



## Adsorptive removal of trace concentration of fluoride ion from water by using dried orange juice residue

Hari Paudyal<sup>a</sup>, Bimala Pangeni<sup>a</sup>, Katsutoshi Inoue<sup>a,\*</sup>, Hidetaka Kawakita<sup>a</sup>, Keisuke Ohto<sup>a</sup>, Kedar Nath Ghimire<sup>b</sup>, Hiroyuki Harada<sup>c</sup>, Shafiq Alam<sup>d</sup>

<sup>a</sup> Department of Applied Chemistry, Saga University, Honjo 1, Saga 840-8502, Japan

<sup>b</sup> Central Department of Chemistry, Tribhuvan University, Kirtipur, Kathmandu, Nepal

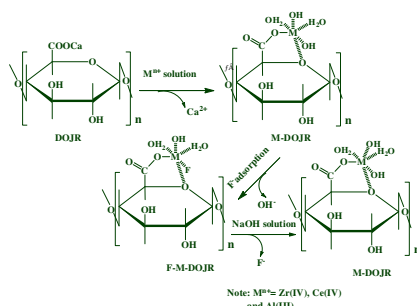
<sup>c</sup> Faculty of Life and Environmental Science, Prefectural University of Hiroshima, 562 Nanatsuka-cho, Shobaru, Hiroshima 727-0023, Japan

<sup>d</sup> Faculty of Engineering and Applied Science, Memorial University, St. John's, NL, Canada A1B 3X5

### HIGHLIGHTS

- Novel adsorbents for fluoride were prepared from low cost cattle food marketed in Japan.
- 100% Removal of trace concentration of fluoride ion from actual plating solution.
- Zr(IV)–DOJR exhibited strong affinity and high adsorption capacity for fluoride ion.
- Zr(IV)–DOJR shows superior durability at least nine repeated adsorption–elution cycles.
- Loaded fluoride could be successfully desorbed by simple alkali solution.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Dried orange juice residue (DOJR) marketed as cattle food in Japan was converted into a promising adsorbent for fluoride as a result of chemical loading with Zr(IV), Ce(IV) and Al(III). The effectiveness of the metal loaded DOJR in adsorbing trace fluoride concentrations from synthetic and actual waste water were investigated. Energy dispersive X-ray (EDX) and infra red (IR) spectroscopic analysis confirmed the effective adsorption of Zr(IV) ions on DOJR in addition to fluoride ion on Zr(IV)-loaded DOJR. The amount of Zr(IV), Ce(IV) and Al(III) loaded on the DOJR were evaluated as 0.90, 0.85 and 0.97 mmol/g, respectively, while the maximum adsorption capacity of fluoride on the Zr(IV), Ce(IV) and Al(III) loaded DOJR were evaluated as 1.43, 1.22 and 0.67 mmol/g, respectively. Application of Zr(IV) loaded DOJR using actual waste plating solutions exhibited effective removal of trace concentration of fluoride to acceptable level. The negligible interference of coexisting anions such as nitrates, carbonates and chlorides makes the Zr(IV) loaded DOJR a promising sorbent for waste water treatment. The adsorbed fluoride was effectively desorbed using an alkali (NaOH) solution for its regeneration. Thus, this work shed light on the potential application of metal loaded DOJR to remediate aquatic environment polluted with fluoride.

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## 1. Introduction

Because of the strict environmental regulations governing fluoride concentrations in water within many countries, safe disposal

\* Corresponding author. Tel.: +81 952 28 8671; fax: +81 952 28 8669.

E-mail address: [inoue@elechem.chem.saga-u.ac.jp](mailto:inoue@elechem.chem.saga-u.ac.jp) (K. Inoue).

of fluoride containing waste water is one of the critical environmental challenges for semiconductor and plating industries, as waste water generated in these factories can sometimes contains 10 mg/l up to several thousand mg/l of fluoride [1–3]. The toxicity of fluoride depends upon the amount of fluoride intake through drinking water, food, and other beverages. It has been known to cause fluorosis, when ingested concentrations exceeding 1.5 mg/l, as recommended

by World Health Organization [4,5]. One of the most extensively employed methods for reducing excess fluoride concentrations in waste water is the lime softening method whereby the low solubility product of  $\text{CaF}_2$  allows fluoride removal to concentrations of approx. 10–20 mg/l. Thus, further treatment is required to meet the legally accepted level (8 mg/l) of fluoride in Japan. To remove such trace concentrations of fluoride, co-precipitation of fluoride with  $\text{Al}^{3+}$  has been extensively employed, which can lower fluoride concentration down to around acceptable levels. However, this method it suffers from disadvantages such as the generation of large volume of toxic sludge with high water content, thereby necessitating secondary treatment for safe disposal of such sludge [6,7]. In recent years, increased attentions have been focused on the development of novel, cost-effective and environmentally benign technology for fluoride ion removal from water.

Ion exchange and membrane technologies including reverse osmosis and nano-filtration have been successfully implemented in the removal of trace fluoride concentrations, however, these methods are expensive and energy consuming [8–11]. Adsorptions of fluoride on natural polymers obtained from agricultural waste are potentially an excellent alternative to the above-mentioned techniques. Because of their low cost and the presence of a variety of functional groups for modification, the uses of agro-waste material has attracted increasing interest in this field [12]. At present, scientists have focused on the development of various adsorbents with high sorption capacity, and selectivity for fluoride ion. The uses of biopolymers loaded with some high valent metal ions such as La(III), Ce(III) and Zr(IV), on suitable functional groups of biomass have been reported to successfully remove fluoride ions even from highly dilute solutions. These metal ions have high resistance to attack by acid or alkali and form stable fluoride complexes, resulting in very high selectivity towards fluoride ions [13–17].

Conventional biosorbents for fluoride ion removal exhibit low selectivity, small uptake capacity and less effectiveness for the removal of trace concentration of fluoride ions from water. In our previous study, adsorption gels for anionic pollutant such as phosphate, fluoride, arsenic and antimony were prepared from orange juice residue immediately after juicing. However, this manner of preparation using raw orange juice residue requires extensive chemical processing consisting of pre-treatment, saponification, multiple water washing and metal loading cycles. This lengthy procedure also consumes large amount of wash water and reagents therefore generating excess waste by-products that subsequently require further treatment prior to being discharged into environment. Furthermore, such preparation is limited only to the orange harvesting season. In the present paper, a new economical technique was developed to prepare the adsorbent from dried orange juice residue, which is now commercially available as cattle food in Japan, regardless of the season.

In the production of orange juice, raw oranges with thick outer covers are mechanically squashed for juicing. In this process, half of an orange is converted into orange juice while another half (solid part) remains as orange juice residue. The majority of orange juice factories in Japan market such orange juice residue as cattle food after drying. In the drying process, raw residue possessing high water content is mixed together with 1% calcium hydroxide in advance as a means of enhancing the drying stage, which is performed using a rotary drier at a temperature of 150 °C. The resulting dried residue is then marketed as cattle food at low cost (~\$0.2 per/kg) in Japan. The production cost, however, particularly that associated with drying, has increased in recent years despite the continuously cheap price of cattle food, thereby reducing the economic benefits for orange juice factories. If such dried orange juice residue, abbreviated as DOJR hereafter, were available for other purposes at a higher price, the financial situations of orange juice factories and orange farmers would be much improved. From

this viewpoint, the current work has focused on the feasibility of employing DOJR as the precursor of the adsorbent for fluoride removal. DOJR typically contains approximately 12% of pectin substances, which is methyl ester of pectic acid in part. In the previous work, raw orange juice residue saponified using calcium hydroxide in aqueous solution (saponified orange juice residue, abbreviated as SOJR, hereafter) was found to function as an excellent cation exchanger and be highly effective for fluoride removal after loading with high valent metal ions [18]. During the mixing of raw orange juice residue with calcium hydroxide in the commercial production of DOJR, it is inferred that some methyl ester part of orange pectin is converted into pectic acid (exactly speaking, calcium pectate) by the aid of calcium hydroxide similar to the case of the saponification in aqueous calcium hydroxide solution in the preparation of SOJR. In the present work, we attempted to employ such commercially available DOJR for the adsorptive removal of fluoride from water.

## 2. Experimental

### 2.1. Preparation of the adsorbents

As a result of the large amounts of calcium and water soluble organic compounds such as citric acid and sugar in DOJR, several water washing steps were required to remove these components in advance. The removal of water soluble organic acids, citric acid in particular, is indispensable as such substances strip the loaded high valent metal ions such as Zr(IV), Ce(IV) and Al(III). Procedurally, 50 g of DOJR was first washed repeatedly with distilled water followed by decantation prior to subsequent filtration. The resulting filter cake was then dried in a convection oven for 24 h at 70 °C, followed by loading with the high valent metal ions, Zr(IV), Ce(IV) and Al(III), according to the reaction shown in Scheme a. This was achieved by mixing 3 g of the dried filter cake with 0.5 l of 0.1 M ( $M = \text{mol/l}$ ) metal solutions at their optimal loading pH, i.e. Zr(IV) at pH 2.21 and Al(III) at pH 4.03, whereas, Ce(IV) loading was performed using 2.5% Ce(IV) solution at pH 2.78. The pH of the solution was maintained constant by adding small amount of 0.5 M  $\text{HNO}_3$  or 0.5 M NaOH solution. The mixture was shaken for 24 h at 30 °C in order to complete the metal loading reaction and then filtered and washed until a neutral pH was achieved, prior to drying. The dried samples of adsorbent particles were isolated within 100–150  $\mu\text{m}$  in size by sieving. The material obtained in this way was termed as metal loaded DOJR, or M-DOJR, hereafter.

### 2.2. Characterization of the adsorbent

Characterization of both the DOJR and M-DOJR were carried out using a JASCO FTIR-410 Fourier Transform Infrared spectrometer for functional group analysis. An energy dispersive X-ray spectrometer (EDX-800 HS, Shimadzu Corp.) was used to determine the chemical composition of the DOJR, Ce(IV)-DOJR and the Zr(IV)-DOJR before and after fluoride adsorption. The total organic carbon leaked from the samples of DOJR and SOJR during different stages of the water washing process were measured using a Shimadzu model TOC-VHS, total organic carbon analyzer.

### 2.3. Measurement of the amount of metal ions loaded on DOJR

The amount of Zr(IV), Ce(IV) and Al(III) ions loaded on the DOJR were evaluated quantitatively via the dissolution of 50 mg of each M-DOJR in 10 ml of aqua regia. After filtration, the metal ion concentration in the aqua regia solution was measured using a Shimadzu model ICPS 8100 inductively coupled plasma-atomic emission (ICP/AES) spectrometer.

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