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Removal of Fluoride Ion by a Porous Spherical Resin Loaded with Hydrous Zirconium Oxide

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A new composite material based on hydrous zirconium oxide and a porous polymer resin has been prepared by the impregnation of tetra(n-butoxy)zirconium into porous polymer beads followed by hydrolysis of the alkoxide. The adsorption properties of the Zr-loaded resin for fluoride ion have been described.

The removal of trace fluoride ion from industrial effluents or drinking water systems has become of increasing importance. Metal-loaded ion-exchange resins (M=La, Ce, Zr, Al) have been examined as the fluoride ion selective adsorbents.[1-3] However, in these systems, a significant leaking of the loaded metals tends to take place upon recycle uses leading to a rapid lowering of the adsorption activity. Hydrous metal oxides (M= Al, Fe, La, Ce, Zr) are also known to have a high selectivity for fluoride ion.[4-6] Among the hydrous metal oxides, those of high valent metals including Zr(IV) and Ce(IV) are very promising due to the high resinstance to attack by acids or alkalis.[7] However a drawback of these inorganic ion-exchangers is the difficulty to obtain the spherical beads of the suitable size for the required applications. Herein we propose a convenient procedure for the preparation of the porous spherical beads in which hydrous zirconium oxide is incorporated over the interior surface of the pores. This paper describes the preparation of the zirconium-loaded polymer beads and their application to the removal of fluoride ion.

The hydrous zirconium oxide loaded resin (Zr-loaded resin) was prepared by the following procedures: Tetra(n-butoxy)zirconium (120 g) was diluted with 300 cm^3 of benzene. To this solution was added 100 g of the dried Amberlite XAD-7 beads (50-100 mesh) and the mixture was stirred under the reduced pressure. After 1 h, benzene was evaporated off. To the residue was added 500 cm^3 of water (pH 2.0), and the mixture was stood at room temperature for 1 h. After filtration, the resin beads were treated with 500 cm^3 of water (pH 2.0), and then the whole content was refluxed for 24 h. The beads were washed with water, ethanol and then dried. The resin beads contain about 15 wt.% of zirconium which corresponds to 1.7 mmol of zirconium per gram of the resin. The broad X-ray diffraction peaks of the resin indicate that the zirconium oxide formed by hydrolysis of the alkoxide is an amorphous gel. However continued refluxing (60 h) resulted in partial crystal growth, as has been observed by Clearfield.[8)]

Table 1. The numerical data of the Zr-loaded resin and the XAD-7

	Specific surface area	Pore volume	Mean pore radius	Zr content
	$m^2\ g^{-1}$	$cm^3\ g^{-1}$	Å	$mmol\ g^{-1}$
XAD-7	390	0.58	30	-
Zr-loaded resin	280	0.28	20	1.7

Table 1 shows the numerical data of the Zr-loaded resin along with those of the XAD-7. The specific surface area and the mean pore radius of the XAD-7 decreased upon incorporation of the oxide. Hydrous zirconium oxide appeared to deposite inside the pores with relatively large radius since most of the pores with 30-60 Å observed in XAD-7 disappeared upon loading of zirconium, although the pores with the radius lower than 20 Å remain unclogged. The titration curves of the Zr-loaded resin and the hydrous zirconium oxide prepared by the hydrolysis of the alkoxide[9)] commonly gave an inflection point at around pH 7-8 which corresponds to the dissociation of the hydroxyl protons on the zirconium.[10)] The Zr-loaded resin can readily adsorb fluoride ion at pH ranging 2-7; the maximum amount of fluoride ion uptake seems to be close to the amount

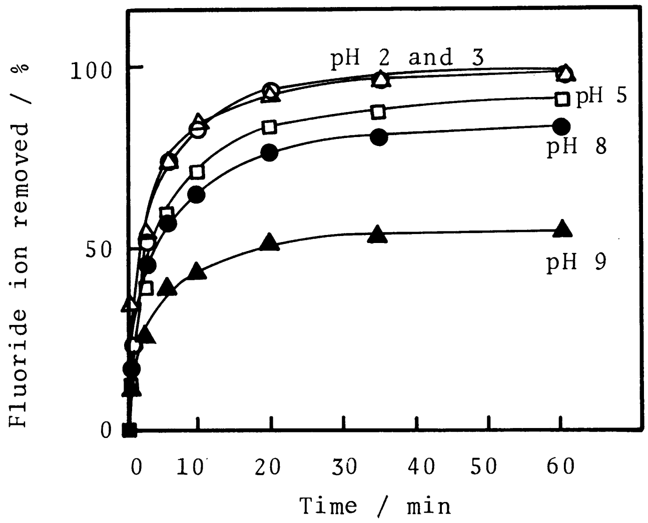

Fig. 1. Time-courses for the adsorption of fluoride ion.
Zr-loaded resin = 3 g,
$[F^-]$ = 50 ppm (200 cm^3)

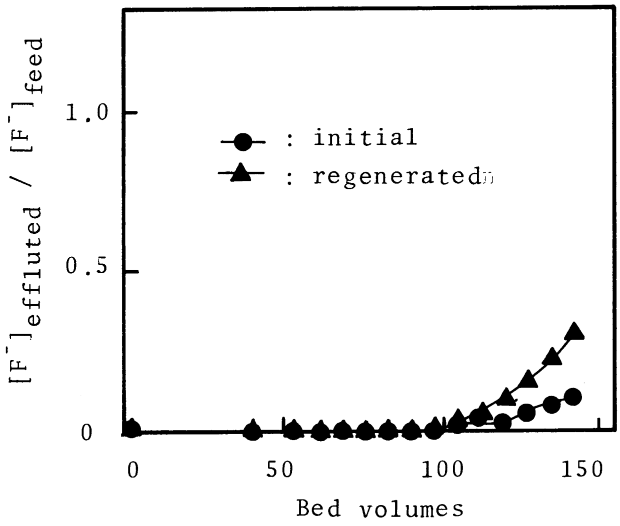

Fig. 2. Breakthrough curves for the adsorption of fluoride ion.
Column bed volume = 14.5 cm^3
$[F^-]_{feed}$ = 100 ppm (pH = 3.0),
Flow rate = 2 cm^3 min^{-1}.

of zirconium loaded on the resin indicating the 1 : 1 molar ratio between zirconium and fluoride ion.[6] The adsorption capacity greatly decreased at pH higher than 9.0. The hydrous zirconium oxide is known to behave as an amphoteric exchanger; the hydroxyl groups can be exchanged at the pH value below the isoelectric point, while for the higher pH value protons can be replaced by cations.[11] The time-courses for the adsorption of fluoride ion is given in Fig. 1. The adsorption rate appears to decrease with increase of pH. This trend is much more marked at the pH region higher than 8.0 where the inflection point is observed in the titration curve. The pH dependence of the adsorption rate is related with the proton dissociation presumably due to the decrease in the number of anion exchange site associated with increase of the pH.

Column adsorption of fluoride ion was examined by using a glass column packed with the present resin (ϕ 1.0 x 18 cm, 5 g). A buffered solution (pH 3.0) containing 100 ppm of fluoride ion was continuously supplied to the column at a rate of 2 cm^3 min^{-1}. The column effluent was fractionated into small portions and then analyzed. Fluoride ion was quantitatively retained on the column until the breakthrough point (ca. 100 bed volumes) as given in Fig. 2. The adsorbed fluoride ion was liberated from the resin by elution with 1 M (M = mol dm^{-3}) sodium hydroxide. The column can be used repeatedly after rinsing with 1 M hydrochloric acid followed by washing with water. The amount of zirconium ion leaked by an adsorption and desorption cycle was appreciably small (less than 2%).

The preparative method presented here may be applicable to various combinations of metal alkoxides and porous polymers, i.e., numerous types of spherical beads loaded with the hydrous oxides of desired metals can be available in a simple procedure.

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