



ADSORPTIVE REMOVAL OF TRACE CONCENTRATION OF FLUORIDE FROM WATER USING CERIUM LOADED DRIED ORANGE JUICE RESIDUE

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(Received: August 8, 2018; Revised: December 17, 2018; Accepted: December 20, 2018)

ABSTRACT

Two adsorbents for fluoride ion removal were developed from dried orange juice residue (DOJR) after loading Ce(III) and Ce(IV) in this study. The characterization of adsorbents was done by an energy dispersive X-ray spectroscopy, X-ray diffraction analysis, electron microscopy and chemical analysis. The experimental results indicated that the fluoride removal efficiency of both the adsorbents was influenced significantly by pH and the optimum operating pH was found to be 4. The equilibrium data were well fitted with Langmuir isotherm model and the maximum adsorption capacity of Ce(III)-DOJR and Ce(IV)-DOJR for fluoride were evaluated to be 0.67 and 1.22 mmol/g, respectively. Leakage of cerium from Ce(IV)-DOJR was negligible for trace concentration of fluoride but it was significant for high concentration of fluoride at pH below 3 resulting fluoride precipitation. Therefore, cerium-loaded DOJR investigated in this study can be considered as an efficient, environmentally benign and promising alternative for the treatment of fluoride contaminated with trace amount of fluoride ion.

Keywords: Fluoride, Adsorption isotherm, Cerium-loaded DOJR, Fluoride precipitation, X-ray diffraction analysis

INTRODUCTION

The contamination of surface and ground water occur due to natural as well as anthropogenic processes. Naturally, the pollution of water with fluoride occurs due to weathering of fluoride rich rocks and minerals whereas anthropogenic pollution takes place by the discharge of industrial waste water generated from semiconductor, plating and other high tech industries (Shen *et al.* 2003). Fluoride ion concentration below 1 mg/L is considered to be beneficial for our dental health. However, consumption of high concentration of fluoride for long period of time can cause mottling of teeth and lesions of endocrine glands, liver, thyroid and other organs in addition to dental and skeletal fluorosis. It is estimated that more than 70 million people are suffering from fluorosis globally due to consumption of fluoride contaminated water (Viswanathan & Meenakshi 2008, Paudyal *et al.* 2011). In order to minimize the risk, WHO has recommended the tolerance limit of 1.5 mg/L of fluoride in drinking water (WHO 1993). Therefore, it is necessary to lower the elevated amount of fluoride in water.

Nowadays, there has been a considerable increase in the prevalence of dental and skeletal fluorosis among population around the fluoride polluted area (Meenakshi & Viswanathan 2007). Moreover, intake of fluoride from sources other than drinking water such as foodstuffs, toothpaste, fluoridated milk, dietary supplements, fluoridated salt, mouth rinses and brick tea are another cause of fluorosis in our body. The highly preferable alternative for the preventive measure is to find a supply of drinking water with safe fluoride levels and one of such

option is defluoridation (Liao & Shi 2005). Most commonly used methods for defluoridation of water are chemical precipitation, membrane process, ion exchange and surface adsorption. The surface adsorption using chemically modified waste biomass material seems to be more promising because of its easy operation and affordable cost (Biswas *et al.* 2009, Zhao *et al.* 2008).

The orange juice residue obtained after juicing is one of the pectin rich biomass that can be easily converted into cation exchanger by basic hydrolysis reaction with lime water (Paudyal *et al.* 2013). In the present work the cattle food of orange juice residue abbreviated as dried orange juice, DOJR, was utilized for the preparation of adsorbents for fluoride by loading Ce(III) and Ce(IV). The fluoride removal potential of cerium-loaded DOJR was investigated batch wise. The effects of varying parameters such as pH and initial fluoride concentration for the removal of fluoride from water were investigated using both the adsorbents.

MATERIALS AND METHODS

Chemicals and instrumentation

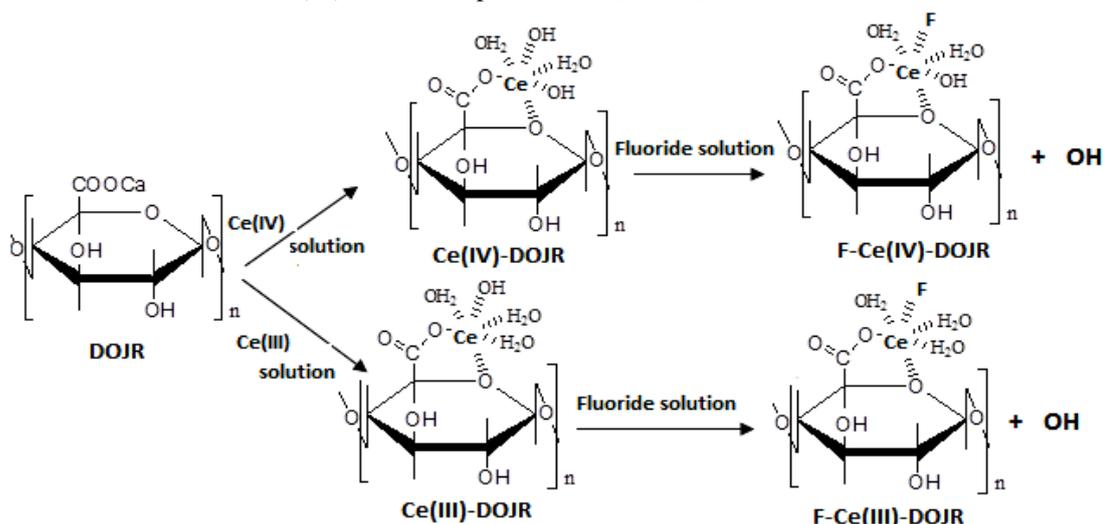
The stock solution of fluoride was prepared from NaF purchased from Wako Chemical Co. Ltd. Japan. The $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ purchased from Wako Chemical and $\text{CeSO}_4 \cdot 4\text{H}_2\text{O}$ purchased from Sigma Aldrich were used to prepare Ce(III) and Ce(IV) solution, respectively, for loading reaction. The pH of the solution was measured using pH meter (TOA DKK, HM-30R pH meter). The surface structure of DOJR before and after Ce(III) loading was analysed by using electron microscope. An elemental

analysis of DOJR before and after Ce(IV) loading were performed by using an Energy Dispersive X-ray spectrometer (Shimadzu model, EDX-800HS). The concentration of metal ion was measured by an inductively coupled plasma atomic emission spectrometer (ICP-AES, Shimadzu model ICPS 8100) where as that of fluoride was analyzed by ion chromatography (Dionex model ICS 1500).

Preparation of cerium loaded DOJR

The chemical modification of DOJR was carried out according to the procedure described elsewhere (Paudyal *et al.* 2012). In the present study, three grams of DOJR was mixed with 500 mL of 0.1 M Ce(III) solution at pH

around 3.4 and shacked for 24 h at 30 °C for the immobilization of Ce(III) ion instead of Zr(IV). Then it was washed with distilled water until neutral pH was achieved and was dried in convection oven at 70 °C for two days. The material prepared was termed as Ce(III) loaded DOJR (i.e., Ce(III)-DOJR) hereafter. Similarly, Ce(IV) sulphate solution was used in order to prepare the Ce(IV) loaded DOJR (Ce(IV)-DOJR). During the loading reaction, Ca²⁺ ions present in the dried orange juice residue (DOJR) undergoes cation exchange reaction with the loaded Ce(III) or Ce(IV) ions and the coordinated hydroxyl group present in both types of cerium loaded DOJR were expected to be substituted with fluoride during adsorption also shown in Scheme 1.



Scheme 1. Plausible mechanism for the loading of cerium onto DOJR and ligand substitution during fluoride adsorption

Batch adsorption studies

The adsorption experiments for cerium loaded DOJR towards fluoride ion was carried out at varying pH (1.5 to 11.5), contact time and fluoride ions concentration using batch adsorption method. In a typical adsorption experiment, 10 mg adsorbent and 15 mL of fluoride solution were mixed in sealed glass bottle and shaken for 24 h at 30 °C. The solid-liquid mixture was separated by filtration and the filtrate was analyzed using ion chromatography. The adsorption percentage and capacity were evaluated by using following relationship

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

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

Where, C_i and C_e are initial and equilibrium concentration (mmol/L) respectively. W is weight of the adsorbent (g) and V is volume of solution (L).

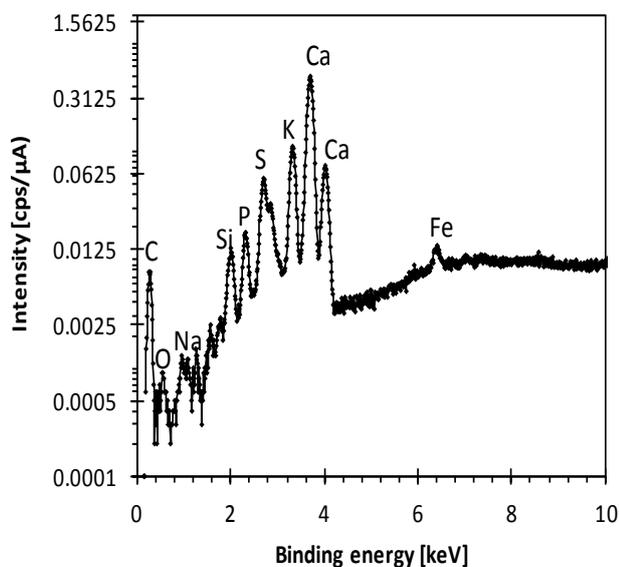
RESULTS AND DISCUSSION

Elemental analysis of DOJR

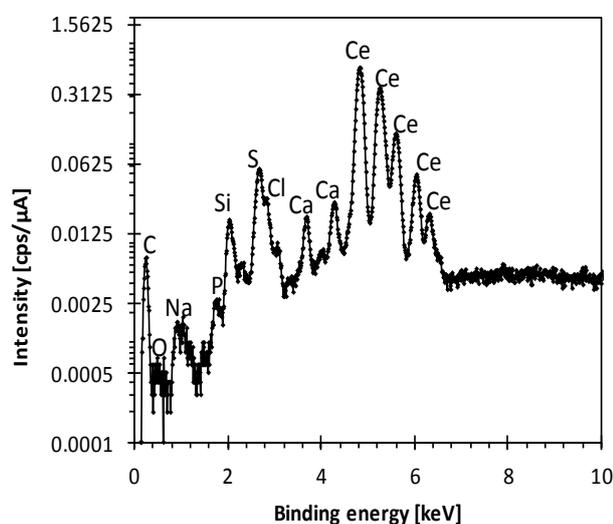
For the qualitative determination of the presence of various elements in the tested sample of adsorbents, an energy dispersive X-ray spectroscopic (EDX) technique was used. The EDX spectra of DOJR and DOJR after Ce(IV) loading is presented in Figs 1(a) and 1(b). It was observed from the EDX spectra of DOJR that it contained the elemental peaks of C (0.28 keV), O (0.32 keV), Na (1.09 keV), Si (1.78), P (2.04 keV), S (2.32 keV), K (2.89 keV), Ca (3.68 and 4.12 keV) and Fe (6.41 keV) as shown in Fig. 1(a). After Ce(IV) loading, new peaks corresponding to cerium element were also observed at the energy value of 4.29, 4.81, 5.24, 5.62, 6.01 and 6.27 keV in addition to the peaks of DOJR as shown in Fig. 1(b) which strongly suggest the effective loading of Ce(IV) onto DOJR.

In addition to this, the intensity of elemental peaks of Ca at 3.68 keV and 4.12 keV were decreased sharply after Ce(IV) loading. The peaks corresponds to Fe at energy

value around 6.41 keV had nearly disappeared in Ce(IV) loaded DOJR as shown in Fig. 1(b). These results strongly suggested that, the metal substitution reaction of Ca and Fe occurred with Ce during cerium loading reaction *via* cation exchange mechanism as demonstrated in Scheme 1.



(a)



(b)

Fig. 1. An energy dispersive X-ray (EDX) spectra of (a) dried orange juice residue (DOJR) and (b) Ce(IV)-DOJR

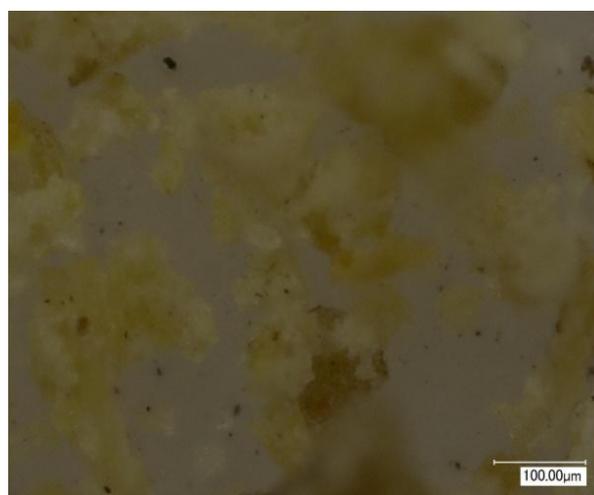
Surface analysis of DOJR and Ce(III)-DOJR

The morphological microstructures and surface characteristics of DOJR and Ce(III)-DOJR were observed with electron microscope as shown in Figs 2(a) and 2(b), respectively. The surface morphology of DOJR had a smooth, golden yellow appearance with low microporosity as shown in Fig. 2(a), while on the surfaces of Ce(III)-DOJR some irregular cracks or deformation were

visible due to chemical modification and removal of low molecular weight water soluble sugar, citric acid and limonene compounds from DOJR as shown in Fig. 2(b). In addition, the observation of the yellow colour pigment on DOJR was due to the presence of limonene compounds, which potentially hindered the metal loading reaction.



(a)



(b)

Fig. 2. Electron microscopic image of (a) dried orange juice residue (DOJR) and (b) Ce(III)-loaded DOJR

Effect of pH solution

The pH of the solution strongly affects the surface charge of the adsorbents and the degree of ionization thus it is one of the controlling factors in the process of adsorption. The removal efficiency of fluoride onto Ce(III)- and Ce(IV)-loaded DOJR is shown in Fig. 3. As shown in Fig. 3, removal efficiency of fluoride increased up to 94.1 % and 87.7 % by Ce(IV)- and Ce(III) loaded DOJR, respectively when pH was 4. At pH > 5.0 and pH < 2, adsorption percentage was noticed to be decreased. The

decrease in fluoride adsorption at pH > 5 was due to the competition of hydroxide ion for the active sites because hydroxide ion concentration was increased with the raise of pH of the solution. At lower pH below 3, some fraction of fluoride ions was present in the form of HF, which was difficult to be adsorbed onto the anion exchange site of metal loaded DOJR that potentially caused the decrease of fluoride adsorption percentage. The adsorption mechanism of fluoride onto both the cerium loaded DOJR is explained as follows. The coordinated hydroxyl ions in cerium loaded DOJR were protonated at pH around 4 to give positively charged surface (reaction a) where negatively charged fluoride ions were interacted and adsorbed with the loss of water molecule (reaction b). The overall reaction indicated the exchange of coordinated hydroxyl ions present in cerium loaded DOJR with fluoride ion from aqueous solution.

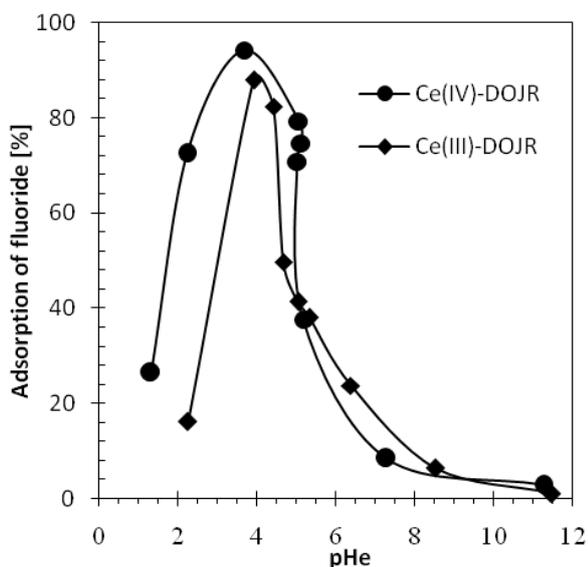
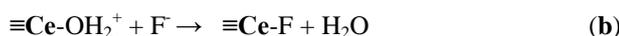
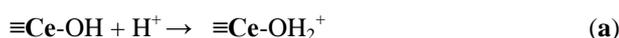


Fig. 3. Effect of pH on the adsorption of fluoride using Ce(III) and Ce(IV) loaded DOJR (condition: volume of solution = 10 mL, weight of adsorbent = 10 mg, fluoride = 0.5 mmol/L, pH = 4, shaking = 24 h at 30°C)

Adsorption isotherm study

Fig. 4 shows the adsorption isotherms of fluoride onto Ce(III)- and Ce(IV)- loaded DOJR from aqueous medium. It is clear from this figure that adsorption capacity of both the adsorbents increased sharply at lower concentration whereas it was ascribed to attain plateau value at higher concentration. Moreover, compared to Ce(III)-DOJR, Ce(IV)-DOJR had relatively high adsorption capability for fluoride ion. The hydroxyl ligand generated on the co-ordination sphere of loaded cerium in both the adsorbent undergoes ligand exchange reaction

between hydroxyl ligands and anionic species of fluoride ion as shown in Scheme 1. A similar type of removal mechanism was observed by Paudyal *et al.* (2018) and Biswas *et al.* (2009) for the removal of fluoride ion, respectively, from Zr(IV) loaded SRP and Fe(III)-Sn(IV) bi-metallic oxide adsorbents. Because of high oxidation state of Ce(IV) followed by Ce(III), more active sites for fluoride ion were created in Ce(IV)-DOJR and hence adsorption capability of Ce(IV)-DOJR was found to be higher than Ce(III)-DOJR.

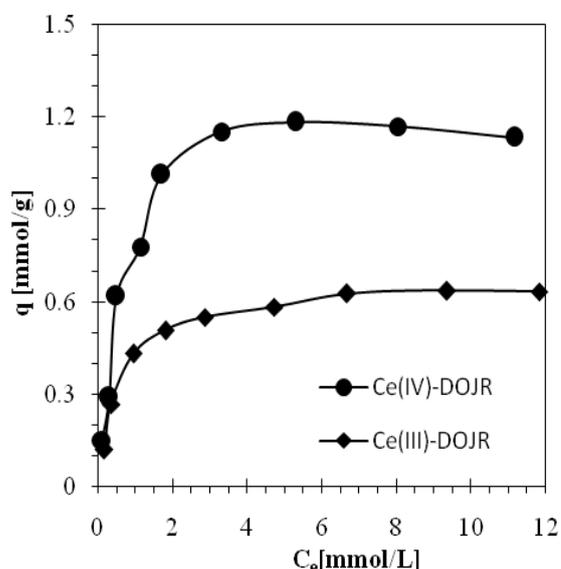


Fig. 4. Adsorption isotherm of cerium loaded DOJR for fluoride ion

The experimental data were modeled by using well known Freundlich and Langmuir isotherm model. The linear form of the Freundlich isotherm model is represented by the equation 3 as (Freundlich 1906).

$$\log q_e = \log K_F + (1/n) \log C_e \quad (3)$$

Where, K_F and n are Freundlich constant related to adsorption capacity and adsorption intensity of the adsorbent, respectively. The values of K_F and $1/n$ were estimated from the intercept and slope, respectively, of the linear plot of experimental data of $\log Q_e$ vs $\log C_e$ as shown in Fig. 5(a).

Similarly, a linear form of the Langmuir isotherm model is given by the equation 4 as (Langmuir 1916).

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \quad (4)$$

Where, C_e (mmol/L) and q_e (mmol /g) are equilibrium concentration and amount of adsorption, respectively, while q_{\max} and b are maximum loading capacity and adsorption equilibrium constant. The values of q_m and b were evaluated from the slope and intercept of straight line plot of C_e/q_e versus C_e as shown in Fig. 5(b).

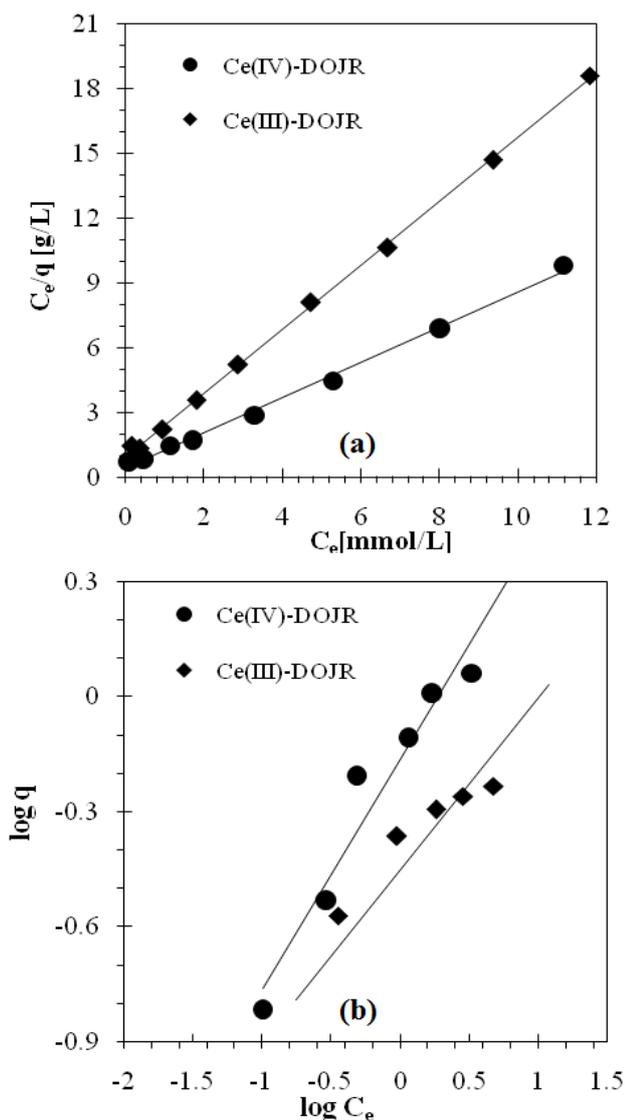


Fig. 5. Modeling of isotherm data using (a) Langmuir and (b) Freundlich adsorption isotherms

The calculated values of Langmuir and Freundlich isotherm constants are listed in Table 1. Although total amount of cerium content in Ce(III)-DOJR (0.91 mmol/g) and Ce(IV)-DOJR (0.89 mmol/g) were nearly the same, adsorption potential of fluoride using Ce(IV)-DOJR was higher than Ce(III)-DOJR which was due to the development of more anion exchange site in Ce(IV)-DOJR owed to higher oxidation state of Ce(IV). Because of the higher value of correlation coefficient obtained for Langmuir isotherm model ($R^2 > 0.99$) than Freundlich isotherm model (R^2 not higher than 0.93), the Langmuir isotherm model is more suitable to describe adsorptions behavior of fluoride ion onto both the adsorbents tested. Therefore, Langmuir type monolayer formation of fluoride on the surface of both the adsorbents took place during adsorption process.

Table 1. Langmuir and Freundlich parameters for the adsorption of fluoride using cerium loaded DOJR

	Isotherm Parameters	Ce(III)-DOJR	Ce(IV)-DOJR
Freundlich	K_F (mmol/g)	0.64	0.85
	$1/n$	0.45	0.60
	R^2	0.88	0.93
Langmuir	$q_{max.}$ (mmol/g)	0.67	1.22
	b (L/mmol)	1.60	1.80
	R^2	0.99	0.99

Effect of fluoride ion and pH for adsorbent stability

The stability of investigated adsorbent is very important for the application purpose. The XRD spectra of Ce(IV)-DOJR at two different condition, that is, first after treating low concentration of fluoride at optimal pH and second after treating high concentration of fluoride at lower pH were recorded to investigate the adsorbent stability and the results are shown in Figs 6(a) and 6(b), respectively.

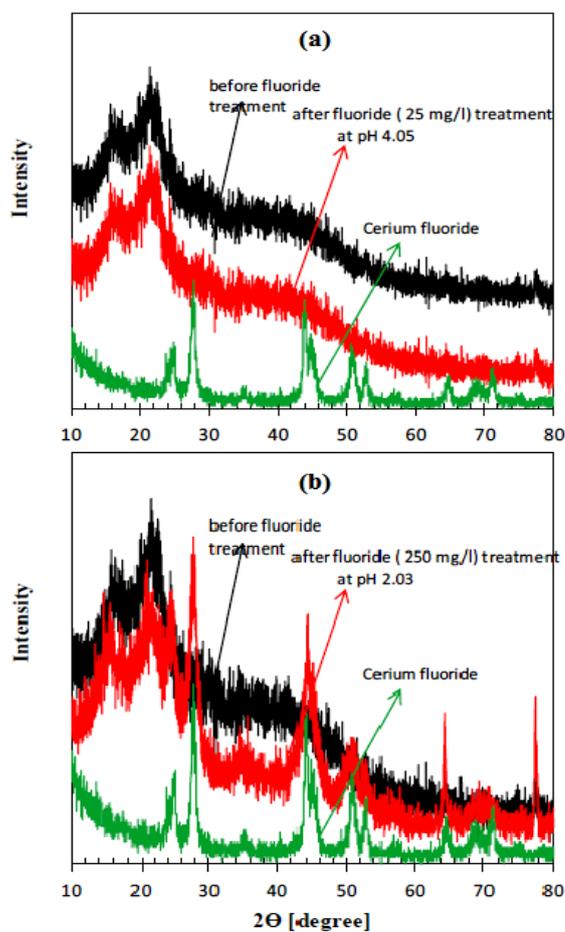


Fig. 6. XRD spectra of (a) Ce(IV)-DOJR before and after treating low concentration of fluoride (25 mg/L) at 4.05 pH and (b) Ce(IV)-DOJR before and after treating high concentration of fluoride (250 mg/L) at 2.03 pH

In the case of using low concentration of fluoride ion as shown in Fig. 6(a), there was no change in XRD spectrum before and after fluoride adsorption indicating that Ce(IV)-DOJR is stable and robust if we use for the treatment of trace concentration of fluoride ion. However, in case of using high concentration of fluoride at low pH as shown in Fig. 6(b), new peaks were observed at 2 θ value at around 24.9, 27.6, 43.8, 50.7, 52.6, 64.8 and 71.4 in the XRD spectrum after fluoride treatment. These peaks were exactly in the same position as observed in the case of pure cerium fluoride purchased from Wako Chemical Co. Ltd. Japan. There was high possibility of combining Ce(IV) leaked at low pH with fluoride ions to form cerium fluoride precipitate which was evidenced from the observation of crystalline peaks of cerium fluoride in the XRD spectrum of Ce(IV)-DOJR obtained after the treatment with high concentration of fluoride at strongly acidic pH as depicted in Fig. 6.b.

CONCLUSION

In this study, two types of cerium loaded DOJR were successfully developed for fluoride ion adsorption by loading Ce(III) and Ce(IV) onto DOJR. The optimum pH for fluoride removal was 4. The adsorption isotherm was fit better with Langmuir isotherm model than Freundlich model. High concentration of fluoride cause significant leakage of Ce(IV) at low pH which was concluded to be combined with fluoride ion to give cerium fluoride precipitate. Adsorption test using trace concentration of fluoride showed negligible leakage of loaded Ce(IV) from Ce(IV)-DOJR, which indicate high stability of this adsorbent at this condition. Therefore, it is expected that the Ce(IV)-DOJR investigated in this study can be effective for the treatment of water polluted with trace amount of fluoride ion.

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