



Adsorptive Removal of Trace Concentration of Fluoride Using Orange Waste Treated Using Concentrated Sulfuric Acid

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Abstract: Novel adsorption gel was prepared from orange juice residue by using boiling concentrated sulfuric acid to create a condensation cross-linking reaction. It was then loaded with Zr(IV) ion to create adsorption sites for fluoride ions. This prepared gel was characterized by IR, EDX, XRD, SEM and chemical analysis. Fluoride adsorption was strongly pH dependent and maximum adsorption occurred at pH 3-4. The maximum adsorption capacity was drastically improved by loading Zr(IV) from 0.21 mmol/g up to 0.71 mmol/g at 303 K. The thermodynamic parameters evaluated from adsorption isotherms at varying temperature suggested that adsorption of fluoride onto the present adsorbent is spontaneous and endothermic in nature. The adsorbed fluoride was successfully desorbed using dilute alkaline solution. Trace concentrations of fluoride contained in the actual waste plating solution was completely removed by adding small amounts of this adsorbent.

Keywords: Fluoride Removal, Adsorption, Orange Juice Residue, Sulfuric Acid Treatment, Zr(IV) Loading

1. Introduction

Fluoride is widespread in the environment: water, air, vegetation and in the Earth's crust which can enter ground water by natural processes [1]. An appropriate concentration of fluoride in drinking water is required for preventing dental damage but long term ingestion of water that contains excess amount of fluoride causes disease such as skeletal and teeth damage, paralysis of volition, cancer etc. [2, 3]. 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, where lime is added in order to convert fluoride ion into water insoluble precipitates of calcium fluoride, CaF₂. However, the lowest fluoride concentration which can be theoretically achieved by this method is 5 mg/dm³ based on the solubility of calcium fluoride, and the lowest fluoride concentration practically achieved is usually in the range of 10-20 mg/dm³ [7], which requires further treatment to meet the maximum acceptable contaminant level of fluoride (< 0.8 mg/dm³) discharged into the environment in Japan [6, 8]. Thus, lime precipitation method is usually coupled with further treatment such as an aluminum

co-precipitation method to remove the remaining trace concentrations of fluoride [9]. In this method, aluminum sulfate or aluminum chloride is added and pH is adjusted to form precipitates of aluminum hydroxide, onto which trace concentrations of fluoride is adsorbed and co-precipitated. Although this method can successfully lower the fluoride concentration down to the WHO (1.5 mg/dm^3) and Japanese environmental standards (0.8 mg/dm^3) [10], it suffers from various disadvantages such as the generation of huge amounts of sludge containing huge amounts of water which requires further treatment [9]. Donnan dialysis [10, 11] and membrane process [12] are also effective techniques for the removal of trace amounts of fluoride from water. However, since these methods are expensive for waste water treatment, their commercialization has not been achieved. Consequently, there is an urgent need to develop more efficient and low cost technology to remove such trace concentrations of fluoride.

In recent years, much attention has been attracted to adsorption technology using natural polymers or biomass wastes, biosorption, as an economical and environmentally benign technology [13, 14]. Adsorptive removal of fluoride effectively making use of natural polymers contained in various biomass wastes can be also expected as alternative to the above-mentioned techniques.

Huge volumes of juice are produced from oranges in many countries and areas including Japan. In orange juice factories in Japan, oranges, after harvesting, are mechanically peeled and pressed for juicing [15], where one half of orange by weight is converted into orange juice while another one half is remained as orange juice residue, which is abbreviated as OJR (Orange Juice Residue) hereafter. Majority of OJR has not been effectively used except for additives of cattle foods in Japan. In our previous work [16], gold (III) can be effectively and selectively adsorbed from acidic

chloride media on the gel prepared from OJR by treating in boiling concentrated sulfuric acid, which is abbreviated as ATOJR (Acid Treated Orange Juice Residue) hereafter, where the maximum amount of gold adsorption was as high as around $2 \text{ kg/kg-dry adsorbent}$, i.e. twice the amount of the dry adsorbent itself.

ATOJR principally consists of polysaccharides such as cellulose, hemicellulose and pectin as well as chlorophyll pigment and other low molecular weight compounds like limonene and so on. Pectin contains carboxyl groups as well as its methyl ester groups, which can be easily converted into carboxyl groups by saponification reaction using alkaline materials such as lime water. In order to effectively use OJR as adsorbents for cationic metal ions, such methyl ester portion should be converted into carboxyl groups which exhibit high affinity for cationic metal ions. In our other previous work [17], we studied the adsorptive removal of some heavy metals such as lead (II) using OJR treated by the saponification reaction using calcium hydroxide, which is abbreviated as SOJR (Saponified Orange Juice Residue) hereafter. Furthermore, we also studied the adsorptive removal of trace concentrations of fluoride using SOJR loaded with high valent metal ions such as aluminum (III), tin (IV), lanthanum (III),

titanium (IV) and zirconium (IV) [18, 19]. Although the metal loaded SOJR was able to successfully remove trace concentrations of fluoride, it suffered from a problem of high production cost because large volume of washing water was required to remove residual calcium and water soluble organics. In order to resolve this problem, we also prepared another type of adsorption gel using dried orange juice residue which is marketed as additive of cattle food [20]. This type of gel is abbreviated as DOJR (Dried Orange Juice Residue) hereafter. In these works, it was demonstrated that high valent metal ions, zirconium (IV) in particular, loaded onto SOJR or DOJR exhibit high selectivity to fluoride ion over other anionic species such as sulfate and chloride. However, both SOJR and DOJR gels suffered from another problem of decaying which generates odor during long time use, impeding its practical use. In the present work, in order to resolve the above-mentioned problems and extend the field of effective use of OJR, we investigated the feasibility of ATOJR to be employed as the adsorption gel for removing trace concentrations of fluoride from aquatic environments. In this case, we selected Zr(IV) ion as the loaded metal ion onto ATOJR because it exhibited highest adsorption capacity for fluoride among the metal ions tested in the case of SOJR [18, 19].

2. Materials and Method

2.1. Chemicals and Instrumentation

All the chemicals employed in this study were of pure reagent grade chemicals and used directly without further purification. Samples of sodium fluoride (NaF), zirconium (IV) oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) and sulfuric acid (H_2SO_4 , 96%) were purchased from Wako Chemical Co. Ltd., Japan. The stock solution (1000 mg/L) of fluoride was prepared by dissolving 1.05 g of NaF in 500 mL of deionized water. The working solutions were freshly prepared by diluting the stock solution at the time of experiment. The sample of the fluoride containing waste plating solution employed in this study was kindly provided by the Federation of Electro Plating Industry Association, Japan. For the pH adjustment, diluted nitric acid and sodium hydroxide (0.1 M each ($\text{M} = \text{mol/L}$)), also purchased from Wako Chemicals Co. Ltd., Japan, were used. The pH of the solution was measured with the help of a TOA DKK, HM-30R pH meter. The elemental compositions of ATOJR before and after metal loading were measured by using an energy dispersive X-ray spectrometer (Shimadzu model, EDX-800HS). The total amount of Zr(IV) loaded onto ATOJR was measured after complete dissolution with aqua-regia by using an inductively coupled plasma atomic emission spectrometer (ICP-AES, Shimadzu model ICPS 8100). The concentration of fluoride before and after adsorption was measured by using an ion chromatography (Dionex model ICS-1500) equipped with separation column (IonPac AS12A, $4 \times 200 \text{ mm}$), guard column (IonPac AG $4 \times 50 \text{ mm}$) and automatic regenerating suppressor (A SRS 300 4mm).

2.2. Preparation of the Adsorption Gel

The OJR, obtained just after juicing, was provided by the JA Beverage Saga Co., Ltd., Japan and it was employed to prepare the ATOJR. To avoid the dissolution of the adsorbent in aqueous solutions, OJR was cross-linked by means of condensation reaction using concentrated sulfuric acid, where it was first washed several times using distilled water and dried in a convection oven at 343K, followed by grinding into fine powder using a Dalton model P-3S power mill. Fifteen grams of this fine powder of OJR was mixed together with 30 mL of concentrated sulfuric acid (96%) in a 250 mL eggplant flask, followed by refluxing the mixture for 24 h at 373K to achieve the cross-linking *via* condensation reaction. After 24 h, the mixture was neutralized using sodium bicarbonate and the cross-linked product was separated by filtration using Advantec 5C 90 mm filter paper. It was further washed several times with distilled water until a neutral pH, after which it was dried in a convection oven at 343K overnight. To create the adsorption sites for fluoride, Zr(IV) was then loaded onto this prepared ATOJR, where 3 g of ATOJR was mixed together with 500 mL of 0.1 M Zr(IV) solution at pH 2.23, which was stirred for 24 h at 303 K for the loading reaction. The mixture was then filtered using the same filter paper and the filter cake was washed several times with distilled water to remove unadsorbed Zr(IV) ions and was dried in a convection oven at 343K. Thus prepared Zr(IV) loaded ATOJR is abbreviated as Zr-ATOJR hereafter.

2.3. Loading Test of Zr(IV) Ion

In order to evaluate the adsorption behavior of ATOJR for Zr(IV), its adsorption test was carried out batch wise at a solid liquid ratio of 1.5 g/L by using 0.5 mM of Zr(IV) solution at varying pH. To investigate the maximum adsorption capacity for Zr(IV) ion, an adsorption isotherm test was carried out by varying the concentration of Zr(IV) ranging from 0.5 up to 11 mM at pH 2.2 at 303K. The percent loading and amount of Zr(IV) loaded onto the tested adsorbents were calculated according to the mass balance relationship expressed by equation (1) and (2), respectively.

$$\%A = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

$$q = \frac{C_i - C_e}{W} \times V \quad (2)$$

% A: percent loading of Zr(IV) loaded onto the tested adsorbents

q : amount of Zr(IV) loaded onto the tested adsorbents

C_i : initial concentrations of fluoride (mM)

C_e : equilibrium concentrations of fluoride (mM)

W : weight of the adsorbent (g-dry)

V : volume of test solution (L)

Further, to evaluate the content of Zr(IV) in Zr-ATOJR, Zr-ATOJR was totally dissolved by mixing 50 mg of the loaded adsorbent together with 10 mL of aqua regia, which was stirred for 24 h to ensure complete dissolution. After filtration, the concentration of Zr(IV) in the filtrate was measured using an ICP-AES.

2.4. Adsorption Tests of Fluoride onto Zr-ATOJR

Although equilibrium was found to be achieved within 2 h for all cases in the preliminary experiment, adsorbents and test solutions were shaken for 24 h in the subsequent adsorption test in order to ensure complete equilibrium. The adsorption test of fluoride ion was carried out by mixing 15 mg of Zr-ATOJR together with 10 mL of 0.5 mM fluoride solution at 303K for 24 h at different pH to investigate the effect of pH on fluoride adsorption onto Zr-ATOJR, where dilute solutions of HNO₃ or NaOH were used to adjust the pH of the fluoride solution. After filtration, the filtrate was analyzed for residual fluoride concentration by using an ion chromatography. The adsorption isotherms tests onto ATOJR and Zr-ATOJR were carried out by mixing 15 mg of the adsorbent together with 10 mL of fluoride solution for 24 h at varying initial concentrations of fluoride ion (0.5 – 6 mM) at pH 4. For the practical application of Zr-ATOJR, the removal of fluoride from actual waste plating solution was tested by mixing 10 mL of actual waste plating solution with different amount of Zr-ATOJR (5 – 100 mg), which was shaken for 24 h at 303K. The percentage adsorption and uptake capacity (q , mmol/g) were calculated according to equation (1) and (2), respectively.

2.5. Desorption of Loaded Fluoride

For the desorption test, fluoride loaded Zr-ATOJR was prepared by shaking 500 mg of Zr-ATOJR together with 500 mL of fluoride solution (0.63 mM) at pH 4 for 24 h at 303K. After filtration, filtrate was analyzed for fluoride ion concentration by using an ion chromatography. The filter cake was washed several times with water to remove un-adsorbed fluoride and oven dried. The dried sample was used for the desorption tests.

The adsorbed fluoride was effectively desorbed from Zr-ATOJR by NaOH solution with insignificant leakage (<1%) of the loaded Zr(IV). To identify the optimum concentration of NaOH, 25 mg of fluoride loaded Zr-ATOJR was stirred together with 10 mL of NaOH solution at varying concentration from 0.01 to 2M for 24 h. After the filtration, filtrate was analyzed for fluoride ion concentration by using an ion chromatography. The percent desorption (% D) was calculated using equation (3).

$$\% D = (D_T/A_T) \times 100 \quad (3)$$

% D : percent desorption of fluoride

D_T : amount of desorbed fluoride (mg)

A_T : amount of adsorbed fluoride (mg)

3. Results and Discussion

3.1. Characterization of the Adsorbent

To identify the various functional groups contained in the adsorbent, analysis of a sample through FTIR spectra is an effective way of obtaining structural and bond information. Figure 1 shows the FTIR spectra of OJR and ATOJR before and after Zr(IV) loading. In the case of OJR, the feed material, sharp peaks were observed at around 3381, 2913, 1742 and 1683 cm^{-1} which are ascribed to the stretching vibration of OH, CH_2 , COO , and $\text{C}=\text{O}$ groups. The hydroxyl peaks observed at 3381 cm^{-1} was flattened or became wider after the acid treatment, which is attributed to the cross-linking condensation reaction between the hydroxyl groups of different polysaccharides in OJR, which was further confirmed by the appearance of new absorption band of C-O-C linkage at 1051 cm^{-1} , suggesting that cross-linking reactions of different orange polysaccharides takes place by the treatment using concentrated sulfuric acid. In the case of Zr-ATOJR, the peaks at 1740 cm^{-1} observed in ATOJR, which is ascribed to carboxylic acid groups, completely disappeared while two new peaks ascribed to metal carboxylate, specifically zirconium carboxylate, were observed at around 1600 and 1398 cm^{-1} , indicating that Zr(IV) ions were loaded onto the carboxylic acid functional groups of ATOJR during the loading reaction. The qualitative analysis of various elements present in the samples of ATOJR and Zr-ATOJR were carried out using EDX and the results are presented in figures 2 (a) and (b), respectively. As seen from figure. 2 (a), there appear the intense peaks of C, O, Na, Si, P, S, K, Ca, and Fe, whereas, after Zr(IV) loading, new peaks corresponding to Zr are appeared at energy values around 7.9, 9.02 and 9.41 keV as shown in figure. 2 (b), which is one of the strong pieces of evidence that

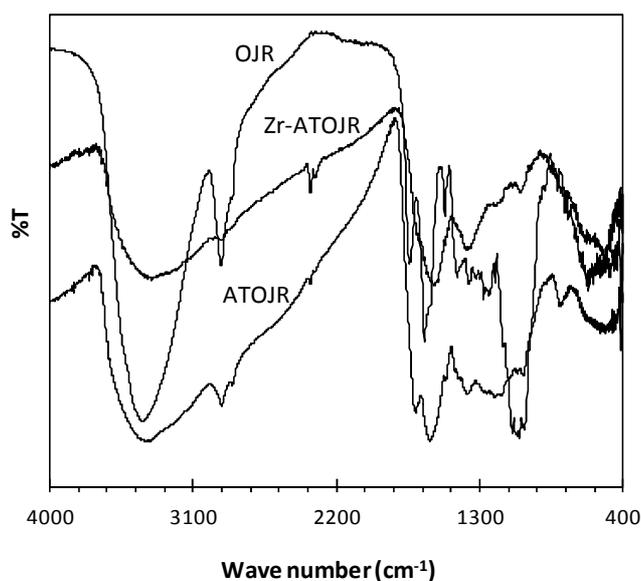


Figure 1. FTIR spectra of OJR, ATOJR and Zr-ATOJR.

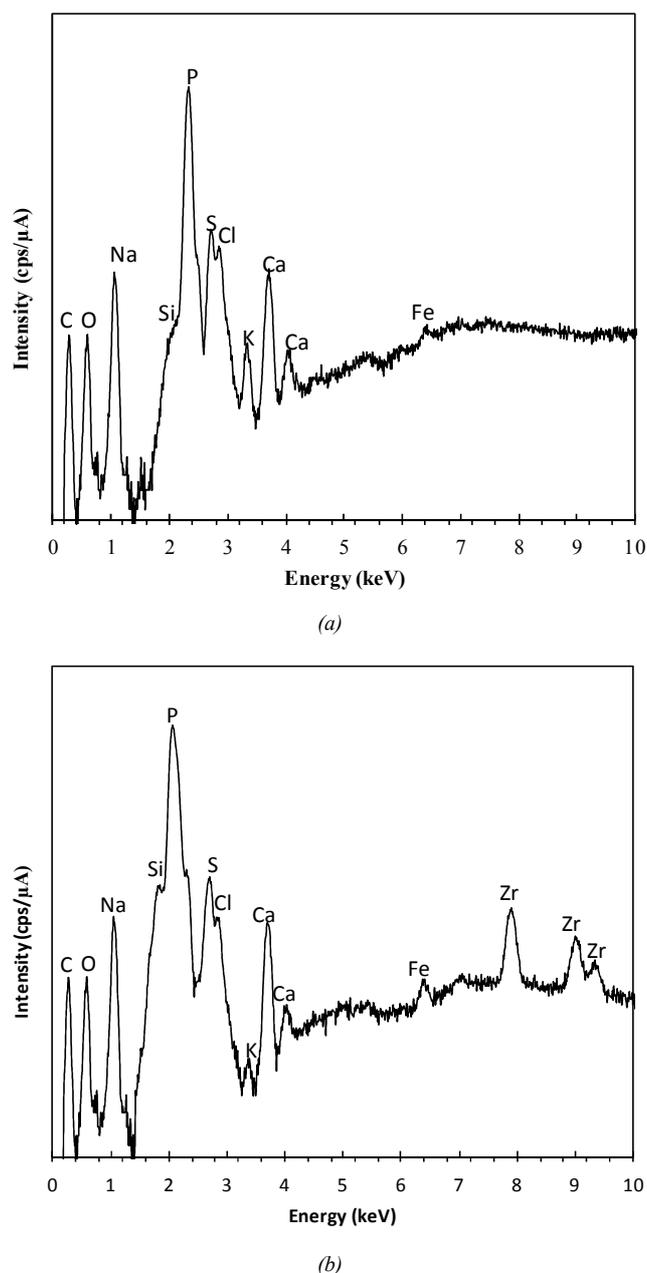


Figure 2. EDX spectra of ATOJR (a) and Zr-ATOJR(b).

ATOJR effectively adsorbed Zr(IV) ion. Figure 3 shows the XRD pattern of Zr-ATOJR where sharp peaks corresponding to crystalline structure are not observed, suggesting the amorphous nature of this adsorbent. Such an amorphous structure allows better accessibility of fluoride ions into the inside of adsorbent particle to reach adsorption sites by easy penetration. The existence of hydrated zirconium oxide in the sample of Zr-ATOJR was confirmed from the observation of broad peaks of hydrated zirconium oxide at 2θ values of 15-34 and 40-61. Figure 4 shows the image of scanning electron micrograph (SEM) of ATOJR. It is evident from this figure that the surface of ATOJR is smooth and lacked any cracks or holes, suggesting a non-porous structure of ATOJR.

The amount of Zr(IV) loaded onto Zr-ATOJR was evaluated to be 0.78 mmol/g by dissolving the sample of

Zr-ATOJR in aqua regia at a solid/liquid ratio of 5 g/L, followed by the measurement of Zr(IV) concentration in the filtrate by using an ICP-AES.

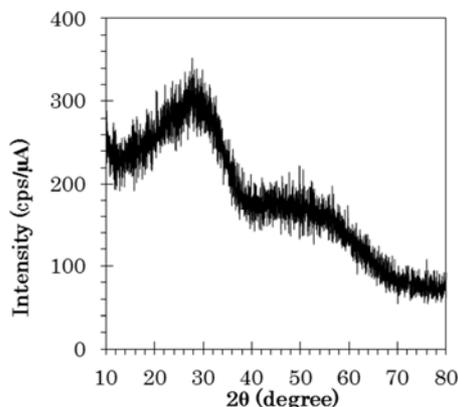


Figure 3. XRD pattern of Zr-ATOJR.

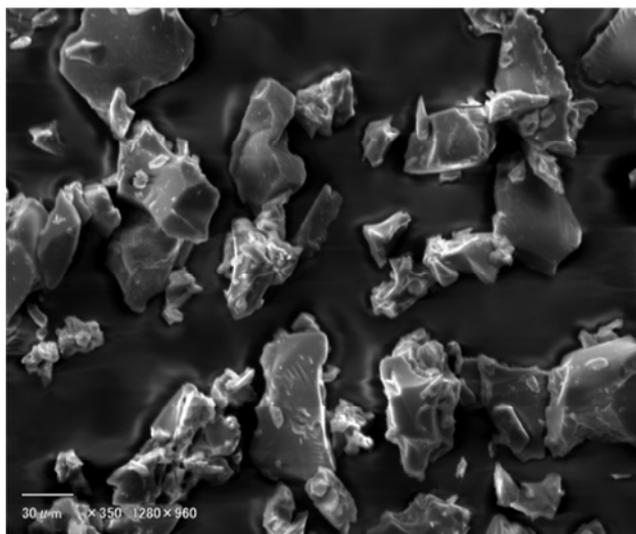
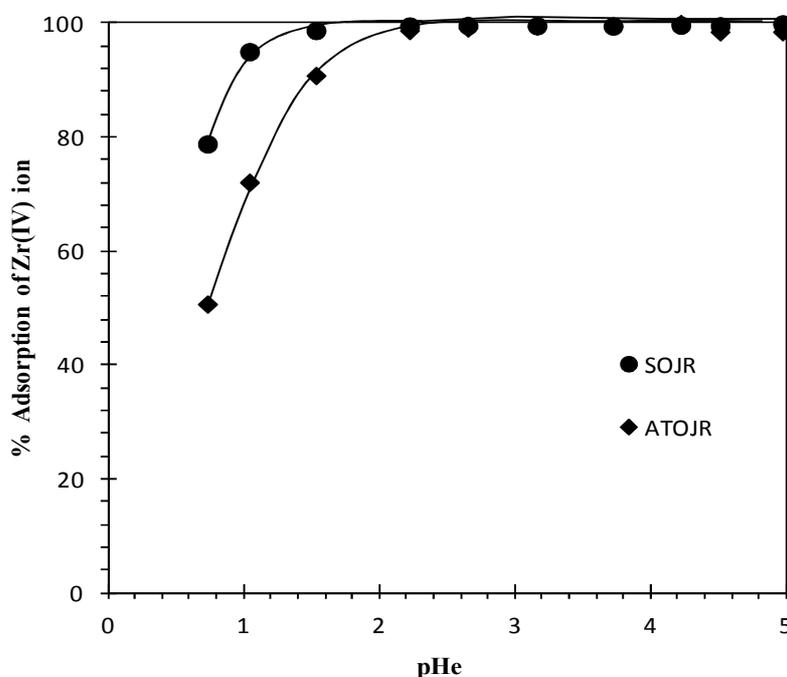


Figure 4. SEM image of ATOJR.Zr(IV).



Conditions: concentration of Zr(IV) = 0.5 mmol/l, solid liquid ratio = 1.5 g/l, temperature = 303K, shaking time = 24 h.

Figure 5. % adsorption of Zr(IV) at different pH at equilibrium on ATOJR and SOJR for comparison.

3.2. Loading Behavior of Zr(IV) onto ATOJR

Because fluoride is adsorbed via Zr(IV) ion loaded onto ATOJR, adsorption behavior of Zr(IV) on ATOJR was investigated prior to the adsorption of fluoride on Zr-ATOJR to find the optimum loading condition of Zr(IV) onto ATOJR. Figure 5 shows the % adsorption of Zr(IV) onto ATOJR at varying pH at equilibrium together with that onto SOJR for comparison, which suggests that adsorption of Zr(IV) increased from 50.2% to 90.8% with increasing pH from 0.75

to 1.53 whereas more than 98% of was adsorbed at pH 2.2, from which the loading of Zr(IV) was decided to be carried out at pH around 2.2 for the preparation of Zr-ATOJR. Similarly, in the case of SOJR reported in the previous work [17], the adsorption of Zr(IV) was also increased from 78.5% to 97.3% by increasing pH from 0.74 to 1.56 and it was nearly 100% at around pH 2.2, which is exactly the similar trend with that of ATOJR.

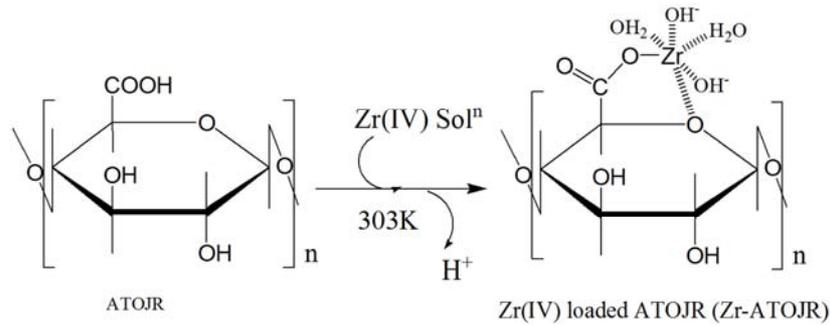


Figure 6. Loading mechanism of Zr(IV) ion onto ATOJR via exchange reaction.

The nature of increasing adsorption of Zr(IV) with increasing pH in both gels suggests that adsorption of Zr(IV) onto these adsorbents takes place in the same manner of cation exchange mechanism between hydrogen ions of carboxylic groups of pectic acid contained in ATOJR and SOJR and cationic Zr(IV) ion as depicted by Figure 6.

Further, pH of Zr(IV) solution after the adsorption on ATOJR was observed to be decreased, which is attributable to the release of hydrogen ions by this cation exchange reaction. For the determination of loading capacity of ATOJR for Zr(IV), adsorption isotherms of Zr(IV) on ATOJR was investigated by varying the Zr(IV) concentration (0.5–11 mM) at pH 2.2. It was found that adsorption of Zr(IV) on ATOJR increases with increasing equilibrium concentration of Zr(IV) at lower concentration and becomes constant or plateau at higher concentration, suggesting the Langmuir type monolayer adsorption of Zr(IV) by ATOJR. From this adsorption isotherm test, the maximum loading capacity of ATOJR for Zr(IV) (q_{\max} , mmol/g) was evaluated as 0.83 mmol/g, which is inferior to those of SOJR (= 1.62 mmol/g [19]) and DOJR (= 0.90 mmol/g [20]). Such difference in the loading capacity is inferred to be ascribed to the treatment of OJR; i.e. in the cases of SOJR and DOJR, number of functional groups of pectic acid effective for metal loading is increased by saponification reaction using calcium hydroxide whereas it is decreased by condensation reaction using concentrated sulfuric acid between functional groups of pectic acid and those of cellulose. The loading capacity for Zr(IV) directly affects the adsorption capacity for fluoride as will be mentioned later.

3.3. Effect of pH and Adsorption Mechanism of Fluoride

Figure 7 shows the effect of equilibrium pH on the adsorption of fluoride onto ATOJR and Zr-ATOJR as well as Zr-SOJR for comparison at varying pH ranging from 2 up to 12. As seen in this figure, adsorption of fluoride is markedly dependent on pH for all cases. It is slightly increased with increasing pH in the pH range 1-4, and decreased sharply at higher pH. Maximum adsorption of fluoride is found to occur at pH around 4-5 for all cases. It is evidently observed that the adsorption is improved drastically after Zr(IV) loading, which is attributed to the development of new adsorption sites caused by the loaded Zr(IV) in addition to those based on Ca for anionic species of fluoride as described as follows. From elementally analysis shown in figure 2(a), ATOJR itself

contains some metal ions like Na, Si, K, Ca, and Fe which may be bonded to orange pectic acid to form metal pectate.

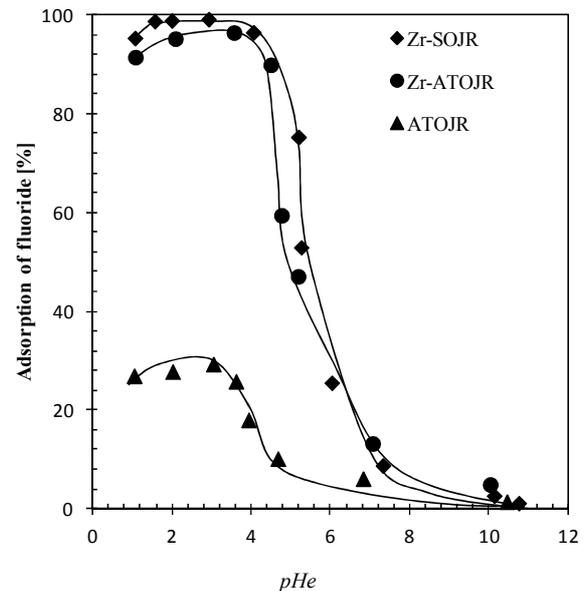
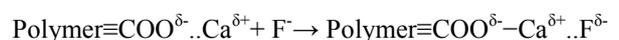


Figure 7. Influence of pH at equilibrium on % adsorption of fluoride on ATOJR and Zr-ATOJR. Conditions: fluoride solution = 0.5 mmol/l, solid-liquid ratio = 1.5 g/l, temperature = 303K, shaking time = 24 h.

Among these metal ions, Ca exhibits some affinity towards fluoride ion where adsorption of fluoride takes place by electrostatic interaction between positive charged calcium ion contained in ATOJR and fluoride fluoride ion as shown below.



The pH effect on the adsorption on Zr-ATOJR quite resembles that on Zr-SOJR. Because adsorption behavior of anionic species onto metal-loaded adsorbents is governed by the nature of the loaded metal ions, this tendency is considered to be natural. In the case of Zr-ATOJR and Zr-SOJR, the % adsorption of fluoride reaches 91.3% and 97.3%, respectively, at pH around 1 which was observed to be increased with increasing pH reaching a maximum at pH around 3-4, where more than 98% removal of fluoride was achieved in both the cases. It was gradually decreased with a further increase in pH of the solution and no or negligible adsorption of fluoride was observed at pH higher than 10 for all three kinds of adsorbents tested. With increasing pH, concentration of hydroxyl ion that

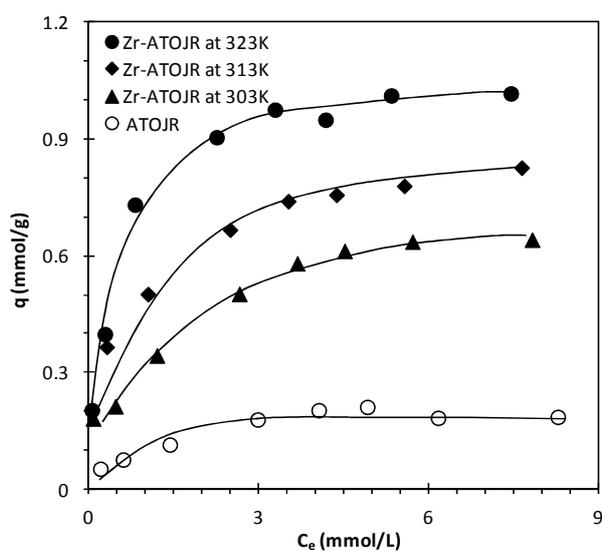
potentially competes with fluoride ions during adsorption process increases, which results in the decrease in adsorption of fluoride. Because, at pH lower than 2, more than 95% of fluoride exists in the form of nonionic form, i.e. hydrofluoric acid (HF), which was hardly adsorbed onto these adsorbents, the adsorption is ultimately decreased. Similar observations have been also reported on the adsorption behavior of other Zr(IV) loaded adsorbents, such as Zr(IV) loaded leather fiber [21], Zr(IV) loaded cross-linked seaweed [22] and Zr(IV) loaded carboxylated chitosan [23], which is attributable to the fact that all of these adsorbents employ Zr(IV) as the loaded metal ion, as mentioned earlier. Consequently, the adsorption mechanism of fluoride on Zr-ATOJR can be clearly interpreted similarly to the case of Zr-SOJR by the following reactions.



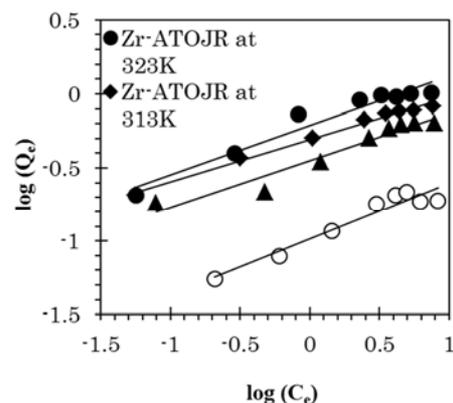
In the case of loading high valent metal ion like Zr(IV) onto the polymer matrix of orange pectic acid, the neutralization of all the positive charge of Zr(IV) only by the carboxylic groups of pectic acid contained in ATOJR or SOJR is impossible because of steric hindrance caused by large polymers of orange pectic acid. Consequently, some of the positive charges of Zr(IV) are neutralized by hydroxyl ions in aqueous solution. These hydroxyl ions are considered to be exchanged with fluoride ions during fluoride adsorption according to the ligand exchange reaction as shown above.

3.4. Adsorption Isotherm of Fluoride

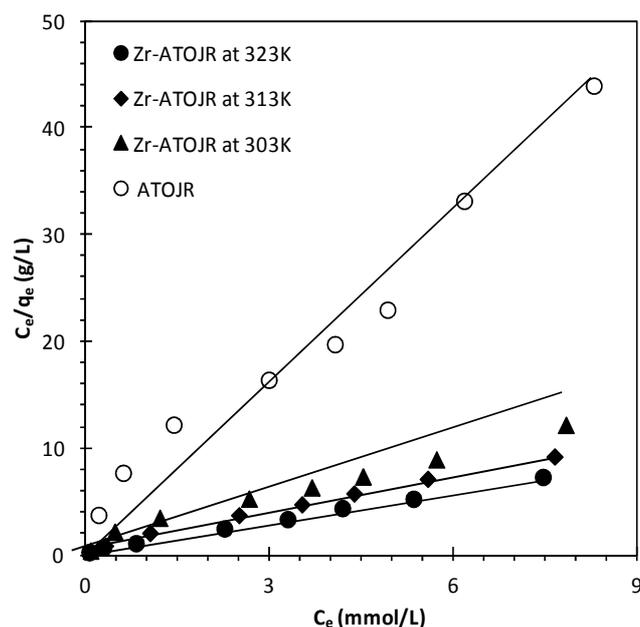
Figure 8(a) presents the adsorption isotherms of fluoride on Zr-ATOJR at varying temperatures from 303 to 323K, as well as that on ATOJR at 303K, for comparison. The result shows that the adsorption of fluoride increases with increasing fluoride ion concentration at low concentration while it tends to approach constant values in all the cases at high concentration and it increases with increasing temperature, suggesting an endothermic nature of adsorption which was further proved by calculating thermodynamic parameters in the later section.



(a). Adsorption isotherm.



(b). Freundlich plot.



(c). Langmuir plot.

Figure 8. Adsorption Isotherm.

Adsorption isotherm of fluoride on Zr-ATOJR at varying temperatures and on ATOJR at 303 K. Conditions: pH = 4, volume of solution = 10 ml, weight of adsorbent = 15 mg, shaking time = 24 h.

Freundlich and Langmuir adsorption isotherm equations expressed by equations (4) and (5), respectively, were used to interpret these experimental results.

$$\log q_e = \log K_F + (1/n) \log C_e \quad (5)$$

C_e : equilibrium concentration of fluoride in solution (mM)
 q_e : amount of fluoride adsorbed per unit mass of adsorbent at equilibrium (mmol/g)

K_F and n ; Freundlich constants related to the adsorption capacity and adsorption intensity.

The values K_F and n can be calculated from the intercept and slope of the linear Freundlich plot of $\log q_e$ versus $\log C_e$ as shown in Figure 8(b). Thus evaluated values are listed in table 1. On the other hand, the Langmuir isotherm model assumes monolayer coverage where all the active adsorption

sites have equal affinity for adsorbate molecules.

$$C_e/q_e = 1/q_{\max}b + C_e/q_{\max} \quad (6)$$

q_{\max} : maximum adsorption capacity of the adsorbent for fluoride ion (mmol/g)

b : adsorption equilibrium constant related to the free energy change during adsorption process (L/mmol)

The values of q_{\max} and b were evaluated from the slope and intercept of the linear plot of C_e/q_e versus C_e as shown in Figure 8(c), which are also listed in Table 1. From this table, it is evident that all experimental data are more satisfactorily fitted with the Langmuir isotherm with a higher correlation coefficient ($r^2 = 0.99$) than the Freundlich isotherm model ($r^2 < 0.91$), suggesting that the Langmuir isotherm model is suitable for the modeling of this adsorption system; that is, it can be concluded that the adsorption of fluoride onto ATOJR and Zr-ATOJR takes place according to the Langmuir's monolayer adsorption model. From the comparison of the maximum fluoride uptake capacity of ATOJR with that on Zr-ATOJR at 303K, it is found to be drastically improved after Zr(IV) loading (from 0.21 up to 0.71 mmol/g) also as mentioned earlier, which is attributable to the development of more active adsorption sites on ATOJR by Zr(IV) loading. A similar type of adsorption behavior was observed in the case of Zr-SOJR in our previous study [19], indicating similar types of adsorption mechanism may take place in both the cases. From the temperature dependency of the adsorption of fluoride on Zr-ATOJR, the thermodynamic parameters were calculated. That is, from the Langmuir's adsorption equilibrium constants, b , at different temperatures, thermodynamic parameters such as Gibbs free energy change, enthalpy change and entropy change were calculated according to the following relationships:

Table 1. Langmuir and Freundlich isotherm parameters for the adsorption of fluoride onto Zr-ATOJR at different temperatures and its comparison with ATOJR itself.

Adsorbents and temperature	pH	Langmuir parameters		
		q_{\max} (mmol/g)	b (L/mmol)	r^2
Zr-ATOJR at 303K	4	0.71	1.14	0.98
Zr-ATOJR at 313K	4	0.86	2.19	0.99
Zr-ATOJR at 323K	4	1.05	3.36	0.99
ATOJR at 303K	4	0.21	1.40	0.98
Adsorbents and temperature	pH	Freundlich parameters		
		K_F	b	r^2
Zr-ATOJR at 303K	4	0.71	1.14	0.98
Zr-ATOJR at 313K	4	0.86	2.19	0.99
Zr-ATOJR at 323K	4	1.05	3.36	0.99
ATOJR at 303K	4	0.21	1.40	0.98

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

$$\Delta G = -RT \ln b \quad (8)$$

ΔG : Gibbs free energy change (kJ/mol)

ΔH : enthalpy change (kJ/mol)

ΔS : entropy change (kJ/mol K)

R : gas constant (kJ/mol K)

T : temperature (K)

Combination of equations (6) and (7) gives

$$\ln b = -\Delta H/RT + \Delta S/R \quad (9)$$

Gibbs free energy change (ΔG) of the system for all temperatures were evaluated according to equation (7) as -0.34, -2.05 and -3.27 kJ/mol for 303, 313 and 323 K, respectively. On the other hand, enthalpy change (ΔH) and entropy change (ΔS) were determined as 44.03 kJ/mol and 146.7 J/mol K, respectively, from the slope and intercept of the Van't Hoff plot of $\ln b$ versus $1/T$, respectively, according to equation (8) as shown in Figure 9. The value of ΔG is negative for all the temperature and is decreased with the increase in temperature, indicating that the adsorption of fluoride on Zr-ATOJR is spontaneous at the tested range of temperatures. The positive value of enthalpy change confirms that the adsorption is endothermic in nature, whereas the positive value of entropy change suggests that the adsorption process leads to an increase in disorderness or randomness at the solid surface during the adsorption, which is possibly due to the release of coordinated hydroxyl ions *via* ligand exchange reaction with fluoride ion during adsorption process.

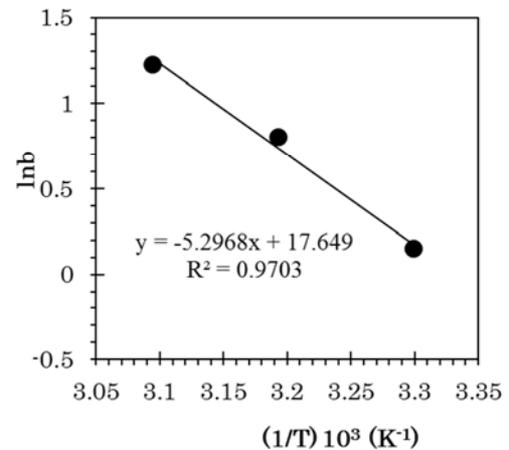


Figure 9. Van't Hoff's plot for the adsorption of fluoride on Zr-ATOJR.

3.5. Desorption of Loaded Fluoride

The desorption of fluoride from Zr-ATOJR is important to determine the extent of its recovery in addition to the regeneration of the adsorbents for repeated use. As shown in Figure 6, because negligible adsorption of fluoride on Zr-ATOJR is observed at pH higher than 10, dilute alkaline solutions are the candidate for the desorption of fluoride. Based on such expectation, the optimization of NaOH concentration was carried out by using varying concentration of NaOH (from 0.001 to 0.5 M) as shown in Figure 10. From the result shown in this figure, 0.1 M NaOH solution was found to be the optimum concentration to effectively desorb fluoride from the loaded adsorbent.

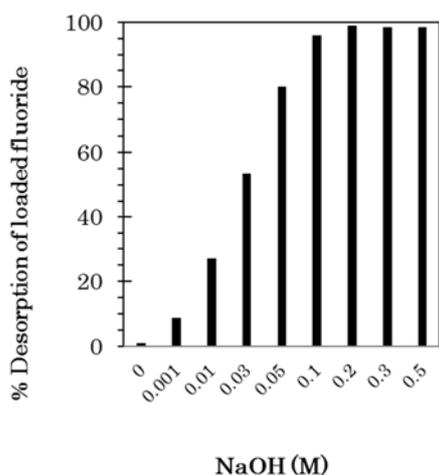


Figure 10. Desorption of fluoride from fluoride loaded Zr-ATOJR using varying concentrations of NaOH solution.

Conditions: amount of fluoride contained in fluoride loaded Zr-ATOJR = 12.8 mg/g, solid liquid ratio = 2.5 g/l, shaking time = 24 h, temperature = 303K

The desorption of fluoride is inferred to take place by the replacement of adsorbed fluoride by hydroxyl ions provided from NaOH solution as shown below.



3.6. Application of Zr-ATOJR to Remove Fluoride from Actual Waste Plating Solution

To evaluate the feasibility of Zr-ATOJR for the treatment of industrial waste water containing trace concentration of fluoride ion, the adsorption behavior for fluoride was investigated using actual waste plating solution containing several cationic species (Al^{3+} : 12.7 mg/L, Ca^{2+} : 28.9 mg/L, Si^{4+} : 37.5 mg/L, Fe^{3+} : 21.6 mg/L, Cu^{2+} : 8.1 mg/L and Zn^{2+} : 0.83 mg/L) as well as anionic species (F^- : 15.2 mg/L and SO_4^{2-} : 524 mg/L) by using Zr-ATOJR at varying solid liquid ratio.

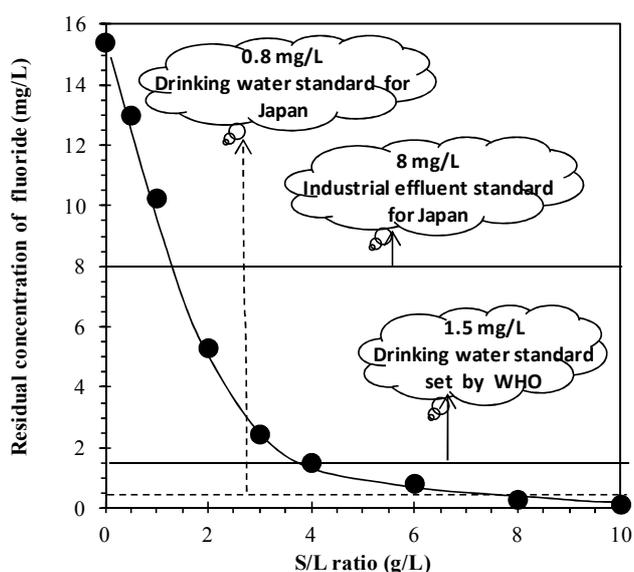


Figure 11. Application of Zr-ATOJR for the removal of trace concentration of fluoride from actual waste plating solution at different solid-liquid ratio.

Conditions: pH = 6.7, fluoride concentration = 15.2 mg/l, volume of test solution = 10 ml, shaking time = 24 h, temperature = 303K.

Figure 11 shows the residual concentration of fluoride ions in the waste plating solution after the adsorption onto Zr-ATOJR at varying solid liquid ratio at its native pH (pH = 6.7). It is evident from this figure that fluoride removal was increased with increasing solid liquid ratio and fluoride concentration was found to be lowered less than industrial effluent standard in Japan (8 mg/L) at the solid liquid ratio of 1g/L. It also suggests that, at the solid liquid ratio higher than 4 and 6 g/L, the maximum permissible level of fluoride in drinking water set by WHO (1.5 mg/L) and Japanese environmental standard (0.8 mg/L) can be cleared, respectively, whereas more than 8 g/L of solid liquid ratio is required to achieve 100% removal. Furthermore, since zirconium leakage from the gel was found to be very insignificant in this case, Zr-ATOJR investigated in this study can be expected as an excellent adsorption material to treat the waste plating solution containing trace amount of fluoride ion.

3.7. Comparative Studies with Other Adsorbents

Table 2 shows the comparison of maximum adsorption capacities of ATOJR and Zr-ATOJR investigated in this study with other adsorbents including Zr-SOJR reported in the literatures. Although the maximum adsorption capacities listed in this table were evaluated at different pH and different temperatures, they can be useful criteria for the comparison of adsorption capacity for process design in the actual operation in large industrial scale. It is clear from this table that the maximum adsorption capacity of Zr-ATOJR investigated in this work is higher than the majority of the adsorbents reported in the literature. The adsorption capacity of some metal loaded adsorbents like La-200CT, READF-(PG) and mixed rare earth oxide exhibits higher adsorption capacity for fluoride ions than Zr-ATOJR. Compared also with Zr-SOJR which uses the same feed material, orange juice residue (OJR), the maximum adsorption capacity on Zr-ATOJR (0.71 mmol/g) is lower than that on Zr-SOJR (1.20 mmol/g) at 303 K. This difference is attributable to the difference in the loading capacity for Zr(IV) between SOJR and ATOJR; i.e. that for SOJR is 1.62 mmol/g [17] while that for ATOJR is 0.83 mmol/g. This difference in the loading capacity is considered to be caused by the difference of the

treatments for OJR; i.e. functional groups of pectin (partly methyl-esterified pectic acid) are effectively saponified into pectic acid resulting in the increase in the number of metal bonding sites in the treatment of SOJR while, in the treatment of ATOJR, some of functional groups of pectin undergo the condensation reaction each other and together with other polysaccharides such as cellulose losing the sites for bonding metal ions though some of pectin functional groups are hydrolyzed into pectic acid by the aid of sulfuric acid. However, high-porous resins like READF-(PG) and La(III) loaded 200CT resins suffer from serious drawback of clogging of micro-pores of the resins by fine particles present in the fluoride containing waste water. The direct application of

mixed rare earth metal oxide looks more costly. In the case of Zr-SOJR, because it is prepared from wet orange juice residue, it should be prepared immediately after juicing to avoid decaying and, further, it requires much water washing as mentioned earlier accompanying the generation of large amount of waste water, which potentially increases the production cost of the adsorbent. Alternatively, Zr-ATOJR investigated in this study can be prepared from dried orange juice residue where more than 70% of waste water generation was reduced by cross-linking using sulfuric acid in addition to the 100% removal efficiency of fluoride from actual waste plating solution. Hence it appears more promising as a potential alternative for the treatment of fluoride polluted water.

Table 2. Comparison of the maximum adsorption capacities on Zr-ATOJR at varying temperatures and those of various adsorbents for fluoride ion.

Adsorbents	pH	q_{max} [mmol/g]	Ref.
Zr-ATOJR at 323K	4	1.05	This work
Zr-ATOJR at 313K	4	0.86	This work
Zr-ATOJR at 303K	4	0.71	This work
ATOJR at 303K	4	0.21	This work
Zr(IV) loaded SOJR at 303K	2.4	1.20	[19]
Zr(IV) loaded DOJR at 303K	4	1.43	[20]
La(III) loaded 200CT resin at 303K	6	1.34	[24]
Waste carbon slurry	7.5	0.23	[25]
Spirogyra species IO1	7	0.06	[26]
Synthetic nano-hydroxyapatite	5-6	0.24	[27]
Fe(III) loaded cotton cellulose	4	0.98	[28]
Alumina/chitosan composite	7	0.20	[29]
KMnO ₄ modified rice straw carbon	2	0.84	[30]
Zr impregnated coconut shell carbon	4	0.19	[31]
READF	3	2.10	[32]
Acid activated mud	5	0.15	[33]
Carboxylated crosslinked chitosan	7	0.58	[23]
Montmorillonite	6	0.01	[34]
Nano-hydroxyapatite/chitosan	7	0.11	[35]
Quick lime	-	0.87	[36]

4. Conclusion

Efficient adsorbent for fluoride was prepared by loading Zr(IV) onto OJR treated with concentrated sulfuric acid. The adsorption behavior of ATOJR for fluoride was drastically improved by loading Zr(IV) on ATOJR. This adsorption was found to be strongly pH dependent; i.e. nearly quantitative adsorption was observed at pH range 2–4 while only negligible adsorption was observed at pH greater than 10. From the adsorption isotherm study, the adsorption can be interpreted in terms of the Langmuir's monolayer adsorption theory. Thermodynamic study suggested that adsorption of fluoride is spontaneous and endothermic in nature. Fluoride loaded on Zr-ATOJR can be effectively desorbed by dilute alkali solutions. Adsorption/desorption mechanism was interpreted by the anion exchange between hydroxyl and fluoride ions. The Zr-ATOJR was found to be successfully applied for the removal of trace concentration of fluoride from actual waste plating solution.

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