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Adsorptive Removal of Fluoride onto Different Waste Materials: Orange Juice Residue, Waste Seaweed, and Spent Cation-Exchange Resin

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Abstract

To effectively use waste materials in developing a sustainable society, adsorbents for removing trace or low concentrations of fluoride, which is difficult to be removed by conventional techniques, were prepared from three waste materials: orange juice residue, waste sea weed, and spent cation exchange resin. These adsorbents were loaded with tri- or tetravalent metal ions such as iron(III) and zirconium(IV), of which zirconium(IV) was found to be most suitable as the loaded metal ion. From the pH effect on adsorption, the adsorption mechanism was inferred, and adsorption and desorption was found to be controlled by changing pH values. The maximum adsorption capacities on zirconium(IV)-loaded orange juice residue, waste sea weed, and spent cation exchange resin were evaluated as 33.1, 18.1, and 37.6 mg/g, respectively, which were higher than those of most other adsorbents reported in literatures. They exhibited high selectivity for fluoride over other anionic species and high durability. Tests to remove trace concentrations of fluoride from actual waste plating solutions revealed that the concentration could be reduced below the acceptable level using small amounts of these adsorbents, i.e., it was reduced lower than 1.5 mg/dm³ (WHO standard) by adding 1 g of the adsorbents into 1 dm³ test solution.

Keywords: adsorptive removal of fluoride, waste materials, orange juice residue, waste seaweed, spent cation-exchange resin, zirconium(IV)-loaded adsorbents

1. Introduction

Fluoride is contained in effluents from various industries, such as plating, productions of silicon semiconductors and solar panels, nuclear fuels, and phosphoric acid from phosphate rocks, as well as the refining of niobium and tantalum. The conventional technique for removing fluoride from such effluents is by precipitation as calcium fluoride by adding calcium, such as in the form of lime; however, because of the low solubility product of calcium fluoride

($K_{sp} = 3.9 \times 10^{-11}$ (e.g., see [1])), it is theoretically difficult to lower the concentration to less than 8 mg dm^{-3} and practically difficult to achieve less than 10 mg dm^{-3} . The maximum acceptable limit of fluoride in drinking water is 1.5 mg dm^{-3} (e.g., see [2]). Consequently, some additional treatment is necessary to meet the regulation for fluoride before discharging industrial waste solutions into the environment. Adsorption techniques, including ion-exchange, are most suitable to remove such trace concentrations of contaminants in water. According to the well-known Hoffmeister's selectivity series of anion-exchange [3], the selectivity of usual anion-exchange resins for fluoride over other anionic species, such as sulfate and chloride (which usually coexist together with fluoride), is low, so it is difficult to selectively remove trace concentration of fluoride from actual solutions using usual anion-exchange resins. It has therefore been proposed to use cation-exchange resins loaded with high-valency metal ions, such as tri- and tetravalent metal ions [4]. **Figure 1** shows, as an example, the mechanism of adsorption of arsenate on a sulfonic acid-type cation-exchange resin loaded with trivalent ferric ion. In this case, all three positive charges of the ferric ion cannot be neutralized only by the sulfonic acid functional groups ($-\text{SO}_3^-$) due to strong steric hindrance of the cross-linked polymer matrix; one or two positive charges are neutralized by anionic species present in aqueous solution, such as hydroxyl ions, which are substituted by the anionic species in question, such as arsenate or fluoride anions. Consequently, the adsorption and desorption of these anionic species are controlled by the pH values of the aqueous solution.

However, ion-exchange resins, which are highly porous materials, suffer from some drawbacks. One disadvantage is clogging of micropores of the resins by fine particles present in actual solutions, making the smooth operation in packed columns difficult; another issue is cracking of the resin, caused by numerous cycles of fluctuations in pH and solute concentrations over long periods of operation, like weathering of rocks. In such cases, the resins are wasted.

In our research, we attempted to develop an inexpensive removal technique for fluoride that is free from the above-mentioned troubles by using waste materials. In this work, biomass wastes such as orange juice residue [5, 6] and waste seaweeds [7] and spent cation-exchange resins [8] were employed. This study also aimed to find effective uses of waste materials to support the sustainable development of near-future society.

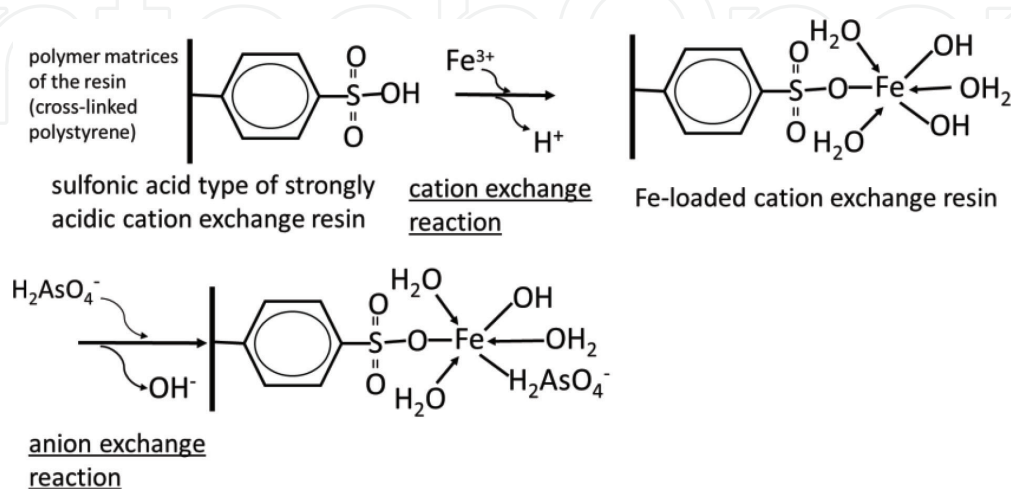


Figure 1.

Mechanism of adsorption of anionic species on cation-exchange resins loaded with high-valency metal ions (example of adsorption of arsenate ion on sulfonic acid type of strongly acidic cation-exchange resin loaded with ferric ion).

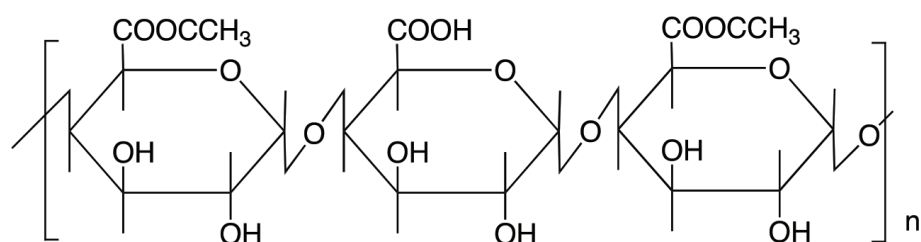
2. Preparation of adsorbents for fluoride removal

2.1 Preparation of adsorbents from orange juice residue

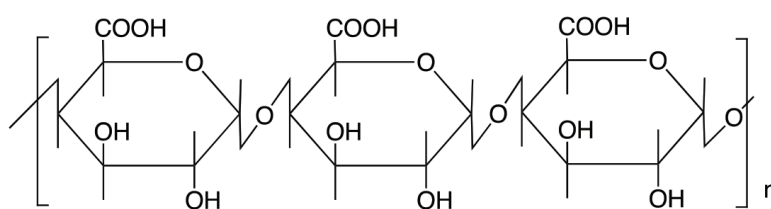
Orange juice is produced from whole oranges by mechanical peeling followed by juicing processes. Approximately, half of each orange is left as orange juice residue, abbreviated as OJR hereafter, which consists of thick outer rind, thin inner peel, seeds, and calyces. Currently, OJR is used as cattle feed and fertilizer in Japan. Its main components are polysaccharides, such as cellulose and pectin, partly methyl-esterified pectic acid, the chemical structures of which are shown in **Figure 2**, together with alginic acid, which is mentioned in Section 2.2.

To prepare the adsorption gel and improve its adsorption capacity for metal ions, OJR was treated with calcium hydroxide to increase the content of carboxylic acid groups, which are the adsorption sites for cationic metal ions. Saponification of the methyl-ester parts of pectin was carried out according to the reaction shown in **Figure 3** [5].

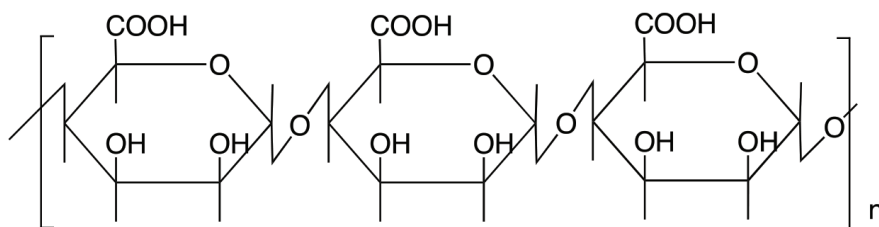
For example, about 100 g OJR obtained just after juicing, kindly donated by JA Saga Beverage Co. Ltd., was added to a juicer with 8 g calcium hydroxide, and the sample was pulverized. The resulting mixture was transferred to a beaker, along with a large volume of water, and the mixture was stirred for 24 h at 200 rpm and room temperature to facilitate the saponification reaction. The initial pH of the mixture was maintained at around 12.5 by adding sodium hydroxide solution. After decantation, the mixture was repeatedly washed using water and decanted until



pectin



pectic acid



alginic acid

Figure 2.
Chemical structures of pectin, pectic acid, and alginic acid.

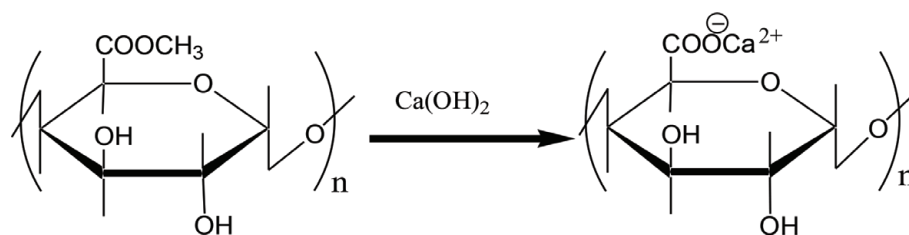


Figure 3.
Saponification of methyl-ester parts of pectin with calcium hydroxide.

it reached neutral pH. In this process, water washing is important because OJR contains citric acid, which functions as a water-soluble chelating agent, impeding adsorption of metal ions or eluting the loaded metal ions. Finally, the mixture was filtered to obtain a wet gel, which was dried in a convection oven for about 48 h at 70°C to obtain dry gel. The prepared dry gel is referred to as saponified OJR gel (SOJR gel). The specific surface area of this gel was measured as 7.25 m² g⁻¹. **Figure 4** shows the outline of the preparation route of SOJR gel and metal-loaded SOJR gel (zirconium(IV)-loaded SOJR gel, in this case), which will be mentioned later.

Figure 5 shows an image of scanning electron microscope of thus prepared SOJR gel. As seen from this figure, SOJR gel is not a porous material.

2.2 Preparation of adsorbents from waste seaweeds

In recent years, big cities adjacent to seas in Japan have been suffering from pollution of their sea sides by waste seaweeds, *Ulva japonica* in particular, caused by their overgrowth due to the eutrophication of the seas around these cities. Large amount of these seaweeds decay on beaches in summer and generating stench; consequently, the treatment of the seaweed wastes has become a serious environmental problem for municipalities of these coastal areas. The development of effective uses of these waste seaweeds is strongly required in Japan. The *Ulva* species of seaweed contains a high content of polysaccharides, including alginic acid (15–65%), lignin

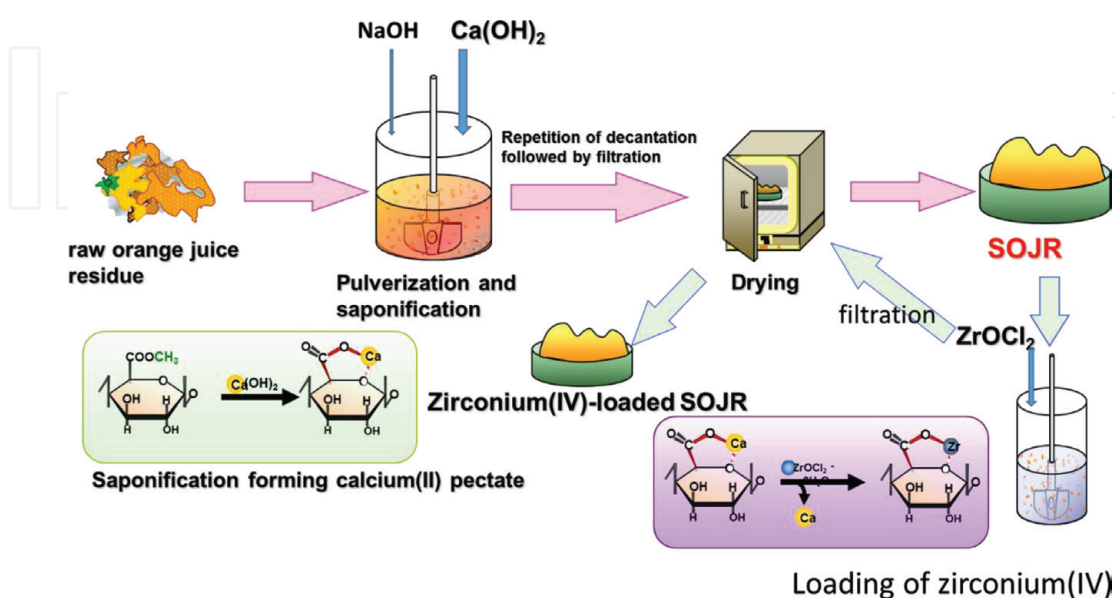


Figure 4.
Preparation route of adsorption gels from OJR.

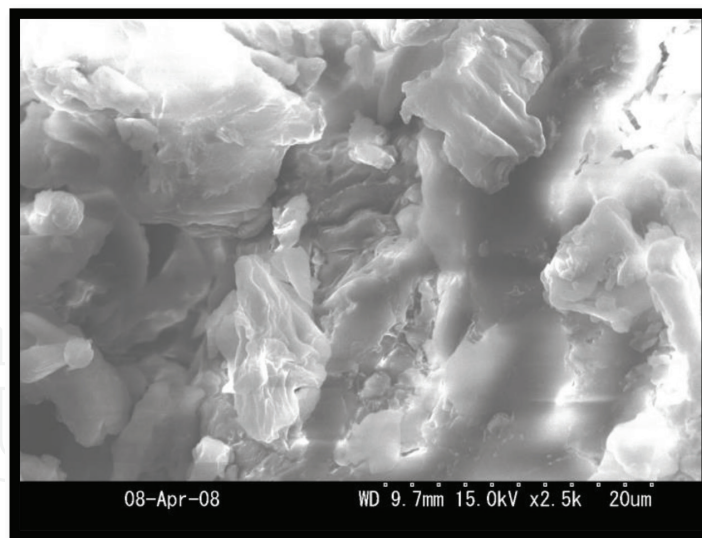


Figure 5.
Scanning electron microscope image of SOJR gel.

(1–3%), protein (6–15%), lipid (1–4%), other amino acids, minerals, and water-soluble organics [9]. Alginic acid presents as calcium alginate with an egg-box structure.

In the present work [7], a sample of *Ulva japonica* collected at Wajiro coast in Fukuoka city, Japan, was washed several times with tap water followed by distilled water to remove impurities. It was pulverized after drying in a convection oven at 70°C for 24 h and sieved to a particle size of <100 µm. The material was then cross-linked with calcium chloride to lower its aqueous solubility. The cross-linked product was washed several times with distilled water and dried in a convection oven at 70°C. Thus, prepared waste seaweed gel is termed as cross-linked seaweed and abbreviated as CSW, hereafter. Similar to the case of SOJR gel, mentioned in Section 2.1, high-valency metal ions, such as zirconium(IV), were loaded on CSW to develop adsorption sites for fluoride, as shown in **Figure 6**.

2.3 Preparation of adsorbents from spent cation-exchange resin

Ion-exchange resins are extensively used in a variety of field, such as water softening, wastewater treatment, precious metal recovery, food industries, and

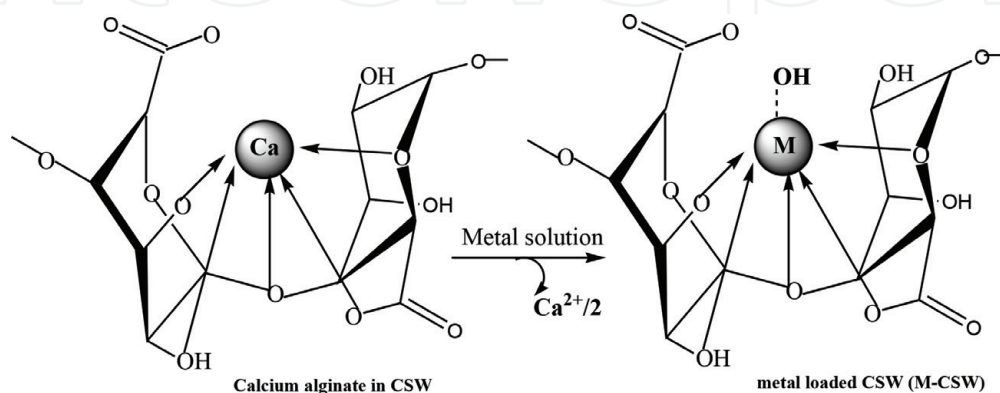


Figure 6.
Preparation of metal-loaded cross-linked seaweed (CSW) gel for fluoride removal [$M = \text{Zr(IV)}$, La(III)].

catalytic processes. Although ion-exchange resins can be regenerated numerous times, they gradually deteriorate owing to the generation of many cracks, which impede smooth column operation and become unusable after many cycles of adsorption followed by elution as mentioned earlier. Tons of spent ion-exchange resins are discarded every year all over the world. Although they are unsuitable for column operation, their functional groups are still active; however, ideas for effective reutilization of such spent ion-exchange resins have not been proposed to date.

In our study [8], we attempted to effectively use such spent ion-exchange resins by pulverizing them into fine powders for use in batch operation together with a coagulating agent, that is, by means of the combined processes of adsorption and coagulation. A sample of spent cation-exchange resin containing sulfonic acid functional groups was pulverized into fine powders and converted to an anion exchanger by loading Zr(IV) ions for fluoride ion removal. The feasibility of using spent resin powder after loading Zr(IV) as ligand exchange-type material for fluoride adsorption was tested in combination with a coagulating agent in a batch system.

A sample of spent strongly acidic cation-exchange resin, MUROMAC MBX8-WH, which had been employed for the production of ion-exchange water, was kindly supplied by Muromachi Chemical Co. Ltd., Omuta, Japan. The polymer matrix of this resin is polystyrene cross-linked by divinylbenzene and it contained functional groups of sulfonic acid. The sample was pulverized into a fine powder, the average diameter of which was less than 20 μm . Thus, prepared resin powder is abbreviated as SRP hereafter. Because of the presence of an exchangeable hydrogen ion in the sulfonic acid group, waste resin powder can effectively adsorb cationic species of metal ions, such as Cu(II), Cd(II), Fe(III), La(III), and Zr(IV), whereas it has low affinity toward anionic species like fluoride ion. Similar to the cases of SOJR and CSW, the adsorption sites for fluoride anion were developed by loading Zr(IV) ion onto the SRP. Here, Zr(IV) was loaded by replacing the hydrogen ion from sulfonic acid functional groups of SRP by the cation-exchange mechanism as shown in **Figure 7**. The material obtained in this way is termed Zr(IV)-loaded spent resin powder and abbreviated as Zr-SRP hereafter.

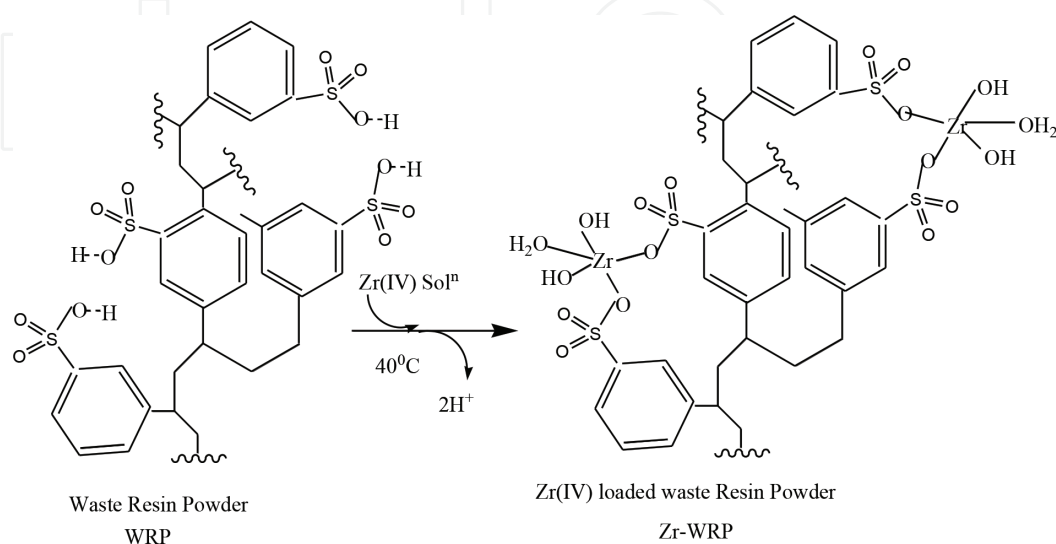


Figure 7.

Development of active sites for fluoride onto spent resin powder (SRP) containing sulfonic acid functional group via Zr(IV) loading.

3. Adsorption behavior of fluoride on saponified orange juice residue gels loaded with various high-valency metal ions

Figure 8 shows the effect of equilibrium pH on the adsorption of fluoride on SOJR gels loaded with various high-valency metal ions. It is apparent that pH greatly influenced the adsorption in the presence of the different metal ions, although the adsorption decreases with increasing pH, regardless of the loaded metal ion. Of the metal ions tested, Zr(IV) exhibits the most effective adsorption, at low pH in particular. The decrease in adsorption at high pH is attributed to the effect of hydroxyl ions, which compete with fluoride ion for adsorption sites on SOJR gel, as depicted in **Figure 9** for the case of Zr(IV)-loaded SOJR gel.

Also from this figure, it is apparent that the adsorption and desorption of fluoride can be easily controlled by changing pH.

Figure 10 shows the adsorption isotherms of fluoride, which is the relationship between the amount of adsorbed fluoride (q) and the fluoride concentration (C_e) in the aqueous solution at equilibrium, on SOJR gels loaded with various high-valency metal ions at 30°C. It is evident that SOJR gel loaded with Zr(IV) exhibited the highest adsorption capacity for fluoride. Consequently, we used Zr(IV)-loaded adsorbent in subsequent work.

Figure 11 shows the effect of coexisting species on the adsorption of fluoride. Although sulfate most effectively interferes with the adsorption of fluoride, it is only less than 2%; consequently, the effect of coexisting species was practically negligible, that is, Zr(IV)-loaded SOJR gel exhibited high selectivity to fluoride over coexisting species. Similar was observed also in the adsorption on Zr(IV)-loaded other adsorbents.

Figure 12 shows time variation in the adsorption of fluoride on Zr(IV)-loaded SOJR gel at various temperatures. Equilibrium was attained within a short contact time (shorter than 100 min), indicating rapid adsorption, regardless of temperature.

Figure 13 shows the effect of initial pH on the elution of fluoride adsorbed on Zr(IV)-loaded SOJR gel. The adsorbed fluoride was quantitatively eluted at pH higher than 12.

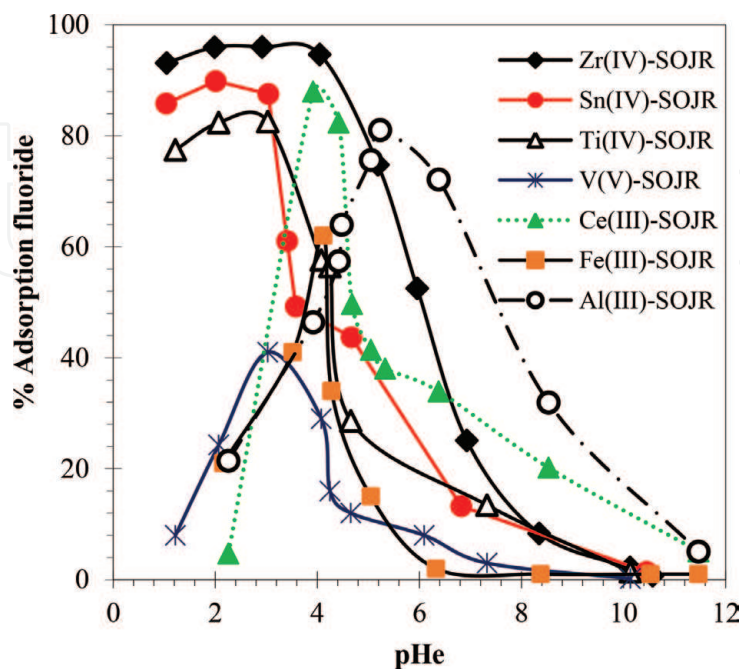


Figure 8.
Effect of equilibrium pH (pHe) on the adsorption of fluoride on saponified orange juice residue (SOJR) gels loaded with various high-valency metal ions.

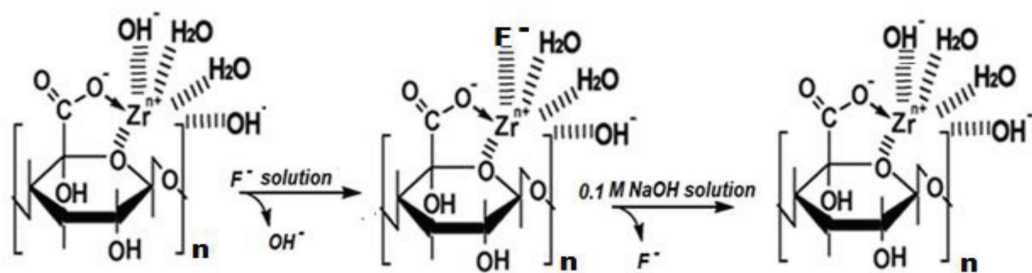


Figure 9.
Adsorption and desorption mechanism of fluoride on Zr(IV)-loaded saponified orange juice residue (SOJR) gels.

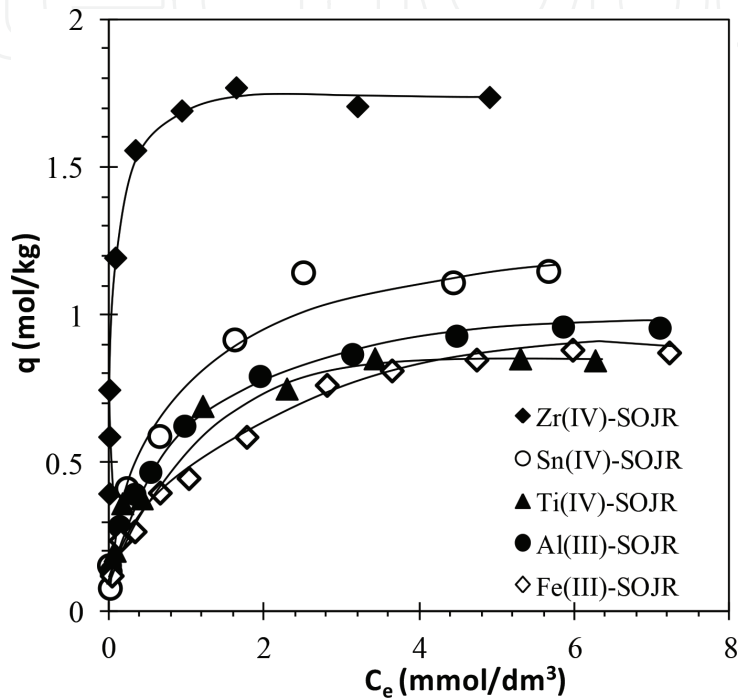


Figure 10.
Adsorption isotherms of fluoride on saponified orange juice residue (SOJR) gels loaded with various high-valency metal ions at 30°C.

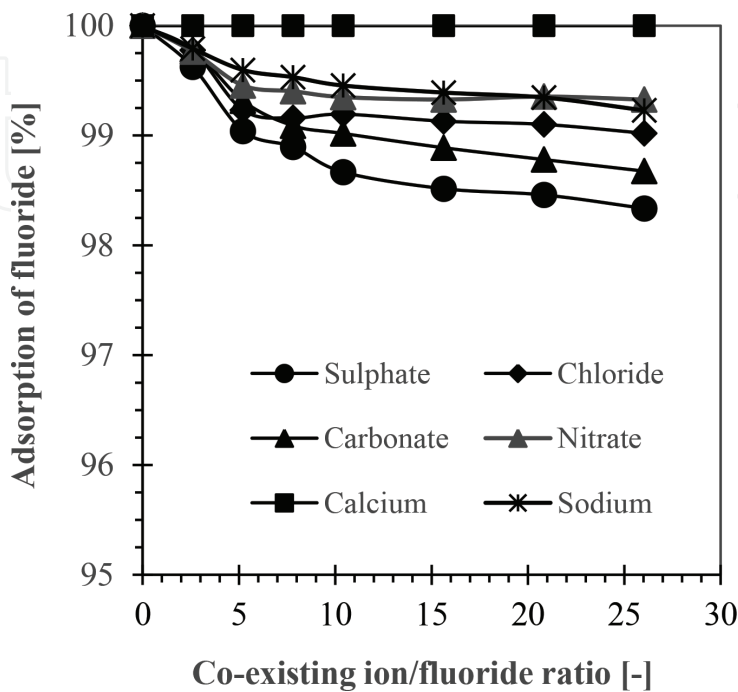


Figure 11.
Effect of coexisting species in the aqueous solution on adsorption of fluoride on Zr(IV)-loaded saponified orange juice residue (SOJR) gel.

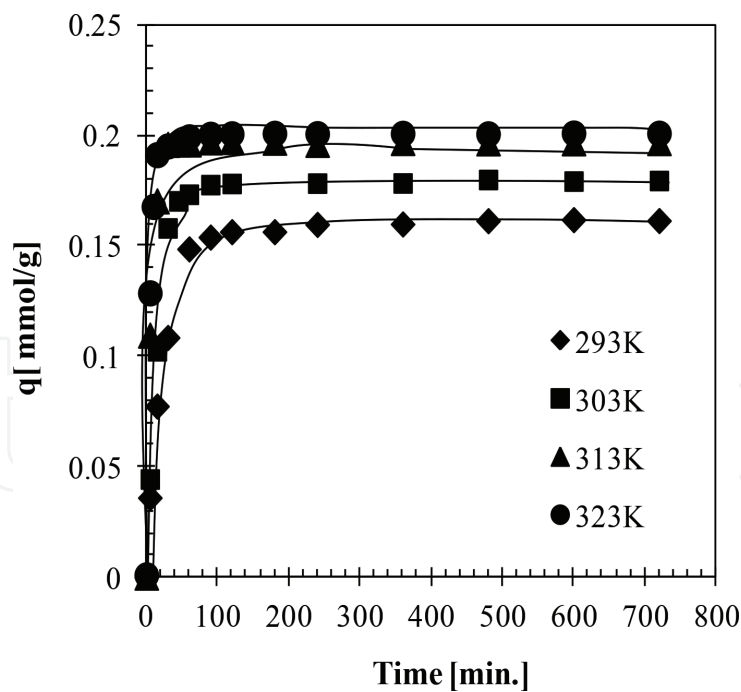


Figure 12.
Time variation in the amount of adsorption of fluoride (q) on Zr(IV)-loaded saponified orange juice residue (SOJR) gel at various temperatures.

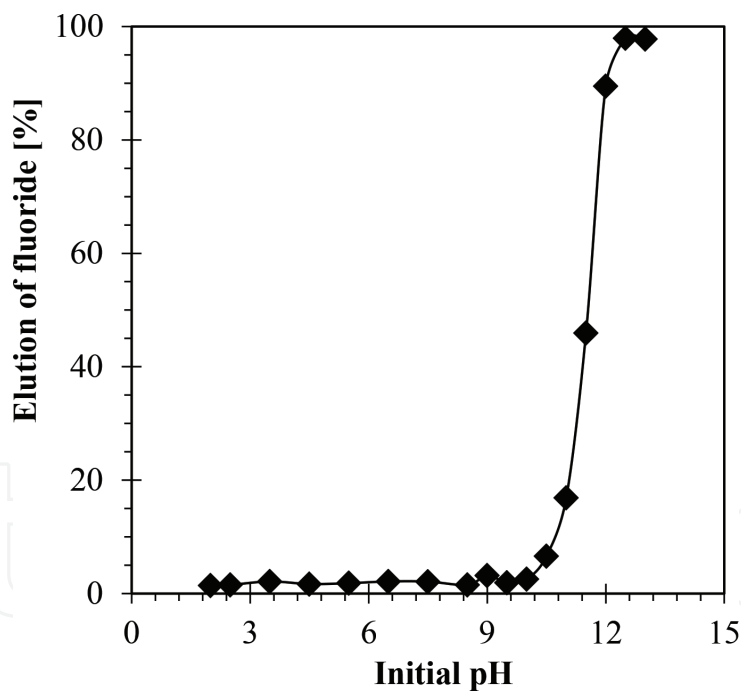


Figure 13.
Effect of pH on elution of fluoride adsorbed on Zr(IV)-loaded saponified orange juice residue (SOJR) gel.

Figure 14 shows effect of initial fluoride concentration at various pH values on leakage of the loaded zirconium(IV) from the SOJR gel. Such leakage, which would cause degradation of the adsorbent, was practically negligible at all pH values, except below pH 3, where the loaded metal ions are replaced by hydrogen ions by cation-exchange mechanism.

Figure 15 shows the result of cycle test of adsorption of fluoride on Zr(IV)-loaded SOJR gel followed by elution using 0.1 mol dm^{-3} NaOH. It can be concluded that the adsorption and desorption behaviors of fluoride on this gel were not significantly degraded, even after 10 cycles of adsorption and elution. The Zr(IV)-loaded SOJR gel exhibited high durability.

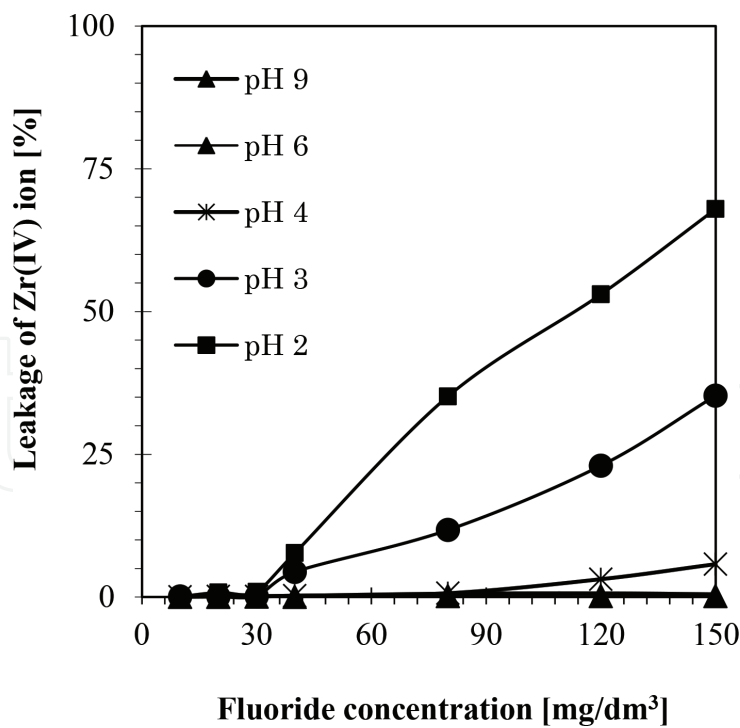


Figure 14. Effect of initial fluoride concentration of fluoride at various pH values on leakage of loaded zirconium(IV) from saponified orange juice residue (SOJR) gel.

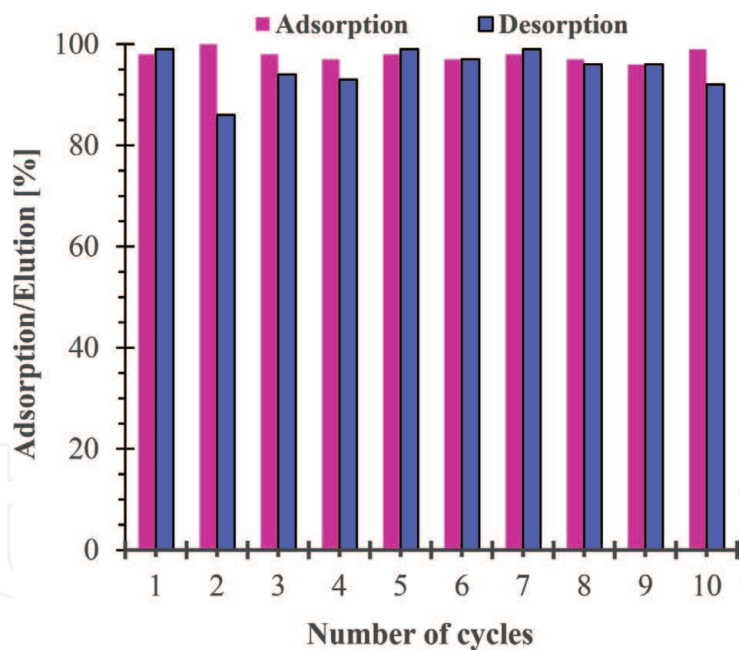


Figure 15. Effect of number of cycles of adsorption of fluoride on Zr(IV)-loaded saponified orange juice residue (SOJR) gel followed by elution using 0.1 mol dm⁻³ NaOH.

4. Adsorption behavior of fluoride on waste seaweed gel loaded with various high-valent metal ions

Figure 16 shows the effect of equilibrium pH on the adsorption of fluoride on the cross-linked seaweed gel (CSW) and CSW gels loaded with Zr(IV) and La(III). Unloaded CSW gel also exhibits some adsorption of fluoride, which is attributable to calcium(II) ion contained in seaweed as calcium alginate. Similar to SOJR gel, the adsorption of fluoride was greatly improved by loading high-valency metal ions, of which Zr(IV) exhibited better adsorption than La(III). The decrease in adsorption

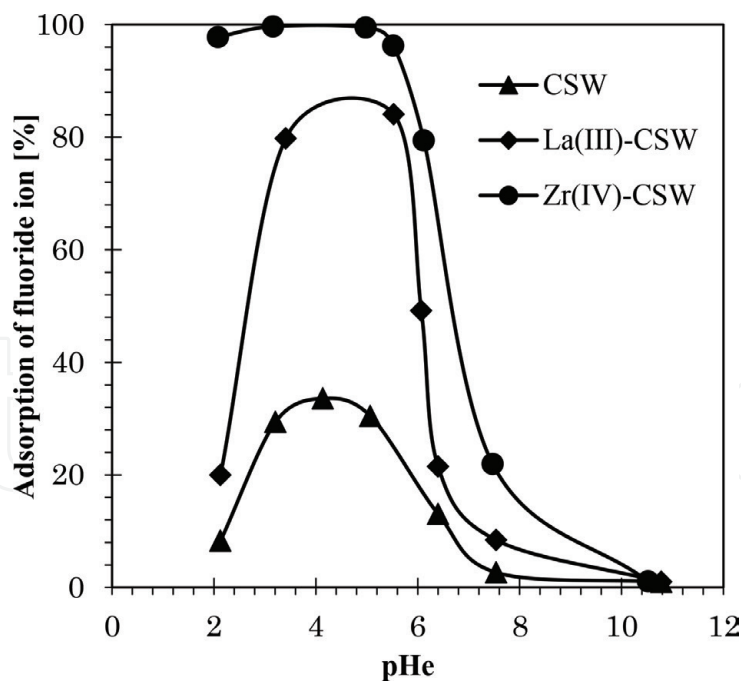


Figure 16.
Effect of equilibrium pH on the adsorption of fluoride on the cross-linked seaweed gel (CSW) and metal-loaded CSW gels [7].

with increasing pH at high pH is attributable to the competition of fluoride ion with hydroxyl ion for adsorption sites on the loaded metal ions; that is, the adsorption and desorption mechanism in this system can also be reasonably interpreted by that depicted in **Figure 9** for SOJR gel.

Figure 17 shows the effect of initial pH on leakage of the loaded metal ions. It is apparent that, compared with La(III), the loaded Zr(IV) is much more difficult to leak from CSW than La(III); that is, Zr(IV) is also more suitable as the loaded metal ion on CSW.

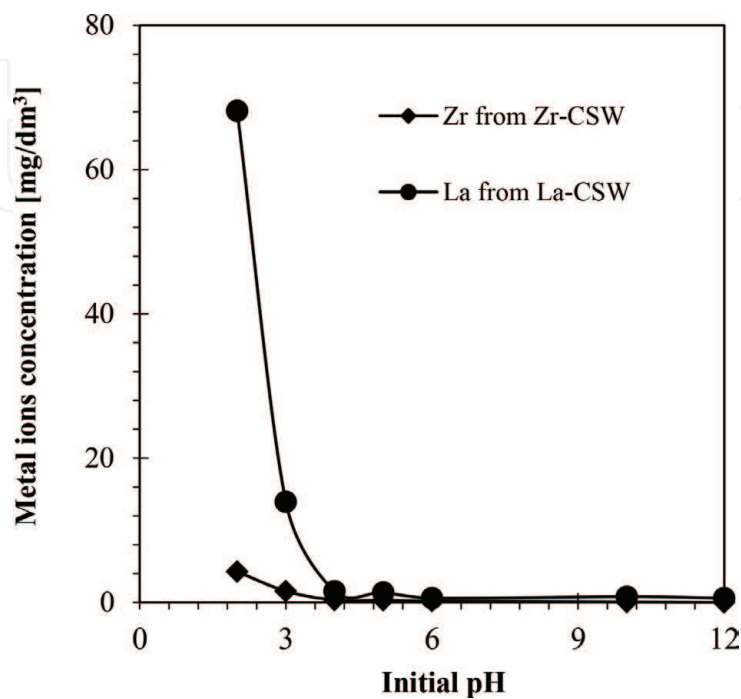


Figure 17.
Effect of initial pH on leakage of the loaded metal ions from cross-linked seaweed (CSW) gels.

5. Adsorption behavior of fluoride on pulverized spent cation-exchange resin loaded with zirconium(IV) ions

A small amount of commercially available inorganic coagulating agent, MAGNETITE III, the main components of which are calcium, aluminum, and iron, was added with Zr-SRP to test solutions containing trace concentration of fluoride to achieve smooth solid/liquid separation or smooth filtration. The coagulating agent is abbreviated as CA, hereafter. It was found that stable floc was formed at a CA/Zr-SRP ratio higher than 0.2.

Figure 18 shows the effect of equilibrium pH on the adsorption of fluoride onto SRP before and after Zr(IV) loading in the presence and absence of CA. Although SRP exhibited only negligible adsorption for fluoride, the adsorption was greatly

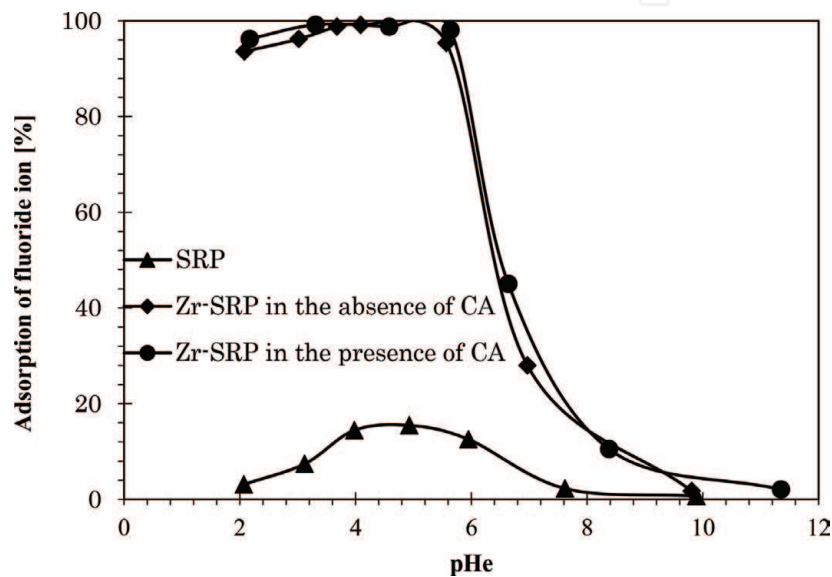


Figure 18. Effect of equilibrium pH on adsorption of fluoride on pulverized spent cation-exchange resin (SRP) before and after Zr(IV) loading [8].

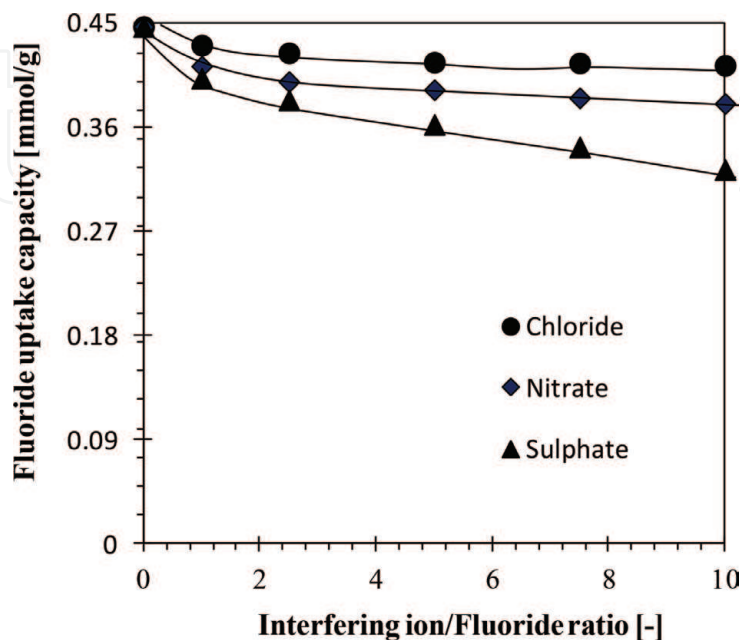


Figure 19. Effect of interfering anionic species on adsorption of fluoride on Zr(IV)-loaded pulverized spent cation-exchange resin (Zr-SRP) [8].

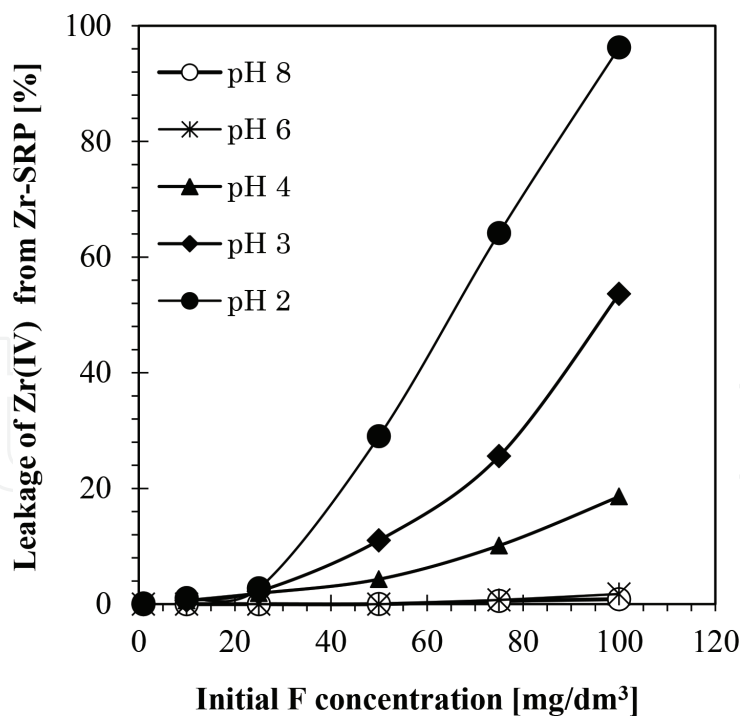


Figure 20.
Effect of fluoride concentration on leakage of loaded Zr(IV) from Zr(IV)-loaded pulverized spent cation-exchange resin (Zr-SRP) at various pH values [8].

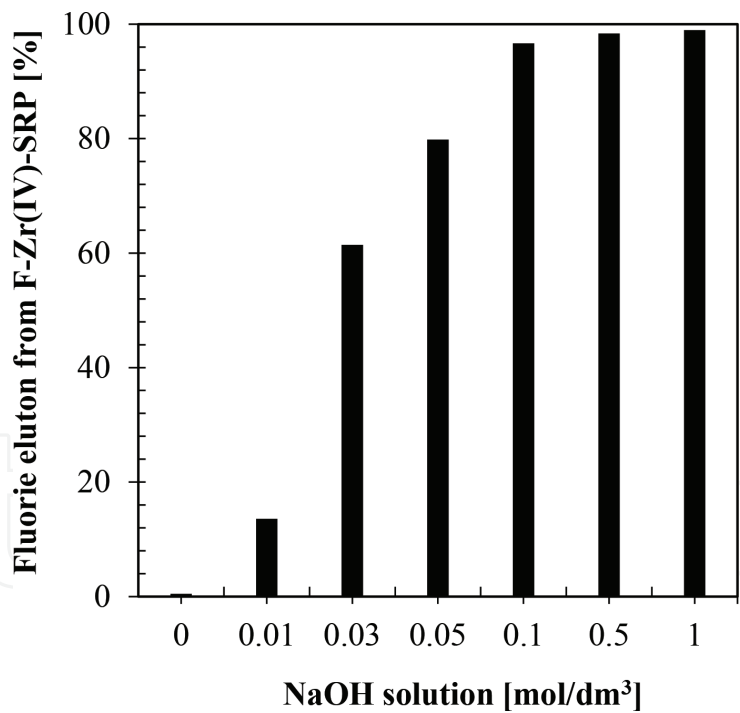


Figure 21.
Effect of concentration of sodium hydroxide on the elution of fluoride adsorbed on Zr(IV)-loaded pulverized spent cation-exchange resin (Zr-SRP) [8].

improved by loading Zr(IV), similar to the cases of SOJR and CSW. The small amount of adsorption on unloaded SRP at pH = 4–6 is considered to be due to calcium accumulated in the resin during its previous function in water treatment. Adsorption of fluoride also rapidly decreased with increasing pH at pH values above 6, similar to the cases of SOJR and CSW, which is attributable to the competition of fluoride ions with hydroxyl ions for the adsorption sites on Zr-SRP. Adsorption of fluoride was not affected by the addition of small amount of CA.

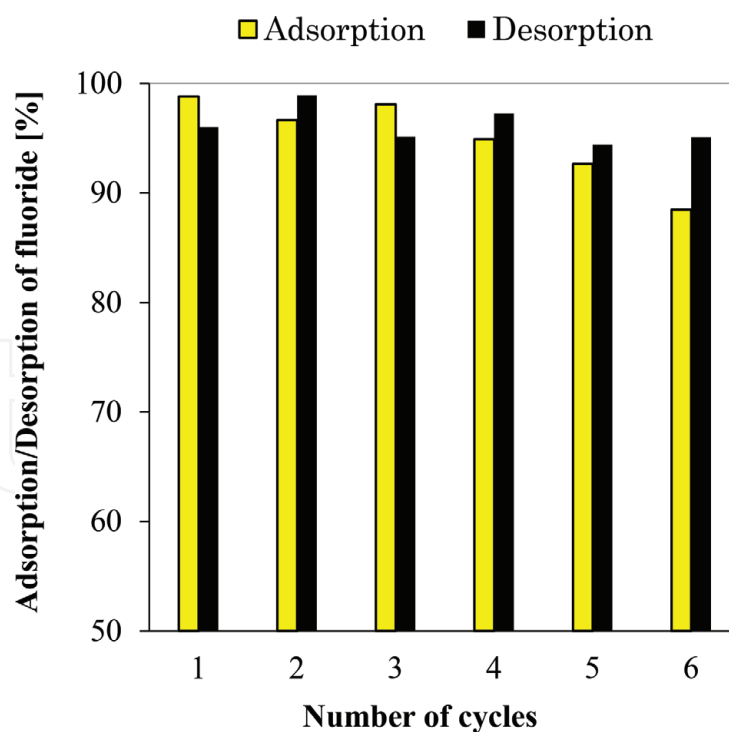


Figure 22.

Effect of number of cycles of adsorption of fluoride on Zr(IV)-loaded pulverized spent cation-exchange resin (Zr-SRP) followed by elution using 0.1 Mol dm^{-3} NaOH solution [8].

Figure 19 shows the effect of interfering anionic species (chloride, nitrate, and sulfate) present in aqueous fluoride solutions on the adsorption of fluoride on Zr-SRP. Also in this case, the effect of coexisting anionic species was relatively low.

Figure 20 shows leakage of Zr(IV) from Zr-SRP by varying concentration of fluoride at various pH values. It is evident that the leakage was negligible at pH values higher than 6, regardless of fluoride concentration.

Figure 21 shows effect of sodium hydroxide concentration on the elution of fluoride adsorbed on Zr-SRP. The results suggest that nearly quantitative elution of fluoride can be achieved by 0.1 mol dm^{-3} sodium hydroxide solution also in this case.

Figure 22 shows the result of durability test of Zr-SRP for repeating adsorption of fluoride followed by elution for up to 6 cycles. This figure suggests that Zr-SRP is not significantly degraded up to at least 6 cycles.

6. Comparison of adsorption capacities for fluoride on Zr(IV)-loaded adsorbents prepared from wastes

Adsorbents are evaluated in terms of their maximum adsorption capacities and selectivity for targeted species over other coexisting species. Selectivity for fluoride of three adsorbents prepared from wastes over other anionic species is discussed in the preceding sections. In this section, the maximum adsorption capacities on Zr(IV)-loaded SOJR, CSW, and SRP for fluoride were compared.

Figure 23 shows adsorption isotherms for fluoride on Zr(IV)-loaded SOJR, CSW, and SRP at 30°C . For all of these adsorbents, the adsorption amount increased with increasing fluoride concentration in the low concentration range and tends to approach a constant value for each adsorbent in the high concentration range, suggesting typical Langmuir-type adsorption.

These adsorption isotherms were therefore replotted according to the Langmuir equation, expressed by Eq. (1) as shown in **Figure 24**.

$$C_e/q = 1/q_{\max} b + C_e/q_{\max} \tag{1}$$

where q_{\max} and b denote the maximum adsorption capacity and adsorption equilibrium constant, respectively, based on the Langmuir's monolayer adsorption theory.

As expected from Eq. (1), the plots in **Figure 24** lay on straight lines. From the values of intercepts of these straight lines with the ordinate and their slopes, the

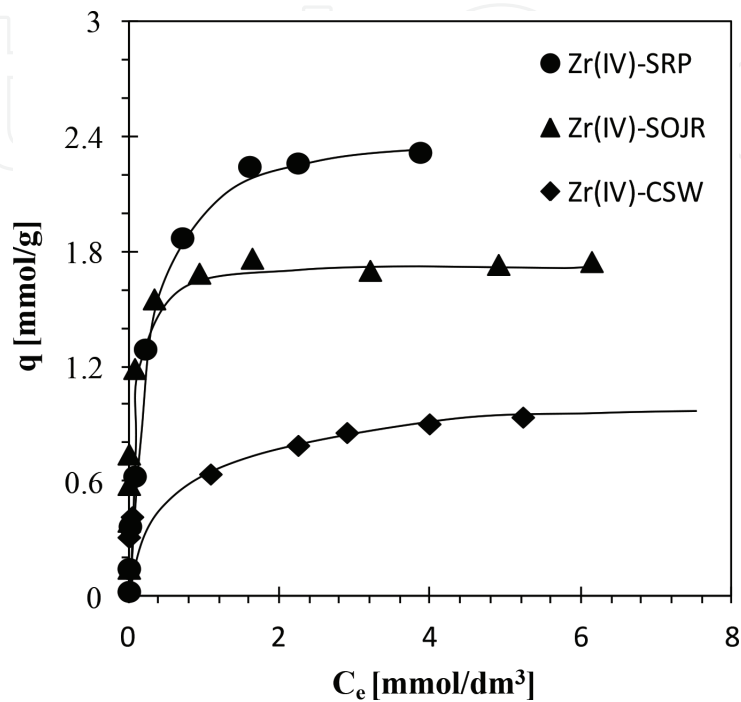


Figure 23. Adsorption isotherms of fluoride on Zr(IV)-loaded saponified orange juice residue (SOJR), cross-linked seaweed (CSW) gels, and pulverized spent cation-exchange resin (SRP) at 30°C.

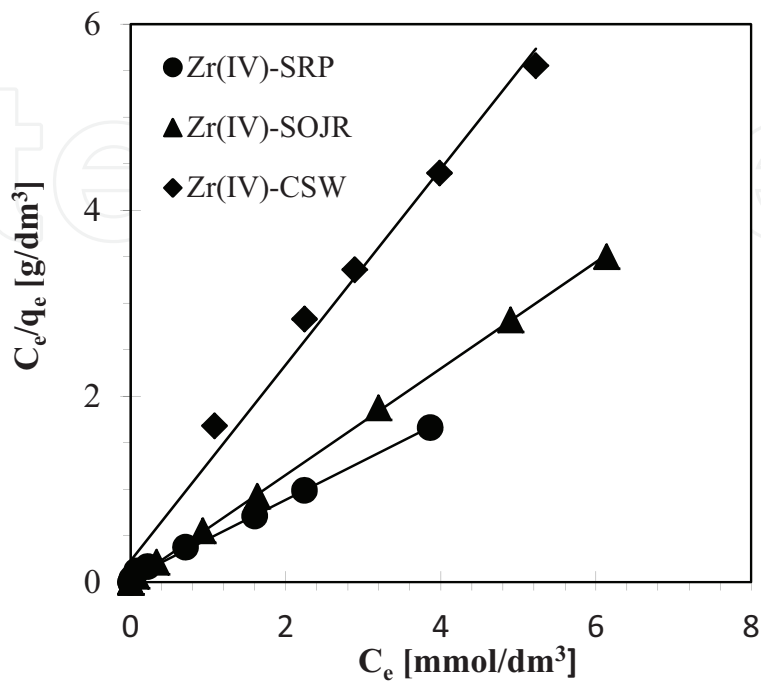


Figure 24. Replots of **Figure 23** according to Eq. (1), the Langmuir's equation.

Adsorbents	q_{\max} (mmol/g-dry weight)	b (dm ³ /mmol)
Zr(IV)-loaded SOJR	1.74	3.11
Zr(IV)-loaded CSW	0.95	5.04
Zr(IV)-loaded SRP	1.98	1.18

Table 1.
Maximum adsorption capacities and adsorption equilibrium constants of fluoride on Zr(IV)-loaded saponified orange juice residue (SOJR) and cross-linked seaweeds (CSW) gels and pulverized spent cation-exchange resin (SRP) at 30°C.

Adsorbents	pH	q_{\max} (mmol/g)	Temperature (°C)	Reference
Zr(IV)-loaded SOJR	4	1.74	30	[6]
Zr(IV)-loaded CSW	4	0.95	30	[7]
Zr(IV)-loaded SRP	4	1.98	30	[8]
Sn(IV)-loaded SOJR	3	1.18	30	[5]
Ti(IV)-loaded SOJR	3	0.93	30	[5]
Al(III)-loaded SOJR	6	1.03	30	[5]
Fe(III)-loaded SOJR	4	0.88	30	[5]
La(III)-loaded SOJR	4	1.06	30	[10]
Sc(III)-loaded SOJR	4	0.60	30	[10]
Sm(III)-loaded SOJR	5	1.22	30	[10]
Ho(III)-loaded SOJR	5	0.93	30	[10]
Ce(III)-loaded SOJR	4	0.91	30	[10]
Ce(IV)-loaded SOJR	4	1.53	30	[10]
READF(PG)	3	2.10	30	[11]
READF(HG)	3	2.35	30	[11]
Zr-impregnated cashew nut shell carbon	3	0.09	30	[12]
La-loaded 200CT resin	6	1.34	30	[13]
Indian FR 10	7	0.068	30	[14]
Ceralite IRA 400	7	0.078	30	[14]
La-loaded CL gelatin	5–7	1.12	25	[15]
Nd-modified chitosan	7	1.17	30	[16]
Fe-loaded cotton	4	0.97	25	[17]
Protonated chitosan	7	0.38	30	[18]
Activated alumina	5–6	0.86	30	[19]
AFB-Pr resin	5	0.026	30	[20]
La-impregnated alumina	5.7–8	0.35	Room temperature	[21]
Spirogyra species IO1	7	0.05	30	[22]
Waste mud	5	0.22	20	[23]
Nanoaluminum hydroxide	5.2	0.17	25	[24]
Magnesia/chitosan composite	10	0.11	Room temperature	[25]
Waste carbon slurry	7.5	0.23	25	[26]
Montmorillonite	6	0.01	25	[27]

Table 2.
Maximum adsorption capacities of fluoride on various adsorbents.

maximum adsorption capacities and adsorption equilibrium constants were evaluated, as listed in **Table 1**. The data indicate that Zr(IV)-loaded SRP exhibits the highest loading capacity.

These maximum adsorption capacities were compared with those on SOJR gel loaded with other high-valency metal ions and with those reported in literature, as listed in **Table 2**. Zr(IV)-loaded SRP and Zr(IV)-loaded SOJR exhibited higher adsorption capacities than other adsorbents, including Zr-containing adsorbents, except for READF, a commercially available porous resin that contains fine zirconium hydroxide powder in its pores.

7. Removal tests of trace concentrations of fluoride from actual waste plating solutions using Zr(IV)-loaded adsorbents prepared from wastes

On the basis of the results of fundamental adsorption tests using Zr(IV)-loaded SOJR, CSW, and SRP discussed above, adsorptive removal of trace concentrations of fluoride was tested from actual waste plating solutions using these adsorbents [6–8]. A sample of the actual waste plating solution was kindly donated by Federation of Electro Plating Industry Association, Japan, Tokyo, Japan. The donated sample solutions contained 12.2 mg/dm³ of fluoride together with about 750 mg dm⁻³ of sulfate, as well as following cationic species (mg dm⁻³): Al 13.8, Ca 10.5, Fe 36.4, Cu 9.8, and Zn 1.9. Its pH value was 6.7. **Figure 25** shows the plots of fluoride concentration after the treatment using these three adsorbents as a function of S/L ratio, defined as the ratio of dry mass of added adsorbent to volume of treated solution together with the permissible level for fluoride in effluents in Japan (8 mg/dm³), WHO standard for drinking water (1.5 mg/dm³), and that in Japan (0.8 mg/dm³). This figure indicates that fluoride concentration can be successfully lowered by adding small amount of adsorbents. The concentration was reduced to less than 0.8 mg/dm³, the Japanese standard for fluoride, by adding only 2 g of adsorbents to 1 dm³ of tested sample solution.

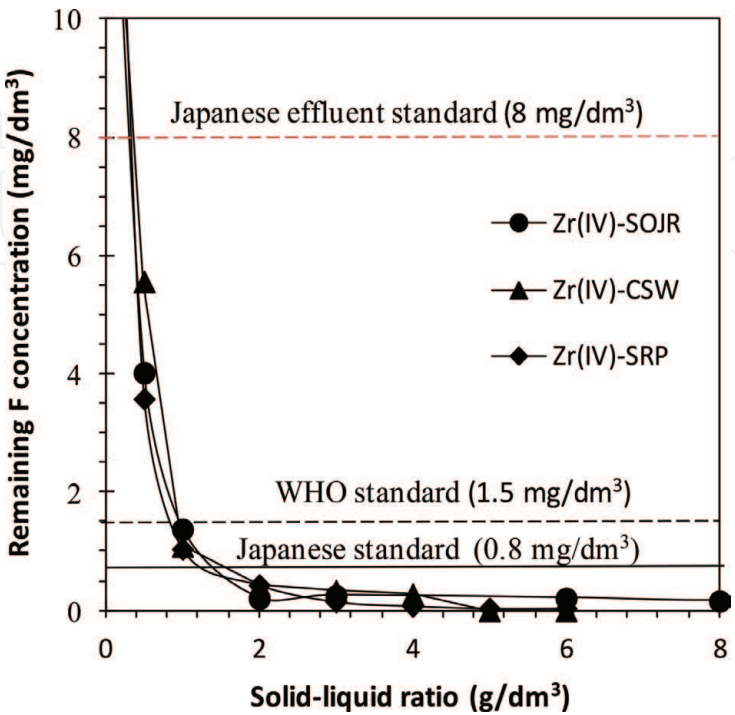


Figure 25.
Adsorptive removal of trace concentrations of fluoride from actual waste plating solution using three adsorbents prepared in the present work, showing relationship between concentration of fluoride remained in aqueous solution after adsorption and mass of adsorbent added to unit volume of solution.

8. Conclusion

For the purpose of removing trace or low concentrations of fluoride from aquatic environments, novel adsorbents were prepared from three waste materials, orange juice residue, waste seaweed, and pulverized spent cation-exchange resin containing sulfonic acid functional groups, by loading with tri- or tetravalent metal ions, such as iron(III), aluminum(III), rare earths(III), and zirconium(IV). Here, the loaded metal ions function as adsorption sites and waste materials function as polymer matrices immobilizing the metal ions. The adsorption mechanisms on these adsorbents were inferred from the results of adsorption tests from aqueous solutions at various pH values. Adsorption and desorption were found to be easily controlled by changing pH. Of the high-valency metal ions tested, zirconium(IV) was found to be the most suitable as the loaded metal ion because zirconium(IV)-loaded adsorbents exhibited highest adsorption of the tested metal-loaded adsorbents in the adsorption isotherm tests. Zirconium(IV)-loaded adsorbents exhibited high selectivity for fluoride over other anionic species present in aqueous solutions. Leakage of the loaded zirconium(IV) ions was found to be negligible, except at low pH, and high durability of these adsorbents was confirmed from repeated cycle tests of adsorption followed by desorption. The maximum adsorption capacities for fluoride on these adsorbents were higher than those of most adsorbents reported in literature. The removal test of trace concentration of fluoride from actual waste plating solutions revealed that the fluoride concentration could be lowered below the acceptable level by using only small amounts of these adsorbents; for example, it was reduced to less than 0.8 mg/dm^3 , the Japanese standard for fluoride, by adding only 2 g of adsorbents to 1 dm^3 of tested sample solution. From these results, it can be expected that trace concentration of fluoride is effectively removed by using adsorbents produced from various waste materials at cheap cost.

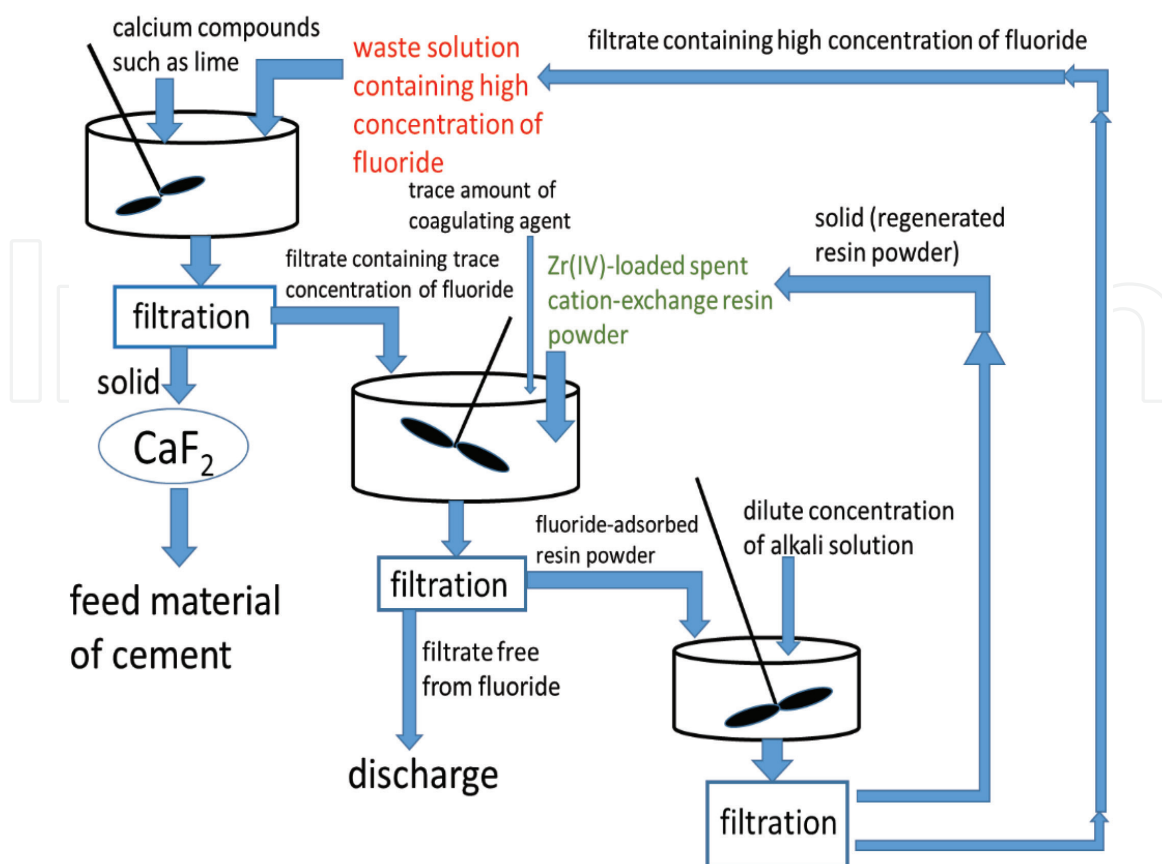


Figure 26. Flow sheet for recovery of fluoride using powder of spent cation-exchange resin loaded with zirconium(IV).

Although it is not noticed in laboratory-scale tests and the small-scale adsorption tests mentioned in this study, the adsorbent prepared from orange juice residue was found to generate considerable stench at larger scale, such as pilot-scale operation. Taking account of this, the adsorbent prepared from spent cation-exchange resins is recommended to be employed in commercial operations. A process for the recovery of fluoride using this adsorbent is proposed as shown in **Figure 26**.

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