Adsorptive removal of fluoride from aqueous solution using orange waste loaded with multi-valent metal ions

Hari Paudyal [a], Bimala Pangeni [a], Katsutoshi Inoue [a,*], Hidetaka Kawakita [a], Keisuke Ohto [a], Hiroyuki Harada [a], Shafiq Alam [b]

[a] Department of Applied Chemistry, Saga University, Honjo 1, Saga 840-8502, Japan
[b] Faculty of Engineering and Applied Science, Memorial University, St. John's, NL A1B 3X5, Canada

ABSTRACT

Adsorption gels for fluoride ion were prepared from orange waste by saponification followed by metal loading. The pectin compounds contained in orange waste creates ligand exchange sites once it is loaded with multi-valent metal ions such as Al^{3+}, La^{3+}, Ce^{3+}, Ti^{4+}, Sn^{4+}, and V^{4+} to be used for fluoride removal from aqueous solution. The optimum pH for fluoride removal depends on the type of loaded metal ions. The isotherm experiments showed the Langmuir type monolayer adsorption. Among all kinds of metal loaded gels tested, Al loaded gel appeared to exhibit the most favorable adsorption behavior. The adsorption kinetics of fluoride on loaded gel demonstrated fast adsorption process. The presence of NO_3^-, Cl^- and Na^+ ions has negligible effect on fluoride removal whereas SO_4^{2-} and HCO_3^- retarded the fluoride removal capacity in some extent. Fluoride removal at different adsorbent doses showed that fluoride concentration can be successfully lowered down to the acceptable level of environmental standard. The fluoride adsorption mechanism was interpreted in terms of ligand exchange mechanism. The complete elution of adsorbed fluoride from the gel was successfully achieved using NaOH solution.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Fluoride is widespread in the environment, water, air, vegetation and in the Earth's crust which can enter ground water by natural process [1]. An appropriate concentration of fluoride in drinking water is required for preventing dental caries but long term ingestion of water that contain excess amount of fluoride causes disease such as skeletal and teeth damage, paralysis of volition, cancer [2,3]. Because of the toxicity of fluoride and danger of overdosing, fluoridation of drinking water has been prohibited in many countries. Fluoride containing waste water is generated in various industries including mines, semiconductor factories, pharmaceutical companies, beryllium extraction plants, fertilizer manufacturing and aluminum smelters [4–6]. Hence, contamination of ground water by fluoride is unavoidable. The most common approach for fluoride removal is by means of lime precipitation. The lowest fluoride concentration which can be theoretically achieved based on the solubility of calcium fluoride by the use of lime is 5 mg/dm^3, but practically the lowest concentration of fluoride achieved is usually in the range of 10–20 mg/dm^3 [7] which requires further treatment to meet the maximum acceptable contaminant

level of fluoride (<0.8 mg/dm^3) discharged into the environment in Japan [6,8].

Other viable technologies so far investigated include Donan dialysis [9,10], membrane process [11], electrochemical technique [12,13], and adsorption using metal loaded sorbents [14–16]. On the other hand, for the treatment of a large amount of aqueous solution containing trace concentration of fluoride, aluminum co-precipitation method is now commercially employed in Japan [17]. According to this method, after aluminum compound like aluminum chloride or sulfate is added to the solution, pH is raised to form precipitate of aluminum hydroxide onto which the trace concentration of fluoride is co-precipitated. However, although it is possible to lower the fluoride concentration down to less than 0.8 mg/dm^3 using this method, large amounts of precipitate of aluminum hydroxide containing fluoride and large amounts of water are generated, which require large amounts of energy for dehydration and drying before wasting, which is not environmentally benign.

Among these methods, adsorption based processes seems to be the most effective. Even though ion exchange process has been used as a promising method, it has some drawbacks for fluoride removal. Because the selectivity of usual anion exchange resins to fluoride over other anionic species like sulfate and chloride which usually co-exist in water together with fluoride is low according to the well known Hoffmeister's selectivity series [18] among anionic species,

* Corresponding author. Tel.: +81 952 28 8671; fax: +81 952 28 8669.
E-mail address: inoue@elechem.chem.saga-u.ac.jp (K. Inoue).
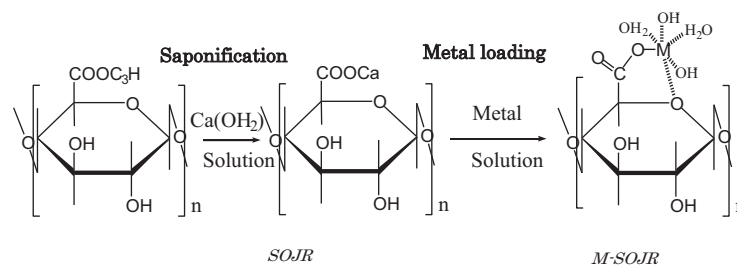
Scheme 1. Synthetic route of metal loaded orange gel M = Al^{3+}, Fe^{3+}, Ce^{3+}, La^{3+}, Ti^{4+}, V^{4+} and Sn^{4+}.

it is difficult to selectively remove small or trace amounts of fluoride from large excess of other anionic species.

Recently, various adsorbents such as bleaching powder [19], quick lime [20], cashew nut shell [21], carboxylated cross linked chitosan bead [22], metal loaded zeolite [23] and spirogyra species [24] have been reported as effective adsorbents for fluoride removal. The improved selectivity and sorption capacities of low cost adsorbents derived from waste bio-mass loaded with metal ions [25–28] have drawn the attention of many scientists in this field.

In this study, we developed the metal loaded orange waste gel for the removal of trace concentration of fluoride from aqueous solution. Various metal loaded adsorbents were prepared from orange waste through chemical modification followed by loading with metal ions to systematically evaluate the adsorption behaviors. The association of various multi-valent metal ions such as Al^{3+}, La^{3+}, Ce^{3+}, Ti^{4+}, Sn^{4+} and V^{4+} with fluoride is high because of their high stability with fluoride ions. Thus, sorption capacity and selectivity of the sorbent are expected to be improved after doping these metal ions on orange waste.

2. Experimental

2.1. Chemicals and analysis

The chemicals used in the present work are pure analytical grade and used directly without further purification. The chloride salts of Sn^{4+}, Ti^{4+}, La^{3+}, Ce^{3+}, Al^{3+}, Fe^{3+} and sulfate salt of V^{4+} were used for the preparation of adsorbent. Sodium fluoride (NaF) solution was used to make fluoride stock solution. All the chemicals were purchased from Wako Chemicals Co., Ltd., Japan. The pH of the fluoride solution was adjusted by adding 0.5 M (M = mol/dm^3) HNO$_3$ or 0.5 M NaOH solution and was measured using DKK-TOA model HM-25G pH meter. The concentrations of metal ions in test solutions were measured using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Shimadzu model ICPS 8100) while that of fluoride was measured by ion chromatography (Dionex model ICS: 1500). The FTIR spectra of SOJR and metal loaded SOJR were recorded using JASCO, FTIR-410 Fourier Transform Infrared Spectrometer whereas total organic carbon leaked from the gel was measured using Shimadzu model TOC-VSH Total Organic Carbon Analyzer.

2.2. Preparation of metal loaded saponified orange waste gel

The orange (*Citrus aurantium*, Linn.) is one of very popular fruits in Japan and easily available in local area. The orange waste after juicing which was applied for the adsorbent preparation, was kindly supplied by JA Beverage Saga Co., Ltd., Japan. Orange waste principally consists of cellulose, hemicellulose, pectin, chlorophyll pigment and other low molecular weight compounds like limonene and so on. Pectin contains carboxyl groups as well as its methyl ester groups. The methyl ester portion of orange pectin can be eas-

ily converted into 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 in Scheme 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 order to evaluate the leakage of some organic compounds from thus prepared SOJR, the total organic carbon dissolved from the gel was measured by TOC analyzer as mentioned in Section 2.1 after shaking SOJR and metal loaded SOJR in water at S/L ratio of 5 g/dm^3 at different pH ranging from 1 to 7.

Thus prepared SOJR was further treated by loading with multivalent metal ions such as Al^{3+}, La^{3+}, Ce^{3+}, Ti^{4+}, Sn^{4+} and V^{4+}. To prepare the metal-loaded gels, 3 g of SOJR was mixed together with 0.5 dm^3 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 on SOJR gel as depicted in Scheme 1. Then, the suspensions were filtered and washed several times with de-ionized water followed by hot water in order to remove the free metal ions from the gel surface. The filter cakes were dried in vacuo and were grinded by mortar to obtain particles in the size range of 100–150 μm by sieving.

The amount of loaded metal ion on SOJR was evaluated by totally dissolving the loaded SOJR in aqua regia by shaking 50 mg of metal loaded SOJR in 10 cm^3 of aqua regia for 24 h, followed by measuring the metal concentration in the aqua regia by ICP-AES.

2.3. Batch wise adsorption test

The adsorption behaviors of fluoride on different metal loaded SOJR gels were examined under the batch-mode of operation. Equilibrium adsorption tests were performed by mixing 10 mg of the adsorbent together with 10 cm^3 fluoride solution (0.52 mmol/dm^3) in a 50 cm^3 conical flask at different pH. The mixture was shaken in a thermo-stated 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 collecting sample solutions at different time intervals. After the adsorption, the samples were filtered and analyzed for fluoride concentration. The percentage adsorption
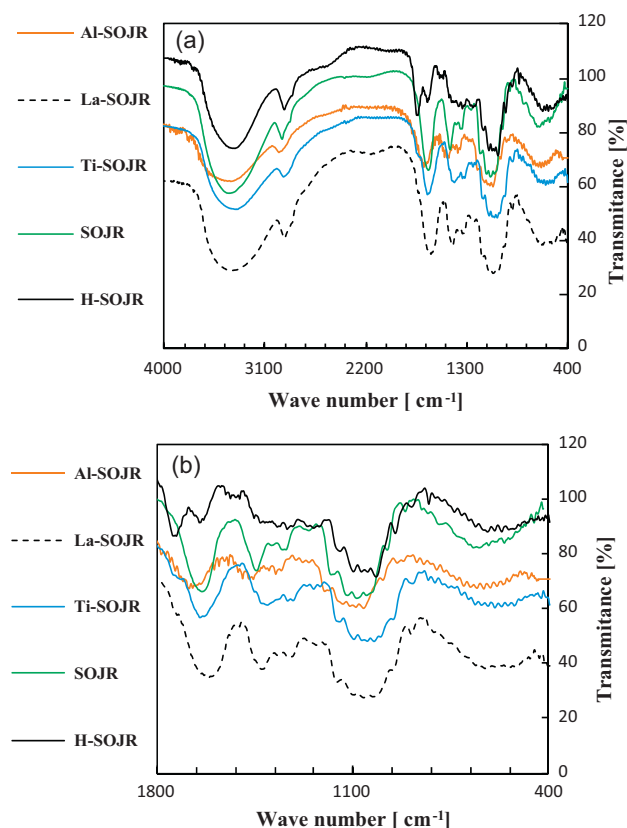
Fig. 1. FTIR spectra of various metal loaded SOJR. (a) FTIR spectra of metal loaded SOJR from 400 to 4000 cm^{-1} (b) Part of FTIR spectra of metal loaded SOJR from 400 to 1800 cm^{-1}.

(%A) and amount of adsorption (q) were calculated according to the following equations:

$$\%A = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

$$q = \frac{C_i - C_e}{W} \times V \tag{2}$$

where C_i and C_e are fluoride concentration (mM) before and after adsorption, respectively, W is the dry weight of adsorbent (g) and V is the volume of fluoride solution (dm^3).

Isotherm studies were conducted by varying the initial fluoride concentration (0.5–8 mM) at optimum pH. The effect of co-existing anions on fluoride adsorption was studied for Al-SOJR at varying the concentration of co-existing ions (SO$_4^{2-}$, Cl$^-$, NO$_3^-$, HCO$_3^-$, Na$^+$, Ca^{2+}, Na$^+$) using their respective sodium salts except for calcium chloride. The elution test was performed at different concentrations of NaOH (0.01–0.5 M) at solid liquid ratio of 1 g/L.

3. Result and discussion

3.1. Characterization of the adsorbent

3.1.1. Fourier transform infrared spectroscopy

Orange waste is one of the pectin rich bio-polymer that can be chemically modified by lime water to SOJR which functions as anion exchanger once it is loaded with multi-valent metal ions. Since SOJR is also a kind of Ca^{2+}-type pectic acid gel, H$^+$-type SOJR gel was prepared by neutralizing SOJR with 0.1 M HCl in order to investigate the effect of loaded metal ions in the FTIR spectra. Fig. 1(a) and (b) shows the FTIR spectra of H$^+$-type SOJR, SOJR and metal loaded SOJR. The FTIR spectrum of H$^+$-type SOJR shows the intense peak at 3436 cm^{-1} which is due to –OH stretching vibration

Table 1
Amount of metal ions loaded on SOJR.

Adsorbent	Metal loading		
	Metal ions	pH of loading	Amount loaded (mol/kg)
Al-SOJR	Al^{+3}	4	1.16
Ce-SOJR	Ce^{+3}	3	0.93
La-SOJR	La^{+3}	3	0.95
Ti-SOJR	Ti^{+4}	1.5	1.2
V-SOJR	V^{+4}	3	1.12
Sn-SOJR	Sn^{+4}	1	0.97

of polymeric compounds such as alcohol, phenol and carboxylic acid, as in pectin, cellulose and lignin. The peak at 2888.28 cm^{-1} is due to –CH stretching vibration. The peak at 1714.21 cm^{-1} is due to stretching vibration of non ionic carboxyl group. The peak at 1638.21 cm^{-1} and 1434.19 cm^{-1} can be assigned to the symmetric and asymmetric vibration of ionic carboxyl group, respectively. In metal loaded SOJR, the peak at 1714.21 cm^{-1} in H-SOJR is shifted to 1658.46 cm^{-1}, 1664.35 cm^{-1}, 1672.52 cm^{-1} and 1684.17 cm^{-1} for La-SOJR, Ti-SOJR, SOJR only and Al-SOJR, respectively. This result reveals that as the molecular weight of loaded metal ions increases the carboxyl peak also shifted to lower frequency region. The changes of stretching frequency of carboxyl functional group in Al^{3+}, La^{3+}, Ti^{4+} loaded SOJR and H$^+$-type SOJR compared to SOJR confirms the chemical modification.

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 amount of different metal ions such as Sn^{4+}, Ti^{4+}, V^{4+}, La^{3+}, Ce^{3+} and Al^{3+} loaded on SOJR at their mentioned loading pH was evaluated to be 0.97, 1.20, 1.12, 0.95, 0.93 and 1.16 mmol/g, respectively, and the results are presented in Table 1.

3.1.3. Aqueous insolubility of gels

Aqueous insolubility of the prepared sorbents was examined by measuring the concentration of total organic carbon (TOC) leached from the gel at varying pH (1–7). Fig. 2 gives the amount of TOC leached, i.e. dissolution of water soluble organic compounds from the various gels as a function of pH. The dissolution of TOC from raw orange juice residue ranges from 247 mg/dm^3 (at pH 1) to 167 mg/dm^3 (at pH 7) whereas it is drastically decreased to 24, 22 and 20 mg/dm^3 (at pH 1) to 4, 4 and 5 mg/dm^3 (at pH 7) from SOJR, Sn-SOJR and Al-SOJR, respectively. Great majority of water soluble organic compounds contained in orange juice residue was
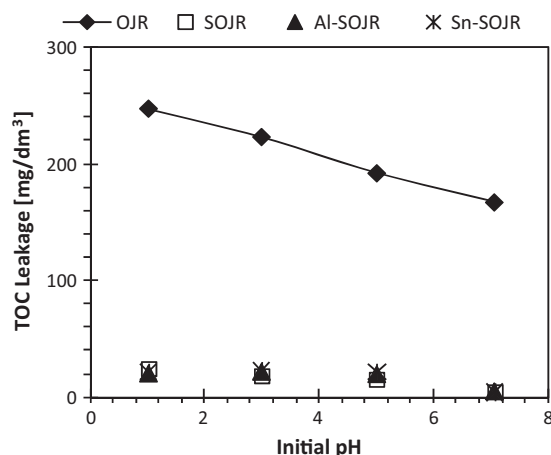

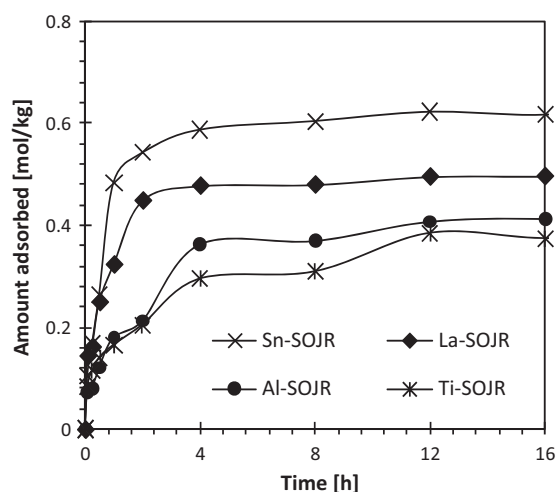**Fig. 2.** Dissolution of total organic carbon from various adsorbents.

Fig. 3. Kinetics of fluoride adsorption on various metal loaded orange gels. *Conditions*: volume of fluoride solution = 10 cm³, feed solution = 1.05 mmol/ dm³, weight of gel = 10 mg, temperature = 30 °C.

Fig. 4. Effect of pH for the adsorption of fluoride by metal loaded orange gel. *Conditions*: volume of fluoride solution = 10 cm³, feed solution = 0.52 mmol/ dm³, weight of gel = 10 mg, temperature = 30 °C, shaking time = 24 h, shaking speed = 150 rpm.

lost during the chemical modification, thus leaving water insoluble stable polymeric compounds in SOJR.

3.2. Kinetics studies

The effect of contact time on fluoride adsorption on different metal loaded SOJR, namely Al-SOJR, La-SOJR, Sn-SOJR and Ti-SOJR, was studied under the applied experimental conditions. Fig. 3 shows the fluoride adsorption on different metal loaded SOJR as a function of contact time. As can be seen from this figure, the adsorption increases rapidly on 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 4 h for all the adsorbents tested, subsequent adsorption experiments were performed for 24 h in order to ensure complete equilibrium.

3.3. Effect of pH

Fig. 4 shows the adsorption of fluoride ion on various metal loaded SOJR at pH 1–12. As can be seen from this figure, the equilibrium uptake of fluoride ion 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^{4+}, Ti^{4+} and V^{4+} 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 La^{3+} and Ce^{3+} loaded SOJR gels. However, optimum adsorption of fluoride by Al^{3+} loaded SOJR has taken place at pH ranging from 5.5 to 6.0, suggesting that Al^{3+} loaded SOJR can be the most preferable candidate for the removal of fluoride from aqueous solution at 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 flu-
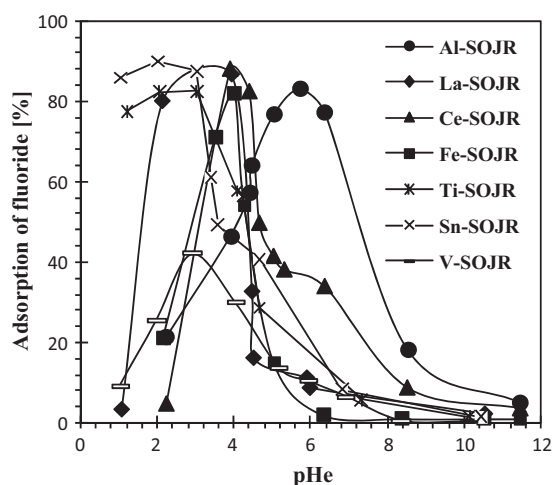
oride adsorption onto Ce–Fe oxide adsorbent after doping Al^{3+} ions [29]. The decrease in fluoride uptake at high pH can be attributed to the competition of hydroxyl ions for the adsorption sites. At pH lower than 2, sparingly soluble hydrofluoric acid (pK_a = 3.2, [30]) is formed and some fraction of fluoride becomes unavailable for the adsorption, resulting in the lowering of adsorption of fluoride. Moreover, at acidic condition (pH <2), leakage of loaded metals ions were observed, which is considered to contribute to the decrease of fluoride adsorption.

3.4. Adsorption isotherms

Adsorption isotherms of fluoride on various metal-loaded SOJR are shown in Fig. 5. 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 according to 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:

$$\frac{C_e}{q} = \frac{1}{q_{max}b} + \frac{C}{q_{max}} \tag{3}$$

where C_e (mmol/dm³) and q (mol/kg) are equilibrium concentration and amount of adsorption, respectively, while q_{max} is the maximum loading capacity and b 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 as shown in Table 2. 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.

Table 2
Isotherm parameters for the adsorption of fluoride on metal loaded SOJR.

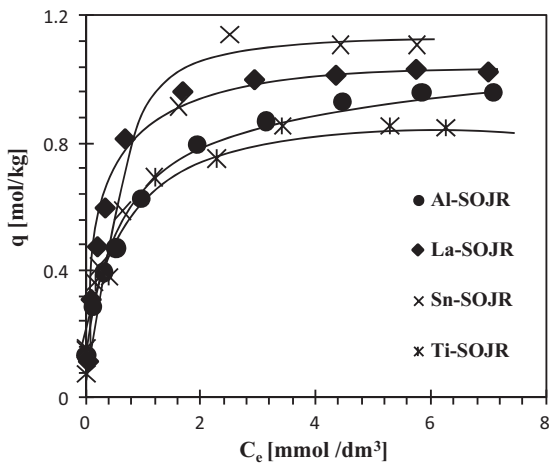| Adsorbent	Loaded M⁺-ions	Langmuir parameters				Freundlich parameters		
		pH	q_{max} (mol/kg)	b (dm³/mmol)	R^2	K_f (mol/kg)	n	R^2
Al-SOJR	Al^{+3}	6	1.01	2.24	0.99	0.78	2.97	0.91
La-SOJR	La^{+3}	4	1.07	3.87	0.99	0.83	2.72	0.81
Ti-SOJR	Ti^{+4}	3	0.91	2.53	0.99	0.77	3.40	0.93
Sn-SOJR	Sn^{+4}	3	1.18	2.79	0.99	0.84	2.53	0.90

Fig. 5. Adsorption isotherm of fluoride on various metal loaded orange gels. *Conditions*: volume of fluoride solution = 10 cm³, weight of gel = 10 mg, temperature = 30 °C.

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

$$\log q = \log K_f + \left(\frac{1}{n}\right) \log C_e \tag{4}$$

The value of Freundlich isotherm constant $1/n$ and K_f were calculated from the slope and the intercept of the straight line for the log–log plot of q versus C_e and presented also in Table 2. The determination coefficient value 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.

Table 3 presents a comparison of the maximum adsorption capacities of fluoride among various adsorbents based on Langmuir isotherm reported in the literatures, which demonstrates that the metal loaded SOJR, prepared in this study, exhibits the highest sorption capacity than any other adsorbents irrespective to metal loading or not. The sorption capacity of SOJR itself which is not loaded with metal ions (0.21 mol/kg) was found to be drastically increased after loading multi-valent metal ion because of increasing the possible adoption sites for fluoride ion which will be described in detail in Section 3.7.

3.5. 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 La-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 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/dm³ as shown in Fig. 6. The result reveals that Al-SOJR dosages of 8 g/dm³ is able to lower fluoride concentration below the Japanese environmental standard (0.8 mg/dm³ or 0.042 mmol/dm³), whereas complete removal of fluoride can be achieved at 15 g/dm³. Thus, it can be expected that Al-SOJR can be a suitable candidates to treat trace concentration of fluoride at neutral pH.

3.6. Effect of co-existing ions

Fluoride contaminated water contains different co-existing ions such as HCO_3^-, SO_4^{2-}, NO_3^-, Cl^-, Ca^{2+}, Na^+ together with fluoride ions. Fig. 7 shows the adsorptive removal of fluoride by Al-SOJR in
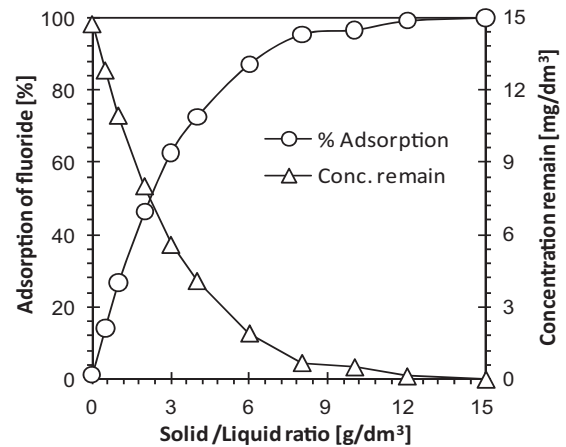

Fig. 6. Adsorption of fluoride onto Al-SOJR at different S/L ratios. *Conditions*: volume of fluoride solution = 10 cm³, feed concentration = 0.77 mmol/dm³ or 14.73 mg/dm³, pH 6.05, temperature = 30 °C.

the presence of 5–40 times higher concentration of co-existing ions from binary solutions. The result signifies that the influence of co-existing NO_3^-, Cl^-, and Na^+ ions for fluoride removal from binary mixture is negligible. But, the presence of Ca^{2+} ions in the fluoride solution enhanced the uptake capacity in small extent whereas HCO_3^- and 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 mg/dm³) with HCO_3^-, SO_4^{2-}, NO_3^-, Cl^- and Na^+ (200 mg/dm³ each) 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 HCO_3^- that may contribute to the lowering of fluoride removal.

3.7. Mechanism of fluoride adsorption

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 with the loaded metal ion [31,32]. Since Al^{3+}, La^{3+}, Ce^{3+}, Ti^{4+}, Sn^{4+} and V^{4+} ions tend to be extensively hydrolyzed even at very low concentration [33], 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 anions. In multi-valent metal loaded SOJR, neutralization of all the positive charges of the
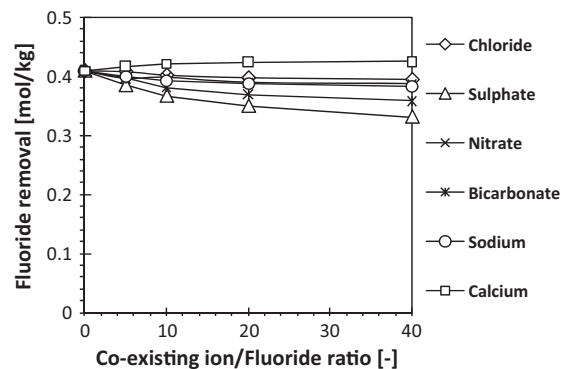

Fig. 7. Effect of competitor ions for the adsorption of fluoride using Al-SOJR gel. *Conditions*: volume of fluoride solution = 10 cm³, weight of gel = 10 mg, fluoride concentration = 0.72 mmol/dm³, temperature = 30 °C.

Table 3
Comparison of the maximum adsorption capacity for fluoride on different adsorbents.

Adsorbents	pH	Dose (g/dm^3)	Temp. (°C)	q_{max} (mol/ kg)	Ref.
Al-SOJR	6	1	30	1.03	This study
Sn-SOJR	3	1	30	1.18	This study
La-SOJR	4	1	30	1.07	This study
Ti-SOJR	3	1	30	0.93	This study
Zr-impregnated cashew nut shell	3	0.015	30	0.09	[21]
Carboxylated cross linked chitosan	7	5	30	0.72	[22]
Spirogyra species	7	1	30	0.06	[24]
La-impregnated cross-linked gelatin	5–7	4	25	1.12	[26]
Fe(III) loaded cotton cellulose	4	6.9	25	0.97	[28]
Modified native cellulose	–	1	25	0.45	[35]
Al(OH)$_2$ Coated rice husk ash	7	1	27	0.78	[36]
Ca-pretreated macrophyte biomass	6	5	25	0.11	[37]
Protonated chitosan bead	7	5	30	0.38	[38]
KMnO$_4$ modified rice straw carbon	2	–	25	0.83	[39]
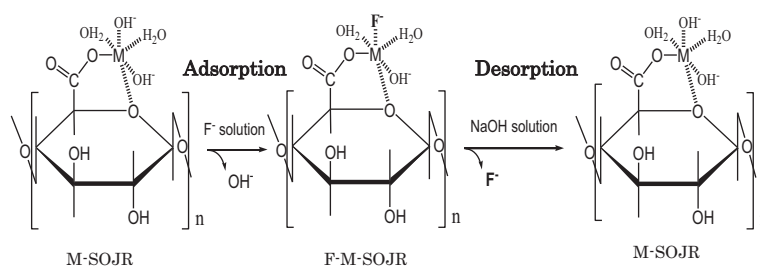
Scheme 2. Mechanism of fluoride adsorption and desorption using alkaline solution M = Al^{3+}, Fe^{3+}, Ce^{3+}, La^{3+}, Ti^{4+}, V^{4+} and Sn^{4+}.

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. Thus, with increasing the oxidation state of the loaded metal ions, there is the higher possibility of increasing number of hydroxyl ions (ligand exchange sites) on the coordination sphere of the loaded metal ions that helps the ligand exchange reaction with fluoride ions. The inferred mechanism of fluoride adsorption is depicted in Scheme 2 which is similar to the removal of phosphate anion by metal loaded orange gel as in our previous study [34].
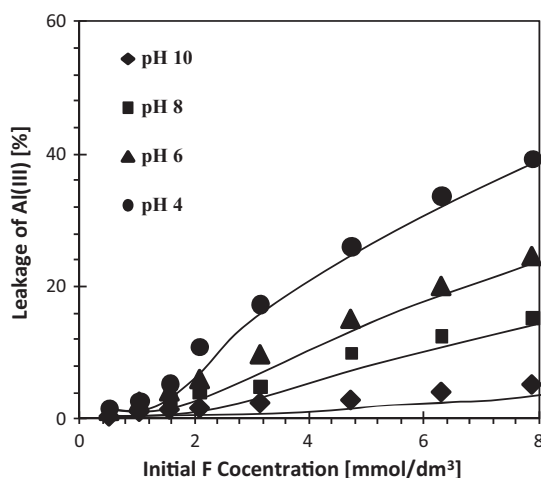
3.8. Leakage of loaded Al(III) ions

In order to investigate the most effective condition for fluoride adsorption on Al-SOJR, leakage of Al^{3+} from Al-SOJR was measured at different pH (4–10) at varying initial fluoride concentration (0.5–8 mmol/dm^3). Fig. 8 shows the percentage leakage of the loaded Al^{3+} from Al-SOJR as a function of initial fluoride concentration. It is clear from this figure that the leakage of Al^{3+} ion increases with increasing fluoride concentration in the high concentration range above 30 mg/dm^3 (1.57 mM) at low pH while it is negligible in the low concentration range at all pH tested, suggesting that the removal of fluoride using Al-SOJR is limited only from dilute solution lower than 30 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.

3.9. Desorption studies

Effective elution of adsorbed fluoride from the saturated gels is very important for the regeneration of adsorbents. The result shown in Fig. 3 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^{3+} ion as mentioned earlier. The desorption studies of fluoride from fluoride adsorbed gel at different concentrations of NaOH is illustrated in Fig. 9, 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.
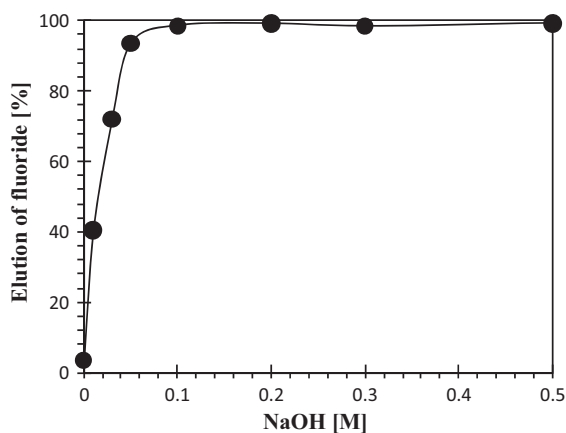

Fig. 8. Leakage of Al(III) from the gel at different fluoride concentrations. *Conditions*: volume of solution = 10 cm^3, weight of gel = 10 mg, shaking time = 24 h, temperature = 30 °C.

Fig. 9. Desorption of fluoride from saturated Al-SOJR using alkaline solution. *Conditions*: volume of eluent solution = 10 cm^3, weight of gel = 10 mg, adsorbed fluoride in the gel = 0.79 mmol/dm^3, temperature = 30 °C.

4. Conclusion

The saponified orange juice residue prepared from orange waste can be easily converted into ligand exchange 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 NO_3^-, Cl^- and Na^+ ions have negligible effect on fluoride removal capacity whereas the presence of co-existing SO_4^{2-} and HCO_3^- retard the fluoride removal capacity in small extent. The adsorbed fluoride was successfully eluted 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.

Acknowledgement

References

[1] S.K. Jha, A.K. Nayak, Y.K. Sharma, Fluoride toxicity effect in onion (*Allium cepa* L.) grown in contaminated soils, Chemosphere 76 (2009) 353–356.
[2] Y. Versessinina, M. Trapido, V. Ahelik, R. Munter, Fluoride in drinking water: the problem and its possible solution, Proc. Estonian Acad. Sci. Chem. 50 (2001) 81–88.
[3] C.J. Huang, J.C. Liu, Precipitate floatation of fluoride containing wastewater from semiconductor manufacturer, Water Res. 33 (1999) 3403–3412.
[4] B.D. Turner, P. Binning, S.L.S. Stipp, Fluoride removal by calcite: evidence for fluorite precipitation and surface adsorption, Environ. Sci. Technol. 39 (2005) 9561–9568.
[5] S. Samatya, H. Mijuki, Y. Ito, H. Kawakita, K. Uezu, The effect of polystyrene as a progen on the fluoride ion sorption of Zr^{4+}-surface immobilized resin, React. Funct. Polym. 70 (2010) 63–68.
[6] T. Wajima, Y. Umeta, S. Narita, K. Sugawara, Adsorption behavior of fluoride ion using a titanium hydroxide derived adsorbent, Desalination 249 (2009) 323–330.
[7] X. Xu, J.O. Burgess, Compressive strength, fluoride release and recharge of fluoride-releasing materials, Biomaterials 24 (2003) 2451–2461.
[8] X. Fan, D.J. Parker, M.D. Smith, Adsorption kinetics of fluoride on low cost materials, Water Res. 37 (2003) 4929–4937.
[9] F. Durmaz, H. Kara, Y. Cengeloglu, M. Ersoz, Fluoride removal by Donnan dialysis with anion exchange membranes, Desalination 177 (2005) 51–57.
[10] J. Wioeniewski, A. Rozanska, Donnan dialysis for hardness removal from water before electrodialytic desalination, Desalination 212 (2007) 251–260.
[11] G. Zhang, Y. Gao, Y. Zhang, P. Gu, Removal of fluoride from drinking water by membrane coagulation reactor, Desalination 177 (2005) 143–155.
[12] N. Drouiche, N. Graffour, H. Lounici, N. Mameri, A. Maallemi, H. Mahmoudi, Electrochemical treatment of chemical mechanical polishing wastewater: removal of fluoride-sludge characteristics-operating cost, Desalination 223 (2008) 134–142.
[13] C.Y. Hu, S.L. Lo, W.H. Kuan, Y.D. Lee, Removal of fluoride from semiconductor wastewater by electro-coagulation flotation, Water Res. 39 (2005) 895–901.
[14] X.P. Liao, B. Shi, Adsorption of fluoride on zirconium(IV)-impregnated collagen fiber, Environ. Sci. Technol. 39 (2005) 4628–4632.
[15] S. Sinha, K. Pandey, D. Mohan, K.P. Singh, Removal of fluoride from aqueous solution by *Eichhornia crassipes* biomass and its carbonized form, Ind. Eng. Chem. Res. 42 (2003) 6911–6918.
[16] L. Fang, K.N. Ghimire, M. Kuriyama, K. Inoue, K. Makino, Removal of fluoride using some lanthanum loaded adsorbent with different functional groups and polymer matrices, Chem. Technol. Biotechnol. 78 (2003) 1038–1047.
[17] http://www.necf.jp/solution-service/eco/environmentalpreservation/fluoride/index.html.
[18] O. Mikeš, High-performance liquid chromatography of biopolymers and biooligomers, part A: principles, materials and techniques, J. Chromatogr. Libr. 41A (1988) A70.
[19] S. Kagne, S. Jagtap, D. Thakare, S. Devotta, S.S. Rayalu, Bleaching powder: a versatile adsorbent for the removal of fluoride from aqueous solution, Desalination 243 (2009) 22–31.
[20] M. Islam, R.K. Patel, Evaluation of removal of fluoride from aqueous solution using quick lime, J. Hazard. Mater. 143 (2007) 303–310.
[21] G. Alagumuthu, M. Rajan, Equilibrium kinetics of adsorption of fluoride on to zirconium-impregnated cashew nut shell carbon, Chem. Eng. J. 158 (2010) 451–457.
[22] N. Viswanathan, C.S. Sundaram, S. Meenakshi, Sorption behavior of fluoride on carboxylated cross-linked chitosan beads, Colloids Surf. B: Biointerfaces 68 (2009) 48–54.
[23] S. Samatya, U. Yusksel, M. Yuksel, N. Kabay, Removal of fluoride from water by metal ions (Al^{+3}, La^{+3} and ZrO^{+2}) loaded natural zeolite, Sep. Sci. Technol. 42 (2007) 2033–2047.
[24] V.S. Mohan, S.V. Ramanaiah, B. Rajkumar, P.N. Sharma, Biosorption of fluoride from aqueous solution onto algal spirogyra IO1 and evaluation of adsorption kinetics, Bioresour. Technol. 98 (2007) 1006–1011.
[25] D. Thakre, S. Jagtap, A. Bansiwal, N. Labhsetwar, S. Rayalu, Synthesis of La-incorporated chitosan beads for fluoride removal from water, J. Fluorine Chem. 131 (2010) 373–377.
[26] Y. Zhou, C. Yu, Y. Shan, Adsorption of fluoride from aqueous solution on La^{3+}-impregnated cross-linked gelatin, Sep. Purif. Technol. 36 (2004) 89–94.
[27] N. Viswanathan, S. Meenakshi, Development of chitosan supported Zr(IV)–tungstophosphate composite for fluoride removal, J. Hazard. Mater. 176 (2010) 459–465.
[28] Y. Zhao, X. Li, L. Liu, F. Chen, Fluoride removal by Fe(III)-loaded ligand exchange cotton cellulose adsorbent from drinking water, Carbohydr. Polym. 72 (2008) 144–150.
[29] X. Wu, Y. Zhang, X. Dou, M. Yang, Fluoride removal performance of novel Fe–Al–Ce trimetal oxide adsorbent, Chemosphere 69 (2007) 1758–1764.
[30] Y. Tang, T. Gaun, N. Gao, J. Wang, Fluoride adsorption on activated alumina: modeling the effect of pH and competing ions, Physicochem. Eng. Aspects 337 (2009) 33–38.
[31] R.P. Dhakal, K.N. Ghimire, K. Inoue, Adsorptive separation of heavy metals from an aquatic environment using orange waste, Hydrometallurgy 79 (2005) 182–190.
[32] K.N. Ghimire, K. Inoue, H. Yamaguchi, K. Makino, T. Miyajima, Adsorptive separation of arsenate and arsenite anions from aqueous medium by using orange waste, Water Res. 37 (2003) 4945–4953.
[33] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, 6th ed., John Wiley and Sons, Inc., Singapore, 1999.
[34] B.K. Biswas, K. Inoue, K.N. Ghimire, S. Ohta, H. Harada, K. Ohto, H. Kawakita, Adsorption of phosphate from aquatic environment using metal-loaded orange waste, J. Colloid Interface Sci. 312 (2007) 214–223.
[35] Y. Tian, M. Wu, R. Liu, D. Wang, X. Lin, W. Liu, L. Ma, Y. Huang, Modified native cellulose fiber – a novel efficient adsorbent for both fluoride and arsenic, J. Hazard. Mater. 185 (2011) 93–100.
[36] V. Gannvir, K. Das, Removal of fluoride from drinking water using aluminium hydroxide coated rice straw ash, J. Hazard. Mater. 185 (2011) 1284–1294.
[37] P. Miretzky, C. Murroz, A.C. Chavez, Fluoride removal from aqueous solution by Ca-pretreated macrophyte biomass, Environ. Chem. 5 (2008) 68–72.
[38] N. Viswanathan, C.S. Sundaram, S. Meenakshi, Removal of fluoride from aqueous solution using protonated chitosan beads, J. Hazard. Mater. 161 (2009) 423–430.
[39] A.A.M. Daifullah, S.M. Yakout, S.A. Elreefy, Adsorption of fluoride in aqueous solution using KMnO$_4$ modified activated carbon derived from steam pyrolysis of rice straw, J. Hazard. Mater. 147 (2007) 633–643.