

Effective Removal of Fluoride onto Metal Ions Loaded Orange Waste

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Abstract

Removal of fluoride is investigated onto several metal ions loaded phosphorylated orange juice residue and commercially available alumina. The experimental results revealed that cerium (IV) loaded phosphorylated orange waste indicated excellent fluoride removal efficiency at acidic pH range and while that lanthanum loaded at neutral pH range. Both the metal loaded adsorbents are found superior to the commercially available activated alumina.

Keywords: *Fluoride, Orange waste, adsorbent, waste water, phosphorylation, activated alumina*

Introduction

The presence of fluoride in industrial effluents has been a matter of problem due to stringent environmental regulation and possible liability to human health. A very small amount of fluoride 1.0-1.5 mg dm⁻³ is especially beneficial for children; however, excess fluorides in drinking water cause dental fluorosis. Fluorides generated as waste from electronic industries exceeds the permissible limit. In such instances, fluorides have been removed by ion exchange, electrolysis, sorption on sludge, on hydroxyapatite, or on zeolites¹⁻¹¹. Dissolved fluoride ions can be removed from polluted water by precipitation with agents containing water-solution rare earth compounds particularly lanthanum (III) and Cerium (IV) and the pH was maintained at 9.0 using Ca or Na compounds by 1 wt.% and then passing the treated water through a solid-liquid separator to obtain clean water. The equivalent weight ratio of the precipitating agent addition to the dissolved fluoride ions is preferably ~1.2:1¹². A 2-column limestone reactor was designed to reduce fluoride concentrations in wastewaters to below the maximum contaminant level (MCL limit) of 4 mg dm⁻³. The reactor functions by forcing calcite (CaCO₃) to dissolve and fluorite (CaF₂) to precipitate in the 1st column. The 2nd column is not necessary to remove fluoride but is used to precipitate the calcite dissolved in the 1st column. The major advantage of this potential technology over existing liming and ion exchange methods is that system monitoring is minimal, regular column regeneration is not required, and chemicals are not permanently added to the water. Because the CaCO₃ dissolved in the 1st column is precipitated in the 2nd, the reactor has potential application to reduce the concentrations of contaminants from wastewaters similar in charge and size to Ca²⁺ and CO₃²⁻ through co-precipitation reactions.

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In a pilot experiment where fly ash leachate was spiked with mg dm^{-3} levels of Cd, As, Cr, and Se and directed through the reactor, reductions in all elements except chromium occurred. Cadmium was the most notable. Influent concentrations of 2-30 mg dm^{-3} were reduced to below detection ($<0.01 \text{ mg/L}$)¹³. Apparatus for treating wastewater-containing fluoride from semiconductor etching process has been investigated. This apparatus for treating fluoride-containing wastewater comprises a 1st means for adjusting pH of the wastewater by adding a pH adjusting agent, a packed tower containing granular CaCO_3 for removing F^- from the wastewater with adjusted pH, a detection means for detecting any one of pH, the Ca^{2+} concentration, and the fluoride concentration of the wastewater flowing out of the tower, and a 2nd means for further adding a pH adjusting agent to the wastewater whose pH is adjusted by the first means before wastewater introduction into the tower. The wastewater may be etching wastewater used for semiconductor materials. While elution of CaCO_3 is prevented, F^- is efficiently removed as CaF_2 to give treated water with stable quality¹⁴. A treatment method for wastewater containing fluoride has been proposed. The removing processes of fluoride ions from the wastewater containing fluoride in presence of CaF_2 dissolving material comprise the following steps: (a) the high concentration fluoride treatment step for making fluoride concentration in wastewater decrease to 20-25 ppm by adding slaked lime and H_2SO_4 to be pH 5.8-8.3; (b) the low concentration fluoride treatment step for making fluoride concentration in the treated wastewater decrease to 15 ppm by adding slaked lime and alum to be pH 5.8-8.3; and (c) the coagulation elimination step for removing the coagulated solids precipitated by adding a flocculant such as polyacryamide¹⁵.

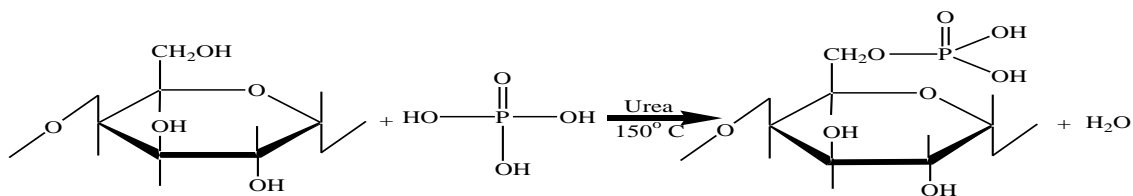
Adsorption of fluoride onto mixed rare earth oxides as adsorbent was studied. The adsorbent, which is a mixture of rare earth oxides, was found to adsorb fluoride rapidly and effectively. The effect of various parameters such as contact time, initial concentration, pH, and adsorbent dose on adsorption efficiency was investigated. More than 90% of the adsorption occurred within the first 5-10 min. Adsorption efficiency was found to be dependent on the initial fluoride concentration and adsorption behavior followed Langmuir adsorption model. The optimum pH was found to be ~ 6.5 . The presence of other ions such as nitrate and sulfate did not affect the adsorption of fluoride significantly (adsorption efficiency reduced from 85 to 79%) indicating the selective nature of the adsorbent. Washing the adsorbent with a pH 12 solutions could easily desorb the adsorbed fluoride. This study clearly shows the applicability of naturally occurring rare earth oxides as selective adsorbent for fluoride from solutions¹⁶. The behavior of D412 resin loaded with Ce (IV) for removing fluoride from water was studied by static and dynamic method. The effects of pH, F^- concentration, and flow of the fluoride containing solution on the adsorption performance were discussed. The adsorbing mechanism of the adsorbent for F^- was analyzed by IR spectra¹⁷. Treatment of industrial wastewaters containing fluorides and heavy metal compounds was studied¹⁸. The method comprises dosing industrial wastewaters containing fluorides (e.g., BF_3 or CHF_3) and heavy metal compounds with alkali metal hydroxides and/or carbonates (e.g., NaOH or Na_2CO_3) at pH 8-12 to form soluble alkali metal fluoride and sparingly-soluble metal hydroxide and/or metal carbonates; filtering the treated waters to separate metal sludge; adding the filtrate with CaCl_2 solution at pH 4-12 to give CaF_2 precipitates; washing the metal sludge with an alkali solution to separate residual fluorides; and then recovering valuable metals from washed sludge.

In the present study, we have examined the fluoride removal efficiency of a novel adsorbent loaded with different metal ions in order to validate its application for wastewater treatment.

Experimental Methods

Materials

Orange waste was kindly provided from JA Saga Beverage, Japan. It was dried for 72 hours in a convection oven at a temperature of 50°C and then dried in vacuo. The dried orange waste was grounded into smaller particles of around 100-200 μm. Cellulose, pectin substances, hemicellulose, chlorophyll pigments and other low molecular weight compounds like limonene are the main chemical constituents of the orange waste¹⁹. The active binding sites for metals are supposed to be functional groups of carboxylic acid in pectin substances. In view of low amount of pectin substances in the orange waste cellulose part of orange waste was phosphorylated after crosslinking in order to convert their abundant hydroxyl groups into phosphate groups with high affinity to metal ions. The detailed procedure of phosphorylation process has been already given in the preceding chapters, which can be represented by the following chemical reaction.



Methods

All chemicals used in this study were of pure analytical grade purchased from Katayama Chemical Co. Ltd. Japan, unless otherwise mentioned. All of the adsorption tests for metal ions and removal tests for fluoride ion were carried out batch-wise. 25 mg of adsorbent was placed in a conical flask together with a 15 ml portion of aqueous metal solution, whose concentration was around 1mM. The pH of the aqueous solutions was adjusted by contacting with HCl or ammonia, while in the case of metal ions adsorption; 2-[4-(2-Hydroxyethyl)-1-piperaziny] ethanesulphonic acid was used as the buffer reagent. The flask was shaken vigorously in a thermostatic shaker at 30°C for about 24 h to attain equilibrium. The metal concentrations before and after adsorption were measured by ion chromatography.

From the metal concentrations measured before and after adsorption (C_0 and C_e , respectively) and dry weight of adsorption gel (W), as well as volume of aqueous solution (V), the amount of adsorption of metals (q) was calculated according to Eq.(1). The removal or adsorption percentage ($R\%$ or $A\%$) defined as the ratio of the decrease in metal concentration before and after the adsorption ($C_0 - C_e$) to initial concentration of aqueous solution (C_0), was calculated according to Eq. (2).

$$q = \frac{C_0 - C_e}{W} \times V \text{ [mol/kg]} \quad (1)$$

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

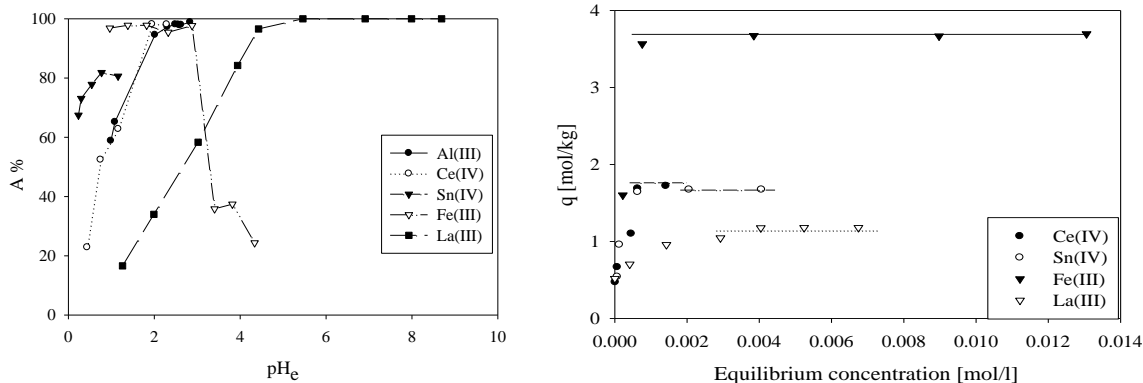


Fig.1 Adsorption of various metal ions as a function of pH. Fig.2 Adsorption isotherm of Ce(IV), Sn(IV), Fe(III), and La(III) and their corresponding loading capacities are 1.7, 1.67, 3.7 and 1.17 mol/kg, respectively.

Results and discussion

Adsorption of metal ions

It is obvious that fluoride ions are adsorbed on the surface of the metal loaded gel, since fluoride ions do exist as anions. Thus the removal mechanism of fluoride anion is exactly similar to the cases of other anions. For this reason, adsorption of several metal ions was tested in order to study the fluoride ion adsorption on the metal loaded gels.

Figure 1 shows the order to study fluoride ion adsorption behavior of aluminum (III), cerium (IV), tin (IV), iron (III), and lanthanum (III) on POJR, whose initial concentration was $1 \times 10^{-3} \text{ mol dm}^{-3}$, expressed as the function of pH. It is seen from the figure that tin (IV) is adsorbed at comparatively lower pH as it forms precipitates at pH around 2, while lanthanum (III) are highly adsorbed at neutral pH region. Similarly, aluminum (III), cerium (IV) and iron (III) are effectively adsorbed in an acidic pH range where the hydrolysis of the corresponding metal ions does not take place.

Figure 2 shows the adsorption isotherms of cerium (IV), tin (IV), iron (III) and lanthanum (III) from which the loading capacities of the corresponding metal ions on phosphorylated gel were evaluated 1.7, 1.67, 3.7 and 1.17 mol kg⁻¹ dry gel, respectively.

Removal of fluoride

The effect of pH on the removal of fluoride ions from various metal ion loaded gel is shown in Fig.3, where the initial metal ion concentration was kept at $1 \times 10^{-3} \text{ mol dm}^{-3}$. It can be seen that iron, aluminum and tin loaded gels are not effective to fluoride ion removal though they can be used for the treatment of trace concentration of fluoride. On the other hand, activated alumina, which is frequently used for the adsorptive removal of fluoride ions, is also shown in the figure for comparison. Although fluoride ions can be removed by using activated alumina in neutral pH range, its removal efficiency seems unsatisfactory. In an attempt to treat it effectively, cerium and lanthanum loaded phosphorylated gels were investigated, whose results are shown in Fig.3. Cerium loaded gels is highly effective for fluoride ion removal in acidic

condition while lanthanum loaded gel is effective in acidic and neutral conditions. Their removal percentage is even higher than commercially used activated alumina. Adsorption isotherms of fluoride ions from cerium and lanthanum loaded gels are shown in Fig.4 from which their corresponding loading capacities were elevated 2.7 and 2.87 mol kg⁻¹ dry gel, respectively. In order to access the complete removal of fluoride ions lanthanum loaded gel, fluoride ion adsorption experiment was carried out batch wisely by keeping the initial fluoride ion concentration constant at 15 mg dm⁻³ and by varying the solid liquid ratio. A complete removal of fluoride was achieved at solid to liquid ratio 0.08g dm⁻³.

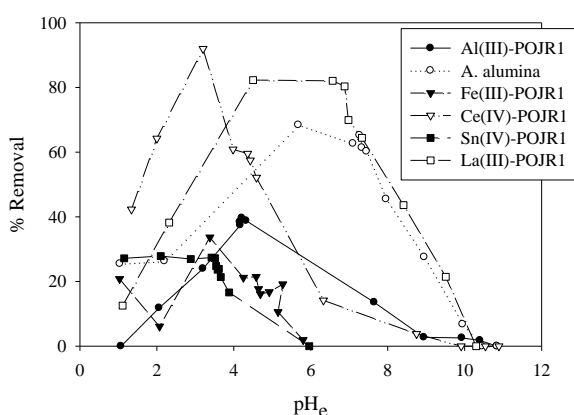


Fig.3 Removal of fluoride on different metals loaded gels as a function of pH.

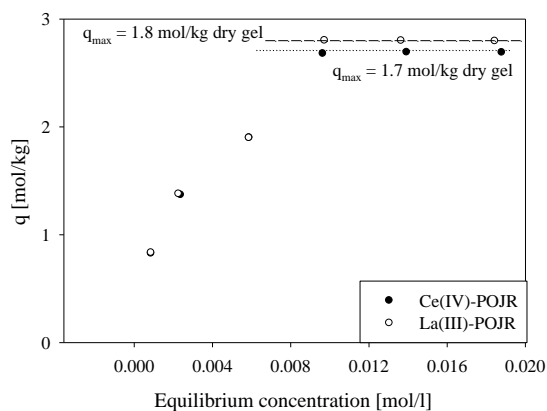


Fig.4 Adsorption isotherm of fluoride from cerium and lanthanum loaded POJR gel.

Conclusion

Cerium and lanthanum metal ion loaded phosphorylated orange juice residue gel is highly effective for fluoride ion removal. The loading capacities of these gels are much higher than those reported in the literature¹. Thus the new material prepared in this work, produced from orange juice waste can be used for the treatment of fluoride contaminated wastewater.

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