using M-DOJR (volume of solution =  $15 \text{ cm}^3$ , shaking time = 24 h, shaking speed = 150 rpm, and temperature =  $30^\circ\text{C}$ )

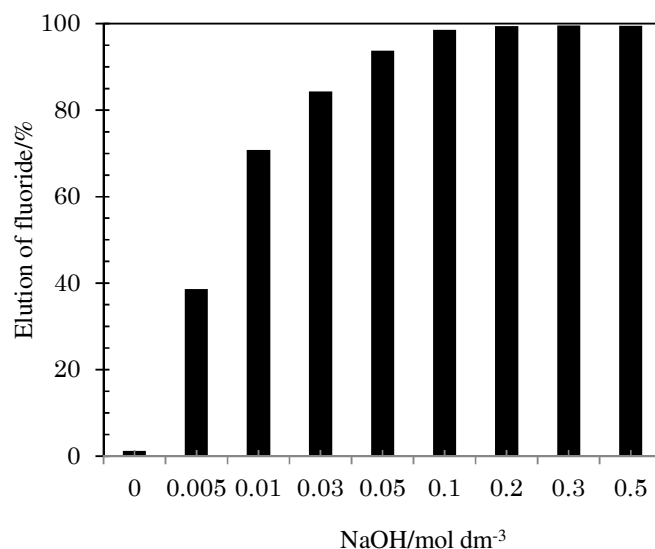
**Table 6.2** Wastewater composition ( $\text{mg dm}^{-3}$ ) of two different plating solutions

	pH	Al	Ca	Fe	Cu	Zn	F	SO <sub>4</sub>
<b>Sample 1</b>	6.7	13.8	10.5	36.4	9.8	1.9	12.3	754.3
<b>Sample 2</b>	6.9	107.6	32.2	6.8	0	217.3	520.4	1461.5

### 6.3.2.7 Stripping of loaded fluoride

Batch wise stripping of loaded fluoride from fluoride adsorbed Zr(IV)-DOJR was investigated to suggest the effective agent for the regeneration. Effect of pH for the fluoride adsorption onto Zr(IV)-DOJR shows that there is negligible adsorption of fluoride at pH higher than 10 without any leakage of loaded Zr(IV), suggesting that alkali solution can be used as a suitable eluting agent. So that, stripping test of fluoride from the loaded gel was performed by changing the concentration of caustic soda (NaOH) solution at varying concentration (0.005-0.5 M) and the result is presented in **Fig. 6.9**. The result shows that the stripping of fluoride

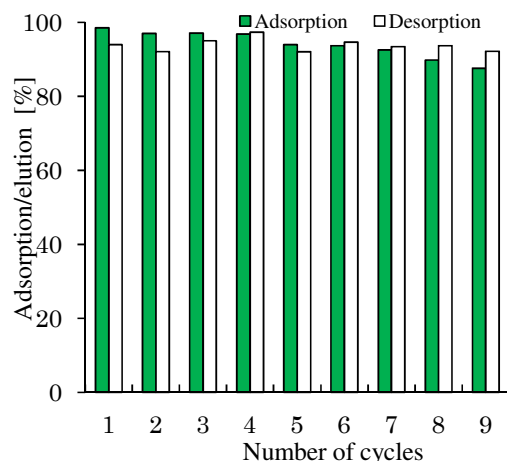
increases from 39% to 98 % by increasing the concentration of alkali solution from 0.005 to 0.1 M and achieved nearly complete stripping. Consequently, 0.1 M caustic soda solution was concluded to be a good eluting agent from fluoride loaded Zr(IV)-DOJR.



**Fig. 6.9** Stripping of adsorbed fluoride from fluoride loaded ( $0.82 \text{ mmol g}^{-1}$ ) Zr-DOJR by using various concentration of caustic soda solution

#### 6.3.2.8 Adsorption followed by elution and re-adsorption cycles

Based on the result of the optimization of elution agent (section 6.3.2.7), the adsorption of fluoride onto Zr(IV)-DOJR followed by elution using dilute NaOH solution was repeatedly performed in order to ensure the durability of Zr(IV)-DOJR. The result up to 9 repeated cycle of adsorption and elution is presented in **Fig. 6.10**, which shows that % adsorption of fluoride on Zr(IV)-DOJR is more than 96% up to 4 cycles whereas it is gradually decreased from 96(%) to 87 % with further increasing the cycle number from 4. The elution of fluoride is more or less the same (>94%) over the entire cycle. Hence, it can be concluded that Zr(IV)-DOJR is stable and robust enough with the negligible deterioration of active adsorption sites.



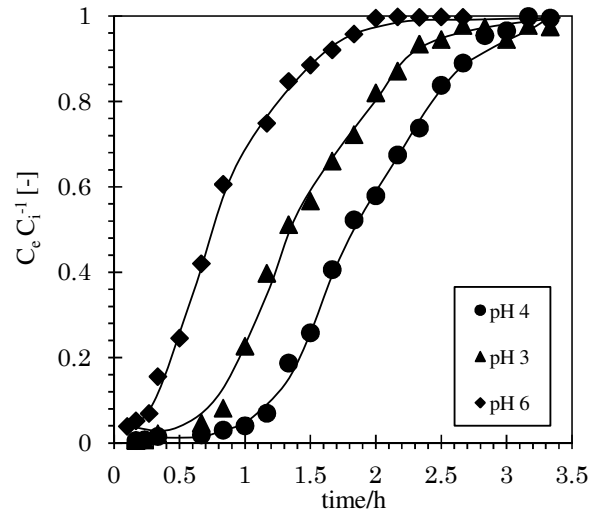
**Fig.6.10** Cycle test of fluoride adsorption onto Zr(IV)-DOJR and its desorption using NaOH solution (solid liquid ratio =  $2.5 \text{ g dm}^{-3}$ , fluoride solution =  $18.6 \text{ mg dm}^{-3}$ , eluent =  $0.1 \text{ M NaOH}$ , and temperature =  $30^\circ\text{C}$ )

### 6.3.3 Continuous adsorption test of fluoride in a packed column of Zr(IV)-DOJR

#### 6.3.3.1 Effect of pH

Effect of solution pH on the adsorption of fluoride was investigated at different pH ranging from 2 up to 6 in continuous packed column of Zr(IV)-DOJR as shown in **Fig. 6.11**. The result shows that, the breakthrough time of the curve increases with increasing pH of the solution from pH 3-4 then, it was found to be decreased with further increase of pH. Breakthrough of fluoride at pH 4 was observed to take place after longest period of time among the tested pH, suggesting that adsorption of fluoride at this pH is the most optimum and effective from the viewpoint of effective utilization of Zr(IV)-DOJR in the continuous mode operation. As in the case of batch wise adsorption test, the adsorption of fluoride at pH values higher than 4 decreased also in continuous system which is clearly demonstrates the observation of earlier breakthrough at pH 6 in **Fig. 6.11**. The decrease of breakthrough time in the case of pH 3 also indicates the decreasing nature of fluoride adsorption capacity. The adsorption capacities of packed column of Zr(IV)-DOJR were determined from the area of breakthrough curve. Uptake of fluoride by Zr(IV)-DOJR in fixed bed column at pH 3, 4 and 6 were found to be  $6.9$ ,  $10.2$  and  $4.3 \text{ mg g}^{-1}$ , respectively. The values were listed in **Table 6.3**.

Consequently, to examine the adsorption behavior of the Zr(IV)-DOJR, pH of the solution is controlled at around 4 to ensure the maximum adsorption of fluoride.



**Fig. 6.11** Effect of pH on the breakthrough profile of fluoride from the column packed with Zr(IV)-DOJR (Feed solution =  $14.3 \text{ mg dm}^{-3}$ , flow rate =  $153.0 \text{ cm}^3 \text{ h}^{-1}$ , and bed depth =  $2.4 \text{ cm}$ )

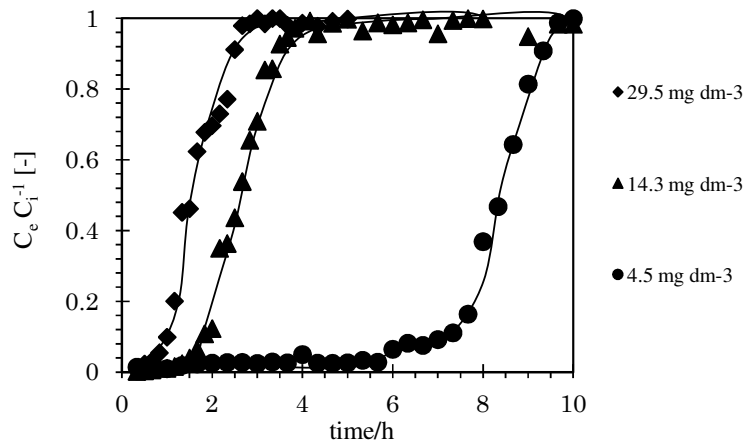
**Table 6.3** Effect of initial pH of the fluoride solution for the adsorption of fluoride by Zr(IV)-DOJR

Parameter	Flow rate $\text{F}/\text{cm}^3 \text{ h}^{-1}$	Column capacity $q/\text{mg g}^{-1}$	pH	Feed solution $C_i/\text{mg dm}^{-3}$	Bed depth $D/\text{cm}$
3	153.0	6.9	3	14.3	2.4
4	153.0	10.2	4	14.3	2.4
6	153.0	4.3	6	14.3	2.4

### 6.3.3.2 Effect of feed concentration

Breakthrough profile of fluoride at different fluoride concentration *viz.* 4.5, 14.3 and  $29.5 \text{ mg dm}^{-3}$  was observed keeping other parameters such as flow rate, bed depth, pH, and temperature constant. The characteristic profiles for different concentrations are shown in **Fig. 6.12**. The result in this figure illustrates that the adsorption of fluoride on Zr(IV)-DOJR reached saturation quickly and the breakthrough time was decreased with increasing influent fluoride concentration. In the case of lowest concentration of influent fluoride ion, breakthrough curve became wider and the treated volume of fluoride solution was highest. The amount of fluoride

uptake increases from 4.5 to 7.2 mg g<sup>-1</sup> (Table 6.4) with the increase of influent fluoride concentration from 4.5 to 29.5 mg dm<sup>-3</sup> in the similar experimental conditions which can be reasonably attributed to the fact that, high influent fluoride concentration providing greater driving force for the transfer process to overcome the mass transfer [7]. In addition, the exhaust time for Zr(IV)-DOJR decreased from 10 h to 2 h as the influent fluoride concentration increased from 4.5 to 29.5 mg dm<sup>-3</sup>. Such a result demonstrated that higher initial fluoride concentrations led to higher driving force for mass transfer; hence the adsorbent achieved saturation earlier [8].



**Fig. 6.12** Effect of influent fluoride concentration for fluoride adsorption on the bed of Zr(IV)-DOJR (flow rate = 153.0 cm<sup>3</sup> h<sup>-1</sup>, pH = 4, bed depth = 4.8 cm, and at rt)

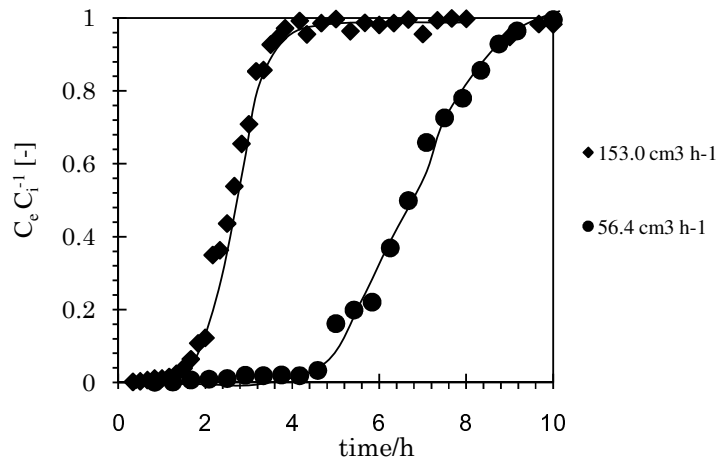
**Table 6.4** Effect of initial fluoride concentration for the adsorption of fluoride by Zr(IV)-DOJR

Parameter	Flow rate F/cm <sup>3</sup> h <sup>-1</sup>	Column capacity q/mg g <sup>-1</sup>	pH	Feed solution C <sub>i</sub> /mg dm <sup>-3</sup>	Bed depth D/cm
4.5	153.0	4.5	4	5.5	4.8
14.3	153.0	5.6	4	14.3	4.8
29.3	153.0	7.2	4	29.3	4.8

### 6.3.3.3 Effect of flow rate

The effect of flow rate of influent solution on the adsorption behavior of fluoride ion onto the Zr(IV)-DOJR column was investigated at the flow rates of 56.4 cm<sup>3</sup> h<sup>-1</sup> and 153.0 cm<sup>3</sup> h<sup>-1</sup>

keeping initial fluoride concentration ( $14.3 \text{ mg dm}^{-3}$ ), bed depth (4.8 cm), and pH of the feed solution ( $\text{pH} = 4$ ) constant at room temperature. Breakthrough profiles of fluoride from the bed of Zr(IV)-DOJR in the mentioned experimental condition are shown in **Fig. 6.13**. It was shown that the breakthrough time decreases with the increase in flow rate. Application of small flow rate increases the time of fluoride contacting with adsorbent surface, which lead to increase the breakthrough time in the continuous adsorption system. It can be reasonably explained in the fact that, at lower flow rate the rate of mass transfer decreased *i.e.* the total amount of fluoride adsorbed onto unit bed height of Zr(IV)-DOJR decreased that lead to the formation of wider breakthrough curve. The column adsorption capacity of fluoride was found to be increased from 5.67 to  $6.33 \text{ mg g}^{-1}$  with the decrease of flow rate from  $153.0$  to  $56.4 \text{ cm}^3 \text{ h}^{-1}$  as shown in **Table 6.5**. Because, the residence time of the fluoride inside the bed of Zr(IV)-DOJR was long enough for adsorption at slow flow rate leading to the increase in column capacity. Similar types of finding were observed for the adsorption of some heavy metal ions by bone char, adsorption of Pb(II) ion by immobilized saw dust of pine and similar other literatures [ 7, 9, 10].



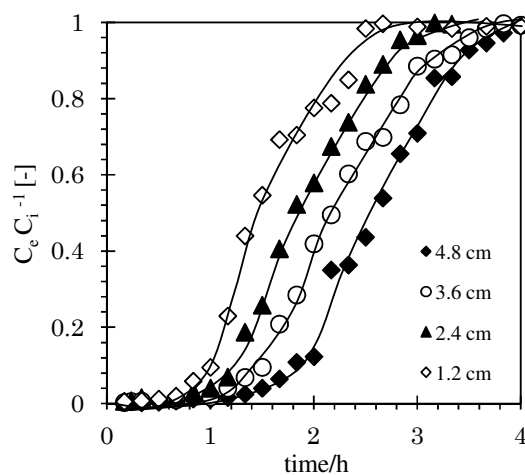
**Fig. 6.13** Adsorption behavior of fluoride ion at different flow rates in bed column of Zr(IV)-DOJR  
(Feed solution =  $14.3 \text{ mg dm}^{-3}$ ,  $\text{pH} = 4$ , bed depth = 4.8 cm, and at rt)

**Table 6.5** Influence of flow rate for the adsorptive removal of fluoride sing Zr(IV) loaded DOJR

Parameter	Flow rate $\text{F/cm}^3 \text{ h}^{-1}$	Column capacity $q/\text{mg g}^{-1}$	pH	Feed solution $C_i/\text{mg dm}^{-3}$	Bed depth D/cm
56.4	56.4	6.2	4	14.3	4.8
153.0	153.0	5.6	4	14.3	4.8

### 6.3.3.4 Influence of bed depth

**Figure 6.14** shows the breakthrough curves of fluoride adsorption on Zr(IV)-DOJR at different bed depths. The results of this figure make clear that, the exhaustion time and amount of treated volume of fluoride solution increases with increasing bed depth of the Zr(IV)-DOJR in the column operation. The reason of such increase in volume of treated feed solution with the increase in bed depth might be due to the increase of residence time of feed solution in the column [7] that results in the more contact between fluoride and actives sites of Zr(IV) loaded dried orange juice residue. It is clear that the removal efficiency of fluoride had an increasing trend in column with the increase in the mass of adsorbent. With the increase of bed depth of Zr(IV)-DOJR in column, the breakthrough curve become sharper that broadened the mass transfer zone [11, 12]. The fluoride adsorption capacity of Zr(IV)-DOJR evaluated from the area of breakthrough curve at 1.2, 2.4, 3.6 and 4.8 cm bed depth were 13.9, 10.2, 6.9 and 5.6 mg g<sup>-1</sup>, respectively as listed in **Table 6.6**. It is attributed that, the channeling effect is increased with increasing height or depth of the column that will ultimately reduces the column capacity. In addition, number of binding sites and adsorbent surface area are increased with the increase of bed depth in the fixed-bed column that will results in the increase of effective bed contact time, thus increase the saturation time of the column [7, 13, 14].



**Fig. 6.14** Influence of bed depth ( $D$ ) for the adsorption of fluoride onto Zr(IV)-DOJR (Feed solution = 14.3 mg dm<sup>-3</sup>, flow rate = 153.0 cm<sup>3</sup> h<sup>-1</sup>, pH = 4, and at rt).



**Table 6.6** Effect of bed depth for the adsorption of fluoride using DOJR loaded with Zr(IV) ion

Parameter	Flow rate $F/\text{cm}^3 \text{ h}^{-1}$	Column capacity $q/\text{mg g}^{-1}$	pH	Feed solution $C_i/\text{mg dm}^{-3}$	Bed depth D/cm
1.2	153.0	13.9	4	14.3	1.2
2.4	153.0	10.2	4	14.3	2.4
3.6	153.0	6.9	4	14.3	3.6
4.8	153.0	5.6	4	14.3	4.8

### 6.3.3.5 Comparative study with other adsorbents

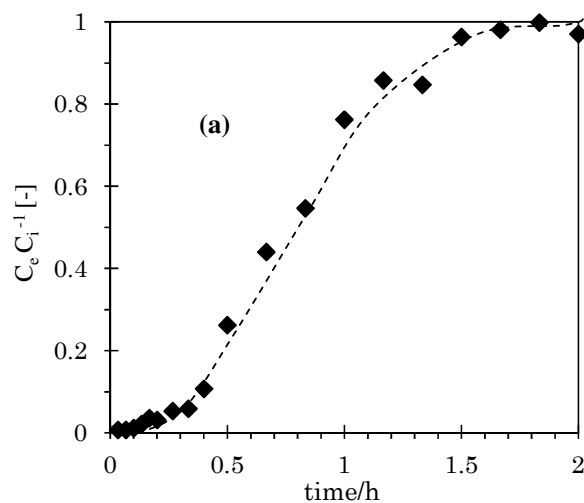
The comparison of adsorption capacities of various adsorbents for fluoride in a fixed bed system together with column capacities of Zr(IV) loaded dried orange juice residue investigated in this work is shown in **Table 6.7** [14-19]. The result shows that, Zr(IV) loaded dried orange juice residue investigated in this study is superior to many other adsorbents reported in the relevant literatures indicating that it can be a promising alternative for fluoride ions removal from aqueous solution in continuous system. The significantly high adsorption capacity for fluoride on fixed bed column of Zr(IV)-DOJR can be reasonably attributable to the development of active adsorption sites on SOJR by Zr(IV) loading. In addition the Zr(IV)-DOJR can be easily regenerated by treatment with dilute alkali solution and can be use again and again.

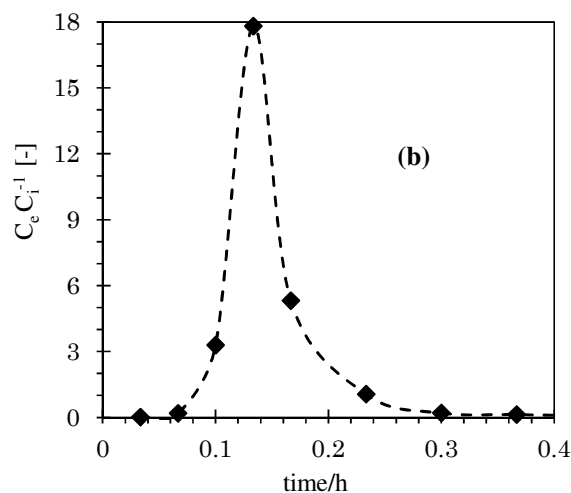
**Table 6.7** Comparison of column capacities of various adsorbent for fluoride

Adsorbents	Flow rate $F/\text{cm}^3 \text{ min}^{-1}$	F solution $C_i/\text{mg dm}^{-3}$	pH	Temp. $^{\circ}\text{C}$	Column capacity $q/\text{mg g}^{-1}$	Ref.
Zr-DOJR	0.9	14.3	4	30	6.2	This study
Zr-DOJR	2.6	14.3	4	30	5.6	This study
Acid treated GHB	8.3	2.8	7.1	25	0.16	15
Granular red mud	5.0	20	4.7	25	0.77	16
Kanuma mud	5.0	20	6.9	30	1.55	17
Biocomposite	-	5	4.8	25	1.70	18
Chitin	-	5	4.8	25	3.40	18
Laterite	5.0	20	6.8	30	0.34	19

### 6.3.3.5 Application of Zr(IV)-DOJR in actual plating solution

In order to evaluate the possibilities of using Zr(IV)-DOJR for the treatment of industrial waste water containing trace concentration of fluoride, adsorption behavior of fluoride in the fixed bed column of Zr(IV)-DOJR by using actual waste water solution was conducted. The ultimate objective of the fluoride bio-sorption technology in continuous mode is application of this technology to the wastewater treatment. For the evaluation of adsorbent ability for the treatment of fluoride from water, continuous adsorption test using model solution may not be effective because fluoride containing wastewater contains fluoride but also several other cationic and anionic species that may interfere fluoride adsorption. Hence, breakthrough profile of fluoride from the column packed with Zr(IV)-DOJR using actual plating solution provided from local plating company at its native pH (6.71) was performed and the results are shown in **Fig. 6.15 (a)**. The result shows that effluent fluoride concentration was found to be less than  $0.1 \text{ mg dm}^{-3}$  at the beginning suggesting that fluoride ions were effectively adsorbed onto the bed of Zr(IV)-DOJR, then after certain period of time, fluoride concentration was found to be gradually increased and reached saturation. The result of this figure also shows that fluoride ion present in plating solution was selectively adsorbed onto the bed of Zr(IV)-DOJR although it contains other interfering cations as well as anions (**Table 6.8**). The column capacity of Zr(IV)-DOJR for plating solution was evaluated to be  $1.65 \text{ mg g}^{-1}$  from the area of breakthrough curve.





**Fig. 6.15** Continuous adsorption of fluoride from plating solution in a fix bed column of Zr(IV) loaded DOJR (a) breakthrough profile (b) elution profile (feed solution =  $\sim 15.2 \text{ mg dm}^{-3}$ , flow rate =  $153.0 \text{ cm}^3 \text{ h}^{-1}$ , bed depth = 1.2 cm, and at rt)

**Table 6.8** Concentration ( $\text{mg dm}^{-3}$ ) of cationic and anionic species in wastewater (Sample 3)

Al	Ca	Fe	Cu	Zn	$\text{F}^-$	$\text{SO}_4^{2-}$
13.8	10.5	36.4	9.8	1.9	15.2	754.3

Desorption of loaded fluoride from the bed of Zr(IV)-DOJR is necessary to regenerate the column for further usage. Dilute alkali (0.1 M NaOH) solution which was observed to be effective in the batch system was employed to desorb the adsorbed amount of fluoride from loaded column of Zr(IV)-DOJR as shown in **Fig. 6.15 (b)**. The adsorbed amount of fluoride ( $1.65 \text{ mg g}^{-1}$ ) from the actual plating solution was quantitatively ( $1.61 \text{ mg g}^{-1}$ ) eluted by using 0.1 M NaOH solution. The fluoride concentration in the eluent solution by using  $20 \text{ cm}^3$  of NaOH solution was found to be  $255.76 \text{ mg dm}^{-3}$  which is 17.8 times higher than the initial concentration of fluoride ( $15.2 \text{ mg dm}^{-3}$ ) in real plating solution. The result shows that 98 % of adsorbed fluoride from actual plating solution was successfully eluted from the loaded column of Zr(IV)-DOJR. This indicate that dilute alkali solution was found to be an effective eluting agent for the desorption of adsorbed fluoride from fluoride adsorbed Zr(IV)-DOJR in continuous mode operation.

#### 6.4 CONCLUSIONS

New economically reasonable adsorption gel for fluoride ions were investigated by loading metal ions onto DOJR and was characterized by EDX and IR spectroscopy. The adsorption experiments showed the effectiveness of M-DOJR for the removal of fluoride from water. The maximum adsorption capacities of Zr(IV)-DOJR and Ce(IV)-DOJR for fluoride were observed at pH 4. The Zr(IV)-DOJR investigated in this study is more effective than Al(III)-DOJR and Ce(IV)-DOJR. Adsorption of fluoride by M-DOJR was highly influenced by pH, fluoride concentration, adsorbent amount and contact time. Langmuir type monolayer model precisely explained the equilibrium data with high correlation regression coefficient. The Zr(IV)-DOJR was effectively used for fluoride removal in continuous system. The performance of fix bed column for the adsorption of fluoride at different operation conditions such as pH, influent fluoride concentration, flow rate and bed depth were investigated. Fixed bed column studies using Zr(IV) loaded dried orange juice residue revealed that column performance was significantly affected by bed height, flow rate and initial fluoride concentration. Effectiveness of continuous operations and the advantages of Zr(IV)-DOJR for fluoride ions can be realized from the effective removal of fluoride in a fixed bed columns of Zr(IV)-DOJR from actual plating solution. The nature of increasing breakthrough time with increasing bed depth suggested that larger bed depth would be required to avoid breakthrough. The uses of less chemicals, short and simple synthetic procedure, easy to store and production of small amount of waste water, utilization of DOJR for the removal of fluoride after metal loading could be cost effective and environmental friendly. Thus, it is expected that, Zr(IV) immobilized dried orange juice residue can be one of the alternative candidate for the removal of fluoride from wastewater.

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## Chapter 7

### **Adsorptive Removal of Fluoride from Water by Using Porous Resins Containing Hydrated Oxide of Ce(IV) or Zr(IV) and Comparison with Other Adsorbents Including Metal Loaded Orange Waste**

To this point, we have successfully prepared 14 different kinds of adsorption gels for fluoride removal from water by using orange waste. It was found that biopolymer derived from orange waste loaded with Zr(IV), Ce(IV), La(III), and Al(III) are very much effective for fluoride removal from water. Among them, tetravalent Zr(IV) and Ce(IV) loaded adsorbents were more superior. For this reason, adsorption behaviors of fluoride by two types of commercial resins that contains hydrated oxide of Zr(IV) and Ce(IV) whose commercial names are READF-(PG) and READF-(HG), respectively, have been investigated and their adsorption capacities were compared with all the metal loaded orange waste gels along with other adsorbents reported in the literature in order to suggest the effectiveness and cost fact of investigated adsorbents. The resins were characterized by XRD, EDX and IR spectroscopy. Fluoride adsorption was found to be strongly pH dependent and optimum adsorption on both types of resins was observed at pH 2-4. The isotherm experiments showed Langmuir type monolayer adsorption. The maximum uptake capacity of READF-(HG) and READF-(PG) were evaluated as 2.35 and 2.10 mmol g<sup>-1</sup>.

#### **7.1 INTRODUCTION**

Because, fluoride is consider as a toxic pollutant for human health, different types of commercial resins were synthesized and marketed for its removal from water. Most of the resins for fluoride ions removal were prepared by loading or impregnating some metal ions or their oxide into suitable polymer matrix [1]. The metal ions such as Al(III), Ce(III), La(III), and Zr(IV) ions possess high affinity with fluoride ions, so that these metal ions are of first choice for the preparation of adsorbents selective to fluoride ion [2-4]. In recent years, two different types of porous resins of ethylene vinyl alcohol (EVOH) containing hydrated oxide of Zr(IV) or Ce(IV) inside the pores of this porous polymer have been commercialized by NIHON KAISUI Co. Ltd. for

fluoride removal. Although they have been marketed for fluoride effluents from plants of semiconductors, the smoke desulfurization equipment of coal incineration power plants and smoke washing equipment of municipal incineration plants, the details of their adsorption behaviors have not been investigated. These resins are produced by impregnating a Zr(IV) or Ce(IV) salt solution into the micro pores of EVOH beads, followed by hydrolysis by using an alkaline solution to form a hydrated metal oxide in the pore. In the present work, we investigated the adsorption behaviors of the two types of commercial resins, READF-(PG) and READF-(HG), containing hydrated Zr(IV) and Ce(IV) oxide, respectively, in details.

## 7.2 MATERIAL AND METHODS

### 7.2.1 Adsorbents

The sample of two types of commercial porous resins READF-(PG) containing hydrated Zr(IV) oxide and READF-(HG) containing hydrated Ce(IV) oxide inside their pores were donated by NIHONKAISUI Co. Ltd., Tokyo, Japan. The total content of Zr(IV) and Ce(IV) in the provided samples of READF resins were measured as follows: Fifty milligrams of READF-(PG) and READF-(HG) were completely dissolved in two different conical flasks with 10 cm<sup>3</sup> of an aqua regia solution. The metal concentration in each of the dissolved aquaregia solutions, *i.e.* Zr(IV) content in REAF-(PG) and Ce(IV) content in READF-(HG), were measured using ICP-AES.

### 7.2.2 Batch wise adsorption test

In order to obtain fundamental information about adsorption behavior of both types of READ-F resins, batch wise adsorption tests of fluoride was performed. In each test, 25 mg of adsorbent and 10 cm<sup>3</sup> of a fluoride solution (~10 mg dm<sup>-3</sup>) were mixed and shaken in a thermostated shaker at 150 rpm at 30°C. After 24 h of shaking, the samples were filtered, and the filtrates were analyzed for fluoride ion. The adsorption isotherm of fluoride on REAF-(PG) and REAF-(HG) were examined by varying the concentration of fluoride (0.5 – 8 mmol dm<sup>-3</sup>) at pH 3 to investigate the maximum adsorption capacity of these resins for fluoride at adsorbent-solution ratio of 2.5 g dm<sup>-3</sup> from aqueous solution.



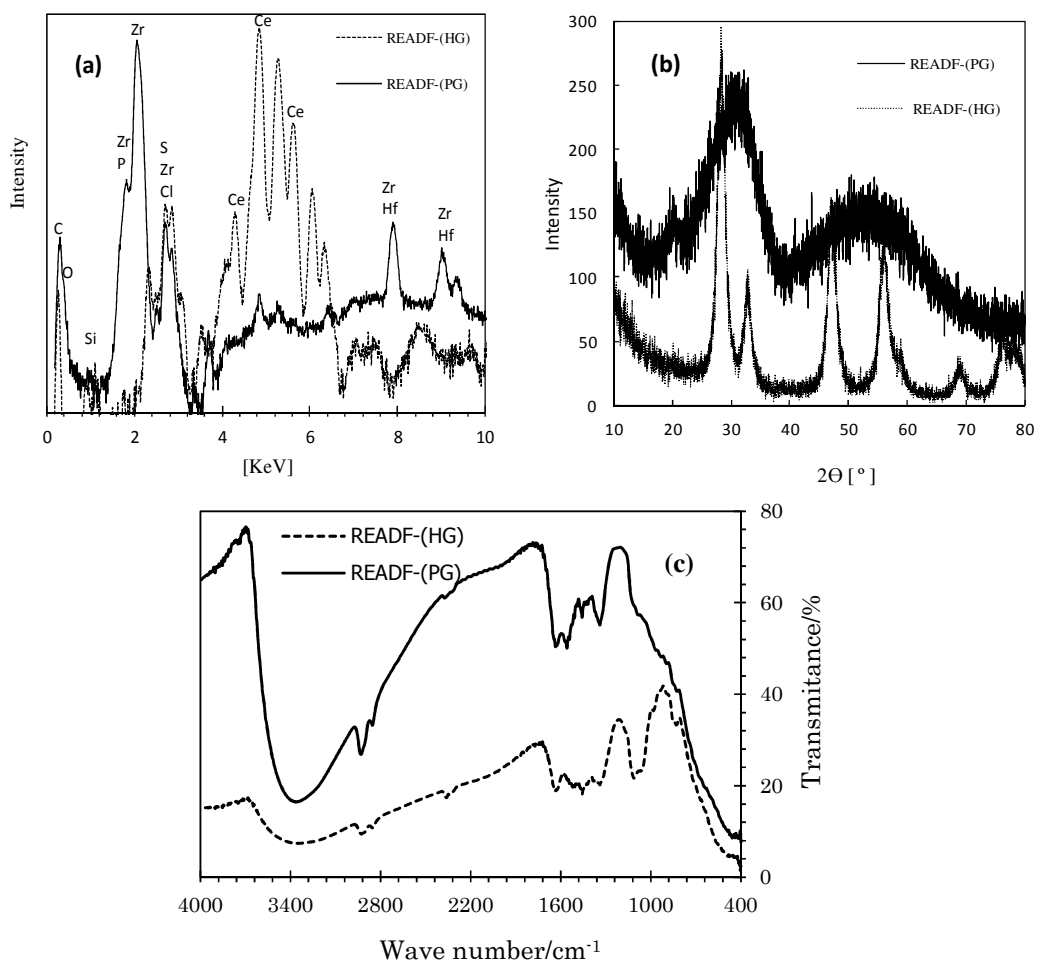
### 7.2.3 Continuous adsorption and elution

A fixed bed column of 20 cm in length and 0.8 cm in diameter packed with 500 mg (wet volume  $0.50 \text{ cm}^3$ ) of READF-(PG) was used for the continuous adsorption/elution test. The column was prewashed with a fluoride free solution overnight at the same pH as the test solution (pH = 3). The fluoride solution ( $35.3 \text{ mg dm}^{-3}$ ) is pumped upward with the help of (Iwaki Model PST 100N) peristaltic pump at the constant flow rate of  $5.3 \text{ cm}^3 \text{ h}^{-1}$ . The flow of the column was continued until the effluent fluoride concentration approached the inlet fluoride concentration. Effluent samples were collected in a regular time interval with the help of (Biorad model 2100) fraction collector to be analyzed by the ion chromatographic system. After complete adsorption, the column was washed with distilled water to remove the unbounded fluoride, and then an elution test was performed using a 0.1 M NaOH solution.

## 7.3 RESULTS AND DISCUSSION

### 7.3.1 Spectral analysis of IR, XRD and EDX

**Figure 7.1 (a)** shows the electron dispersive X-ray spectroscopic analysis of READF-(PG) and READF-(HG) resins. It is clear from these figures that observation of the elemental peak corresponding to cerium in the case of READF-(HG) and zirconium in the case of READF-(PG). This confirms the presence of respective metals in the tested samples. **Figure 7.1 (b)** shows the powder XRD pattern of READF-(HG) and READF-(PG) at  $2\theta$  values ranging from 10–80 degrees. The pattern of READF-(HG) shows intense peaks of Bragg's reflection at  $2\theta$  values of 28, 33, 47, 56, 69 and 76, suggesting the presence of a crystalline form of hydrated cerium oxide, whereas two broad peaks centered at around 18 – 36 and 40 – 66 in READF-(PG) shows the amorphous nature tested sample.



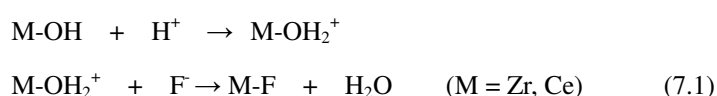
**Fig. 7.1** Spectroscopic characterization of READF-(PG) and READF-(HG) resins (a) EDX- (b) XRD- and (c) FT-IR spectra

**Figure 7.1 (c)** shows the FT-IR spectra of READF-(PG) and REAF-(HG) resins, which shows the intense peak at  $3400 \text{ cm}^{-1}$  which is assigned to the stretching vibration of hydroxyl group of hydrated oxide of Zr(IV) in case of READF-(PG) and Ce(IV) in case of READF-(HG) resin. The peak at  $2888 \text{ cm}^{-1}$  is assigned to C-H stretching vibration. The peak at  $1533 \text{ cm}^{-1}$  is assigned to vibration of  $\text{CH}_2$  group, the peak near  $1300 \text{ cm}^{-1}$  in both resins is assigned to C-O-C stretching vibration. The peak at  $1631 \text{ cm}^{-1}$  corresponds to the stretching vibration of the C-O bond. Because, the vinyl alcohol in EVOH mainly exists as its tautomer acetaldehyde which is attributed to the appearance of C-O stretching vibration in the IR spectra of READF resins.

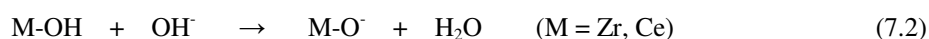
### 7.3.2 Batch wise adsorption test of fluoride

#### 7.3.2.1 Effect of pH

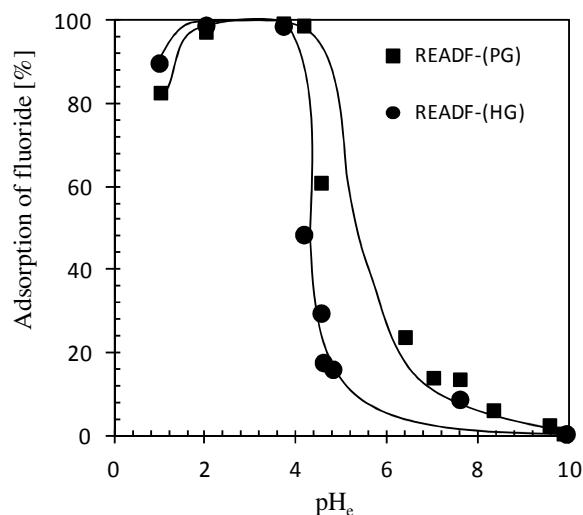
The equilibrium adsorption of fluoride on both types of READF resins over the pH range 1-10 is presented in **Fig. 7.2**. The results reveal that the % adsorption increases with increasing pH at equilibrium pH 1- 2. Maximum sorption is observed at pH 2- 4, and then sorption decreased with a further increase in equilibrium pH for both resins tested. The decrease in fluoride adsorption at high pH can be attributed to the competition of hydroxyl ion for the same adsorption sites. In addition, fluoride is converted into a weakly ionizable hydrofluoric acid at strong acidic conditions, thus some fraction of fluoride is unavailable for adsorption, resulting in the decrease in adsorption at pH 2-1 [5]. The result is similar to the adsorption of fluoride by using various types of metal loaded orange waste gels and some other metal loaded adsorbents [6, 7]. It was found that the pH of the solution after fluoride adsorption increased for both sorbents tested in the low pH region, which is one of the strong evidence of ion exchange reaction mechanism, as will be mentioned later. The mechanism of fluoride adsorption on hydrated metal oxide takes place by the following two steps. At first, protonation of hydrated metal oxide by the consumption of hydrogen ions from an acidic solution takes place, which is followed by adsorption of fluoride with the release of water molecule in the second step as shown below [1].



However, the pH of the solution was decrease after the contact with READ-F resins at high pH region, which can be attributed to the hydrolysis reaction of hydrated oxide as shown in reaction (b).



In addition, the protons released during the hydrolysis reaction consume hydroxyl ions that lead to the lowering of the solution pH after contact with the resin. The repulsion of fluoride anion to the negatively charge  $\text{Zr-O}^-$  or  $\text{Ce-O}^-$  formed after hydrolysis is another reason of reducing the fluoride adsorption efficiency under alkaline conditions.



**Fig. 7.2** Effect of pH for the adsorption of fluoride on READ-F resins (volume of solution = 10 cm<sup>3</sup>, weight of gel = 25 mg, fluoride concentration = ~10 mg dm<sup>-3</sup>, and temperature = 30°C)

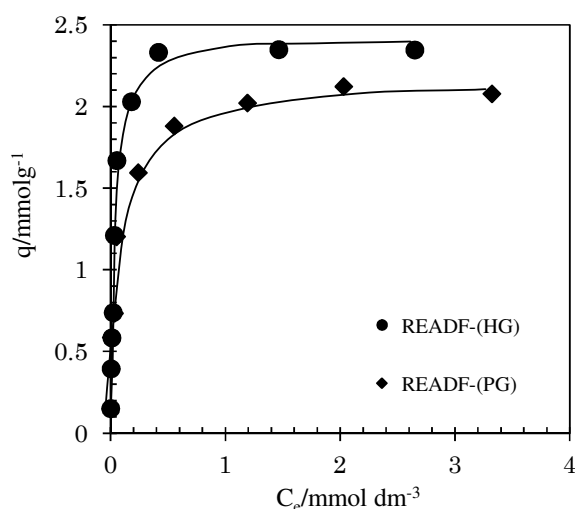
### 7.3.2.2 Adsorption isotherm

**Figure 7.3** shows the sorption isotherms of fluoride on two different types of READF resins. The result shows that the adsorption of fluoride increases with increasing concentration of fluoride and reaches saturation at higher concentration. It was found that the experimental data was in good agreement with the Langmuir isotherm with high correlation, as shown **Table 7.1**. The evaluated values of  $q_{max}$  and  $b$  are also listed in **Table 7.1**. The results show the higher sorption capacity of READF resins that contain hydrous **Ce(IV)** oxide compared to that of the resin containing hydrated **Zr(IV)** oxide.

The observation of high adsorption capacity of fluoride by using READF-(HG) compared that using READF-(PG) can be reasonably attributed to the presence of a larger amount of cerium (3.05 mmol g<sup>-1</sup>) in the sample of READF-(HG) compared to that of zirconium (2.47 mmol g<sup>-1</sup>) in the tested sample of READF-(PG). Although adsorption capacity of both of these READ-F resins for fluoride is higher compared to metal loaded orange waste adsorbents, application of READ-F resins is suffer from serious problems during fluoride adsorption. Because of this, application of READ-F resin appears more complicated which will be discussed in detail in section 7.3.4 in detail.

**Table 7.1** Isotherm parameters for fluoride adsorption on READ-F resins from water

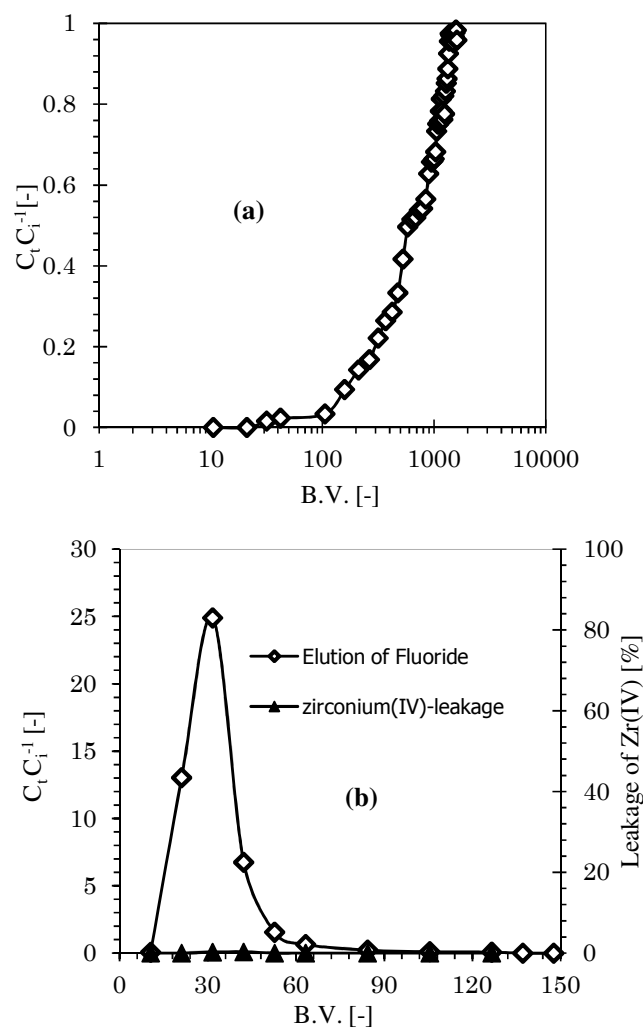
Adsorbents	Langmuir parameters			
	pH	$q_{\max.}/\text{mmol g}^{-1}$	$b/\text{dm}^3 \text{mmol}^{-1}$	$R^2$
READF-(PG)	3	2.10	56	0.99
READF-(HG)	3	2.35	157	0.99

**Fig. 7.3** Adsorption isotherm of fluoride on two different READ-F resins (volume of fluoride solution = 10 cm<sup>3</sup>, weight of gel = 25 mg, pH = 3, and, temperature = 30°C)

### 7.3.3 Dynamic adsorption followed by elution of fluoride in a fixed bed of READF-(PG)

**Figure 7.4 (a)** shows the breakthrough profile of fluoride from the column packed with READF-(PG) resin shown as a semi-log plot to stress the breakthrough behavior at the initial stage. It is observed from this figure that the breakthrough of fluoride started from 21 B.V., but complete saturation of the column occurs at 1265 B.V. The effective adsorption capacity of READF-(PG) in the fixed bed system under the present conditions was evaluated as 0.92 mmol g<sup>-1</sup>, which is 49% of the sorption capacity calculated from the batch wise test. The evaluated lower value of the adsorption capacity of READF-(PG) in a continuous system compared to that in the batch system can be reasonably attributed to the fact that the space velocity of the fluoride solution is not enough for equilibration. **Figure 7.4 (b)** shows the elution profile of fluoride with a 0.1 M NaOH solution

from the column after complete saturation of the bed. It is seen from this figure that fluoride was effectively eluted and concentrated to high concentrations as much as 24.8 times higher than that of the feed solution. The amount of eluted fluoride from the packed column was evaluated as  $0.89 \text{ mmol F g}^{-1}$ . The adsorbed fluoride can be quantitatively eluted at a high concentration without any leakage of loaded **Zr(IV)** ion.



**Fig. 7.4** Continuous adsorption followed by elution of fluoride in a fixed bed column of READF-(PG) resin (a) breakthrough profile, and (b) elution profile (weight of gel =  $500 \text{ mg}$ , flow rate =  $5.3 \text{ cm}^3 \text{ h}^{-1}$ , pH = 3, wet volume of resin =  $0.5 \text{ cm}^3$ , feed solution =  $1.85 \text{ mmol dm}^{-3}$ , and eluent =  $0.1 \text{ M NaOH}$ )

### 7.3.4 Comparative study of adsorption capacities

Most of the adsorbent reported for fluoride are partially or totally contains some metal ions or their oxide. The metal ions or metal oxides are either impregnated into the micro-pores of porous polymer or loaded onto the polymer containing suitable functional groups [1, 4]. The comparative study of maximum adsorption capacities of different types of metal loaded orange waste gels investigated in this study and some other adsorbents reported in the relevant literatures along with READF resins is presented in **Table 7.2**.

**Table 7.2** Comparison of adsorption capacities of fluoride ions by using metal loaded SOJR and DOJR together with those of some other adsorbent reported in literatures

Adsorbents	pH	$q_{\max.}$ $\mu\text{mol g}^{-1}$	Temp. $^{\circ}\text{C}$	Ref.
READF-(PG)	3	2.10	30	This chapter
READF-(HG)	3	2.35	30	This chapter
Sn(IV)-SOJR	3	1.18	30	Chapter 2
Ti(IV)-SOJR	3	0.93	30	Chapter 2
Al(III)-SOJR	6	1.03	30	Chapter 2
Fe(III)-SOJR	4	0.88	30	Chapter 2
Zr(IV)-SOJR	4	1.74	30	Chapter 3
La(III)-SOJR	4	1.06	30	Chapter 4
Sc(III)-SOJR	4	0.60	30	Chapter 4
Sm(III)-SOJR	5	1.22	30	Chapter 4
Ho(III)-SOJR	5	0.93	30	Chapter 4
Ce(III)-SOJR	4	0.91	30	Chapter 5
Ce(IV)-SOJR	4	1.53	30	Chapter 5
Zr(IV)-DOJR	4	1.43	30	Chapter 6
Ce(IV)-DOJR	4	1.32	30	Chapter 6
Zr-impregnated cashew nut	3	0.09	30	[2]
La-loaded 200CT resin	6	1.34		[4]

Indian FR 10	7	0.068	30	[7]
Ceralite IRA 400	7	0.078	30	[7]
La-loaded CL gelatin	5-7	1.12	25	[8]
Nd- modified chitosan	7	1.17	30	[9]
Fe-loaded cotton	4	0.97	25	[10]
Protonated chitosan	7	0.38	30	[11]
Activated alumina	5-6	0.86	30	[12]
AFB-Pr resin	5	0.026	30	[13]
La-impregnated alumina	5.7-8	0.35	R.T.	[14]
Spirogyra species IO1	7	0.05	30	[15]
Waste mud	5	0.22	20	[16]
Nano aluminium hydroxide	5.2	0.17	25	[17]
Magnezia	10	0.11	R.T.	[18]
Waste carbon slury	7.5	0.23	25	[19]
Montmorilonite	6	0.01	25	[20]
Metal loaded zeolit	-	0.1-0.21	30	[21]

The result shows that, the native adsorbent such as spirogyra IOI, protonated chitosan, waste carbon slury, waste mud without any chemical modification possesses low adsorption capacity. However, the result demonstrate that adsorbent that contains multivalent metal ions or their oxide such as metal loaded orange waste, READF resin, Nd-modified chitosan, nano aluminium hydroxide and La-loaded 200CT resin, have high adsorption capacities. In addition, some commercial resins such as Indian FR 10, Ceralite IRA 400 and AFB resins [7, 13] which does not contains multivalent metal ions also shows low adsorption capacity for fluoride which indicate that presence of high valent mental ions improved the adsorption efficiency. Among the adsorbent compared (**Table 7.2**), Zr(IV) loaded orange waste containing ligand exchange type hydroxyl ion posses adsorption capacity for fluoride much higher than ion exchange resin containing sulphonic acid or exchangeable chloride ion [7, 13] and other adsorbents reported in the literatures except READF resins.



Although both types of READ-F resins showed maximum adsorption capacity of fluoride little bit higher than Zr(IV)-loaded orange waste adsorbents *i.e* Zr-SOJR and Zr-DOJR. However, READ-F resins are the porous resins of ethylene vinyl alcohol (EVOH) that contains hydrated oxide of Zr(IV) or Ce(IV) inside the micropores. During the adsorption of fluoride, some of the suspended particles in polluted water or waste water also enter into the micropores and caused the clogging of micropores of the resins. So that the entire active sites of the resin for fluoride ion removal were blocked or destroyed. The resins can not be use again and again for fluoride removal which is the main limitation of READ-F resins. In addition, for the commercial production of READF resin, EVOH polymer is required as a raw material for impregnation reaction of Zr(IV) or Ce(IV). The polymer (EVOH) synthesis required complicated procedure and use expensive chemical which ultimately increases the production cost of adsorbent. Because of such a serious drawbacks or disadvantages of READ-F resins, uses of READ-F resins now become more complicated and non economic.

On the other hand, the preparation of metal loaded orange waste adsorbents investigated in this study is very simple, environmental friendly and economical because the feed material is an orange waste itself and uses fewer chemicals. The metal loaded orange waste especially Zr-SOJR or Zr-DOJR showed high adsorption capacity and high selectivity towards fluoride. The adsorbent can be regenerated by simple method of alkali treatment and can be used for several cycles without any reduction of adsorption efficiency. Therefore, the utilization of orange waste for the preparation of a more sophisticated adsorbent for fluoride appears more promising for environmental remediation.

#### 7.4 CONCLUSIONS

Adsorption studies of two different types of READF resins have been investigated. The maximum adsorption of fluoride was observed at around pH 2 - 4. The equilibrium data obtained in this study was closely fitted with the Langmuir isotherm, which indicated that the monolayer adsorption was involved in the process of fluoride removal. The maximum uptake capacities of fluoride on READF-(PG) and READF-(HG) were evaluated as 2.10 and 2.35 mmol of F g<sup>-1</sup> of sorbent, respectively. A study of column adsorption followed by elution in a packed column suggests that READF-(PG) resins is one of the promising commercial sorbent. The comparative study of sorption capacities of various commercial and other adsorbent reported in the literature shows that metal loaded orange waste adsorbents investigated in our study shows very good adsorption capacities suggesting that metal loaded orange waste can be an alternative to the expensive commercial adsorbents like READ-F resins for the treatment of trace concentration of fluoride from aqueous solution.

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## Chapter 8

### Concluding Remarks

Although small amount of fluoride is required for improving dental caries, pollution of water with fluoride is the main cause of fluoride toxicity and possesses the various types of health hazards in human beings. In the present investigation, 14 different types of metal loaded orange waste adsorbents were successfully prepared from orange juice residue and cattle food of orange juice residue by simple chemical modification. Prior to the metal loading reaction, orange juice residue was converted into SOJR to give M-SOJR whereas dried orange juice residue (DOJR) was directly utilized for loading reaction after water washing. Analysis of total organic carbon (TOC), FT-IR, EDX, TG-DTA, chemical analysis, along with a series of batch experiments were utilized to characterized the adsorbents and investigate the effects of the major parameters, including contact time, pH, fluoride concentration, and adsorbent dosages for the fluoride removal. Moreover, series of adsorption experiments in a packed column of Zr(IV) loaded dried orange juice residue (DOJR) were executed to investigate the effects of different experimental parameters such as flow rate, pH, fluoride concentration, and bed depth on the removal process. Based on the results of these experiments,, following conclusions were drawn :

- a. Fabrication of novel adsorbent for high valent metal ions and rare earth metal ions was performed from orange juice residue by saponification reaction with lime water. During saponification, methyl ester part of orange pectin was converted into calcium salt of orange pectic acid, which was abbreviated to be saponified orange juice residue (SOJR). Creation of active sites for fluoride on SOJR or DOJR was achieved by loading high valent metal ions such as Al(III), Fe(III), Sc(III), Sm(III), La(III), Ho(III), Ce(III), Ce(IV), Ti(IV), V(IV), Sn(IV), and Zr(IV) ions onto their carboxyl framework.
- b. The participation of carboxyl functional group of SOJR or DOJR was confirmed by infrared

spectroscopic measurement before and after metal loading reaction. Direct evidence of loading reaction was achieved from the analysis of EDX spectra of samples.

- c. The increase trend of metal ion adsorption with increasing equilibrium pH of the solution, and reduction of calcium ion peaks in EDX spectra of SOJR or DOJR from their respective metal loaded samples after loading reaction, concluded to be cation exchange reaction with the substitution of calcium ions by loaded metal ions during loading reaction.
- d. The removal efficiency of fluoride by metal loaded orange waste adsorbents strongly dependent on solution pH and types of metal ions loaded. The optimum adsorption of fluoride was observed at around pH 6 in the case of Al loaded orange waste sample whereas in the case of other metal loaded adsorbents, it was found to occur at around 2-5.
- e. Adsorption kinetics of fluoride using M-SOJR and M-DOJR showed fast adsorption.
- f. Adsorption capacity of M-SOJR increase with increasing oxidation state of loaded metal ions. Langmuir isotherm model precisely described the adsorption data for the adsorption of fluoride by metal loaded adsorbents, which indicated that monolayer adsorption of fluoride, was involved in the process of fluoride adsorption.
- g. To achieve maximum permissible level MPL of fluoride ( $1.5 \text{ mg dm}^{-3}$  WHO) in the treated water, the solid liquid ratio of M-SOJR or M-DOJR needed to be increased. The small amount of Zr-DOJR, Zr-SOJR, La-SOJR, and Al-SOJR successfully lowers the fluoride concentration down to the accepted environmental standard ( $0.8 \text{ mg dm}^{-3}$ ) in Japan. Complete removal of fluoride from waste plating solution was achieved regardless of the presence of other cationic and anionic species by using Zr(IV) loaded adsorbents.
- h. The presence of high concentration of coexisting carbonate, sulphate, nitrate, chloride, sodium and calcium ions had negligible influence during fluoride adsorption by Zr(IV) loaded adsorbents. However, in the case of Al(III) loaded gel, presence of sulphate and bicarbonate retard fluoride adsorption capacity in small extent which is concluded that Zr(IV) loaded orange waste gels *i.e.* Zr-SOJR and Zr-DOJR are more selective towards fluoride ion.
- i. Fluoride containing waste water produced from plating factories can be successfully treated by using Zr-DOJR both in batch and packed column.
- j. Metal loaded adsorbents were easily regenerated by washing with dilute alkali solution. High stability of Zr-SOJR and Zr-DOJR during fluoride adsorption more than 9 cycles without deteriorating loaded Zr(IV) ions, suggest that zirconium ions were effectively immobilized.

- k.** At high concentration of fluoride at acidic pH, there was the leakage of loaded metal ions which was observed to be negligible at lower concentration of fluoride. Leakage test of loaded Al(III), La(III), Sm(III) and Zr(IV) from metal loaded adsorbents indicate that metal loaded adsorbent could be used for the treatment of water polluted with trace concentration of fluoride.
- l.** Thermodynamic study shows that positive value of enthalpy change ( $\Delta H$ ) and negative value of Gibbs free energy change ( $\Delta G$ ) of a system which elucidated that adsorption process is endothermic and spontaneous in nature.
- m.** The performance of fixed bed column of Zr-DOJR for the adsorption of fluoride at different operation conditions such as pH, influent fluoride concentration, flow rate and bed depth showed effective adsorption of fluoride also in continuous system.

It is concluded from the results of above studies that, Al(III), La(III), Sm(III), Zr(IV) and Ce(IV) loaded orange waste adsorbents investigated in this study have high adsorption potential than other Ho(III), Sc(III), Ce(III), Fe(III), Ti(IV), V(IV), and Sn(IV) loaded adsorbents. The Al(III) loaded adsorbents are better to remove fluoride around neutral pH thus can be a better alternative for the treatment of drinking water containing trace amount of fluoride ions. Other La(III), Sm(III), Zr(IV) and Ce(IV) loaded orange waste adsorbents remove fluoride at around pH 3-5. Among them, Zr(IV) loaded orange gels possess very high adsorption capacity, high selectivity with fluoride and durable which can be a better candidates for the treatment of water polluted with fluoride ion. The metal loaded adsorbent showed better performance only for the treatment of trace concentration of fluoride, suggesting that adsorbent can not be used for the treatment of wastewater containing high concentration of fluoride which is the main limitation of these adsorbents.

## **APPENDIX**



### List of published papers:

1. **Hari Paudyal**, Bimala Pangeni, Katsutoshi Inoue, Hidetaka Kawakita, Keisuke Ohto, Hiroyuki Harada, Shafiq Alam, Adsorptive removal of fluoride from aqueous solution by using orange waste loaded with multivalent metal ions, *J. Hazard. Mater.*, **192** (2011) 676-682.
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### Patent

1. Keisuke Ohto, Hidetaka Kawakita, Katsutoshi Inoue, **Hari Paudyal**, Removal method of fluoride (フッ化物イオンの除去方法), *Japanese patent*, **Accepted 2012-6-14**.

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1. **Hari Paudyal**, Bimala Pangeni, Katsutoshi Inoue, Hidetaka Kawakita, Keisuke Ohto, Hiroyuki Harada, Kedar Nath Ghimire, Shafiq Alam, Novel utilization of orange juice residue for the removal of trace concentration of fluoride ion from aqueous solution (will be submitted soon).
2. **Hari Paudyal**, Bimala Pangeni, Katsutoshi Inoue, Hidetaka Kawakita, Keisuke Ohto, Shafiq Alam, Continuous adsorption of fluoride by using fixed bed column of zirconium(IV) loaded dried orange juice residue (DOJR) from aqueous solution (will be submitted soon).

### **Participation at different scientific forum:**

- 1. Hari Paudyal**, Katsutoshi Inoue, Miyuki Matsueda, Ryosuke Suzuki, Biplob Kumar Biswas, Hidetaka Kawakita, Keisuke Ohto, Adsorption behavior of Zr(IV)-loaded orange waste gel for fluoride from aqueous solution, *Water and Environment Technology Conference 2010 organized by Japan Society on Water Environment*, Yokohama National University, (2010) June 25-26, (won **WET-2010 best presentation award**).
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