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Removal of Fluoride from Water by Metal Ions (Al^{3+}, La^{3+} and ZrO^{2+}) Loaded Natural Zeolite

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Abstract: In this study, the ion exchange of metal ions (Al^{3+}, La^{3+} and ZrO^{2+}) on modified zeolites was carried out using batch method. Fluoride removal from water using Al^{3+}-, La^{3+}- and ZrO^{2+}- exchanged zeolite was subsequently investigated to evaluate the fluoride sorption characteristics of the sorbents. Natural zeolite samples ($<45\ \mu m$) were pre-conditioned with HNO_3 solution (ZEO-1), $NaNO_3$ solution (ZEO-2), and deionized water (ZEO-3) before loading Al^{3+}, La^{3+}, and ZrO^{2+} on zeolite. ZEO-1 type zeolite had a higher capacity than ZEO-2 and ZEO-3 type zeolites. Metal exchange capacities are 0.233, 0.089, 0.090 mmol/g for ZrO^{2+}-, La^{3+}-, and Al^{3+}- exchanged zeolite (ZEO-1), respectively. Equilibrium isotherms fitted well to Langmuir and Freundlich models. Percent removal of fluoride from aqueous solution containing 2.5 mg F/L was 94% using metal loaded zeolite (ZEO-1 type) at an adsorbent concentration of 6.00 g/L.

Keywords: Drinking water, fluoride removal, ion exchange, metal loaded zeolite

INTRODUCTION

Fluoride pollution of water is widespread in many parts of the world. Fluoride in the environment occur through two different channels; natural sources and

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anthropogenic sources. Fluoride exists fairly abundantly in the earth's crust and can enter groundwater by natural processes; the soil at the foot of mountains is particularly likely to be high in fluoride from the weathering and leaching of bedrock with high fluoride content (1, 2). Toxic wastes containing fluorine/fluoride are generated in all industries using fluorine or its compounds as a raw material (1). Surface and groundwater levels near industrial sites using fluorides may be higher than normal if fluorides are released.

The optimum fluoride level in drinking water for general good health is considered to be between 0.5 and 1.0 mg/L (3). In a number of small villages in Sicily, Turkey, and India there is naturally occurring fluoride in the water ranging from 0.7 to 5.4 mg/L (4). But, the surface, subsurface, and thermal water sample analysis indicate the fluoride concentration ranging from <0.2 to 18 mg/L in the States of Jammu and Kashmir, <0.2 to 6.5 mg/L in Himachal Pradesh, >1.5 mg/L in Rajasthan, 0.2 to 0.6 in Haryana, 0.35 to 15 mg/L in Bihar, on an average 12 mg/L in West Bengal, 15 to 20 mg/L in Chattisgarh, 8.2 to 13.2 mg/L in Orissa, and 0.7 to 6.0 in Maharashtra, indicating that except in Haryana, the concentration of fluoride is very high up to 20 mg/L (5). Excessive ingestion of fluoride can damage the tooth-forming cells, leading to a defect in the enamel known as dental fluorosis. Teeth impacted by fluorosis have visible discoloration, ranging from white spots to brown and black stains (6). Long-term drinking of water containing high fluoride content can result in softening of bones, ossification of tendons and ligaments, and abnormal bone growth in both humans and animals called as skeletal fluorosis (7). Fluoride with a concentration of 1 mg/L causes breakdown of collagen, the most abundant of the body's protein at 30%. It also leads to irregular formation of collagen which serves as a major structural component of skin, ligaments, tendons, muscles, cartilage, bones and teeth (4, 8, 9). Consequently, treatment of fluoride has become a worldwide important subject nowadays (10).

Many methods have been developed to remove excessive fluoride from water; adsorption (11–13), ion exchange (14–16), precipitation (17), electrodialysis (18–20), and reverse osmosis (21, 22). Precipitation is a traditional method of removing fluoride from wastewater. Recently, an alternative fluoride-precipitation technique using a limestone reactor has been proposed. However, these methods are not suitable for drinking waters (23). Adsorption is an effective technique to remove fluoride from aqueous solutions. The viability of adsorption techniques is greatly dependent on the development of adsorptive materials. Ion exchange, electrodialysis, and reverse osmosis are effective methods and can remove fluoride to a suitable level, but require frequent regeneration of resin beads or membrane cleaning of the scaling and fouling (24). Table 1 summarizes removal methods for fluoride from water (25).

Researches on the removal of fluoride by various synthetic resins were reported in the literature. An aluminum-formed cation resin, Indion 225,

Table 1. Removal methods for fluoride from drinking water (23)

	Advantages	Disadvantages	Relative cost
Precipitation	Established process	Sludge produced, treated water is acidic, high chemical dose, Low efficiency, high residual	Low-med high
Adsorption	Locally available Effective, well-established High capacity	Large pH changes before and after treatment May give taste; degenerates Not universally accepted	Low-med high
Ion Exchange	Locally available High capacity	Disposal of chemicals used in resin regeneration	Medium
Electrodialysis	Can remove other ions. Used for high salinity	Skilled operators High cost. Not much used Concentated disposal	High
Reverse osmosis	Can remove other ions. Used for high salinity	Skilled operators High cost	High

used to study the removal of fluoride from aqueous solutions (14). Kaneseto et al. 1988 studied La(III) loaded chelating resin containing phosphonomethylamino groups for fluoride removal. Fluoride is effectively adsorbed on the column packed with La(III)-loaded resin at pH ranging 3-4. La(III)-loaded resin can adsorb fluoride ions without significant loss of the metal ion (26). It was reported that metal-loaded chelating resins (M: La(III), Ce(III), Zr(IV)) could selectively remove fluoride ions due to the complex formation of fluoride with these metal ions with high oxidation states (15). The large internal surface area of zeolite was utilized to create active sites for fluoride sorption by exchanging Na^+-bound zeolite with Al^{3+} or La^{3+} ions. Fluoride removal from water using Al^{3+}- and La^{3+}-exchanged zeolite F-9 was subsequently investigated to evaluate the fluoride sorption characteristics of the sorbents (27). Kabay and Kodama studied the ion exchange behavior of $BiO(NO_3) \cdot 0.5H_2O$ towards fluoride ions. The ion exchange reaction was rapid at pH 1, 6.6, 12. It was observed that $BiO(NO_3) \cdot 0.5H_2O$ is capable of removing 99% of the fluoride ions from the solution at pH 1-12 under optimal conditions (15). The same authors also studied the reactivity of anion exchanger $BiPbO_2(NO_3)$ regarding fluoride ions in solution (16). Wu et al. investigated the characteristics and conditions for removing fluoride ions from water by Inner-Mongolia natural zeolite. The results showed that activated natural zeolite possessed an ability to remove fluoride from water (28). A natural Mexican zeolite (heulandite-clinoptilolite from Sonora) was studied for the sorption of fluoride ions from aqueous solutions and well-water (29).

In this paper, preparation of metal loaded clinoptilolite type natural zeolite obtained from Manisa, Turkey using Al^{3+}, La^{3+} and ZrO^{2+} was defined. Removal of fluoride from aqueous solution by these metal-loaded zeolites was presented.

EXPERIMENTAL

Materials

Clinoptilolite type zeolite samples ($<45\mu m$) were taken from the Enli Mining Company. Zeolite samples were characterized by X-Ray diffraction (XRD) and chemical analysis (30). Chemical composition and the physical properties of zeolite given in Table 2.

Inorganic chemicals supplied by Merck were analytical-grade reagents. The solutions of lanthanum, aluminum, and zirconium ions were prepared by using their nitrate salts; $La(NO_3)_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $ZrO(NO_3)_2 \cdot xH_2O$, respectively, in deionized water. The solution of fluoride ion was prepared by dissolving NaF in deionized water. The tap water sample was obtained from Isparta, Turkey. Table 3 summarizes the content of ions in tap water sample.

Preparation of Metal-Loaded Zeolite Adsorbents

ZeO-1: 15 g of natural zeolite sample (<45 μm) was treated with 100 mL of 2 M HNO_3 solution. This mixture was continuously stirred at 40°C for 4 h and then filtered, washed with deionized water. Then, it was contacted with 100 mL 2 M $NaNO_3$ aqueous solution at pH 8–8.5 by continuous stirring

Table 2. Chemical composition and physical properties of zeolite sample

Chemical composition	(%)	Physical properties	
SiO_2	70.90	Appearance porosity (%)	44.20
Al_2O_3	12.40	Appearance density (g/cm^3)	2.25
Fe_2O_3	1.21	Weight of per unit volume (g/cm^3)	1.32
CaO	2.54	Water adsorption (original), (%)	31.30
MgO	0.83	Water adsorption (grinding), (%)	105
Na_2O	0.52	Oil absorption (g oil/100 g sample)	66
K_2O	4.46	Whiteness (%)	68
SO_3	0.10	Original bleaching (g sample/g tonsil)	1.90
H_2O	6.88	Active bleaching (g sample/g tonsil)	1.70
Si/Al	4.66		

Table 3. Composition of tap water

Species	Concentration (mg/L) pH:8.0
Sodium	109.0
Potassium	1.30
Calcium	3.00
Magnesium	19.00
Fluoride	2.90
Nitrate	1.60
Chloride	2.10
Bicarbonate	358.0
Sulphate	18.10
TDS	101.0

for 4 h. Later on, pH of the solution was adjusted to 6.5–7 with HNO_3 solution. It was filtered, washed, and dried at 105°C for 24 h. Thus prepared sample was defined as ZEO-1.

ZeO-2: 15 g of zeolite sample was treated with 100 mL 2 M $NaNO_3$ solution for 4 h with a continuous stirrer. The treated sample was filtered, washed, and dried at 105°C for 24 h. It was as ZEO-2.

ZeO-3: 15 g of zeolite sample was contacted with 100 mL of deionized water. Then, the sample was filtered, and dried at 105°C. It was as ZEO-3.

The loading of metal ions on pre-conditioned zeolites (ZEO-1, ZEO-2, ZEO-3) was carried out using batch method. An amount of 3 g zeolite samples was contacted with 50 mL of 5000 mg-La^{3+}/L, 1000 mg-Al^{3+}/L and 2000 mg-ZrO^{2+}/L solution at 30°C for 24 h with a continuous shaking.

To load metal ions on zeolite as the other way, metal hydroxides were precipitated on the zeolites. An amount of 1 g ZEO-1 type zeolite was contacted with 50 mL of different amounts of Al^{3+} (20, 30, 40, 50 mg), La^{3+} (25, 50, 75, 100 mg), Zr^{4+} (25, 50, 75, 100 mg) ions for 24 h at 30°C with a continuous shaking in a shaker. By doing this, metal ions (Me) were first loaded onto ZEO-1 type zeolite by ion exchange. After then, the remained metal ions in the solution are treated with an ammonia solution (pH 8–8.5) with continuous mixing at 80–90°C. These metal ions were quantitatively precipitated as metal hydroxides on zeolites ($Me(OH)_x$-ZEO-1). The mixture was filtered and washed several times using demineralized water. Finally, metal loaded ($Me(OH)_x$-ZEO-1) was dried at 105°C.

Batch-Mode Sorption Studies

Various amounts of metal ions loaded zeolites (0.1 to 0.4 g) were contacted with 50 mL of NaF solution containing 2.5 mg–F/L for 24 h at 30°C with continuous shaking in order to find the optimum amount of zeolite concentration for fluoride removal from the aqueous solution.

For the adsorption isotherm study, 0.1 g of metal ions loaded zeolites was contacted with 50 mL of NaF solution at concentrations of 1, 2.5, 5, 10, 15, 20 mg-F^-/L at 30°C for 24 h with continuous shaking.

The fluoride sorption abilities of zeolite (Me(OH)-ZEO-1) on which metal hydroxide were precipitated were tested using sample of tap water obtained from Isparta, Turkey. In this study, an amount of 0.3 g zeolite was contacted with 50 mL tap water sample for 24 h at 30°C with continuous shaking.

Analysis

The analysis of fluoride ion and the other anions were carried out using a Shimadzu model ion chromatography equipment (Model LC 10 A). The cations were determined by using the atomic absorption spectrophotometer (Model Varian Plus 10 *Ai*).

RESULTS AND DISCUSSION

Adsorption of Metal Ions (Al, La, Zr) onto Zeolite

Ion exchange capacities of metal loaded zeolites are given in Table 4. As seen in Table 4, ZEO-1 type adsorbent has a higher capacity than ZEO-2 and ZEO-3 types.

During the preparation of ZEO-1, divalent ions on zeolite structure were removed by treatment with HNO_3. Then zeolite was treated with $NaNO_3$ and NaOH solutions, respectively. During these treatments, sodium ions derived

Table 4. Adsorption of metal ions on zeolite

Modified zeolite	mmol M^{n+}/g-zeolite
Zr-ZEO-1	0.233
Zr-ZEO-2	0.212
Zr-ZEO-3	0.185
La-ZEO-1	0.089
La-ZEO-2	0.086
La-ZEO-3	0.058
Al-ZEO-1	0.090
Al-ZEO-2	0.061
Al-ZEO-3	0.053

from $NaNO_3$ or NaOH in solution can take the position of divalent ions removed by acid wash. Sodium ions on ZEO-1 could easily exchange with metal ions (Al, La, Zr). This was considered to be the reason of the higher metal loading of ZEO-1 than other zeolite adsorbents.

Effect of Zeolite Amount

This experiment was studied using ZEO-1 type zeolite. The effect of zeolite amount on fluoride removal from aqueous solutions was investigated using various amount of zeolite. Figure 1 shows the results obtained. In general, an increase in the amount of zeolite increased the percent removal of fluoride. In order to remove fluoride quantitatively (95%) from aqueous solution, the amount of zeolite needed was found as 6.00 g-zeolite/L-fluoride solution.

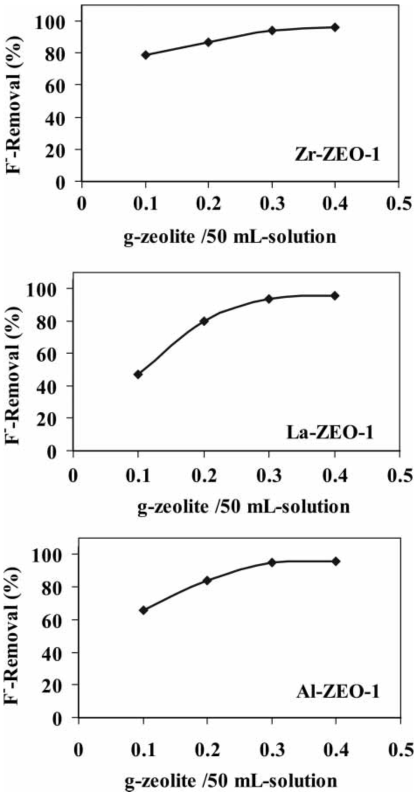

Figure 1. Effect of modified zeolites amount on removal of fluoride ion from aqueous solution.

Adsorption Isotherm Models

The distribution of fluoride between the liquid and solid phases is a measure of the position of equilibrium in the adsorption process and can be expressed by the Freundlich and Langmuir (31, 32).

The Langmuir adsorption isotherm model (Eq. (1)) is valid for monolayer sorption onto a surface with a finite number of identical sites, is given by

$$Q_e = \frac{Q_o b C_e}{1 + bC_e} \tag{1}$$

where C_e is the equilibrium concentration (mg/L), Q_e the amount adsorbed at equilibrium (mg/g), and Q_o and b are the Langmuir constants related to the capacity and a constant related to the affinity of the binding sites, respectively. The Langmuir adsorption isotherm model can be rearranged as follows (Eq. (2)):

$$\frac{C_e}{Q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \tag{2}$$

The equilibrium relationships for zeolites and linearized forms of Langmuir isotherm model are shown in Figs. 2 and 3, respectively. The values of Q_o and b were calculated from the slope and the intercept of the linear plots C_e/Q_e versus C_e (Table 5). The applicability of the Langmuir isotherm suggests the formation of monolayer coverage of the adsorbates (fluoride) on the surface of the zeolite. The correlation coefficient values, R^2, indicate favorable adsorption for the Langmuir isotherm. The Langmuir isotherm is linear with concentration and surface saturation is reached at higher concentration. Fluoride sorption capacities for Zr-exchanged zeolite were higher than those of La^{3+} and Al^{3+} -exchanged zeolites.

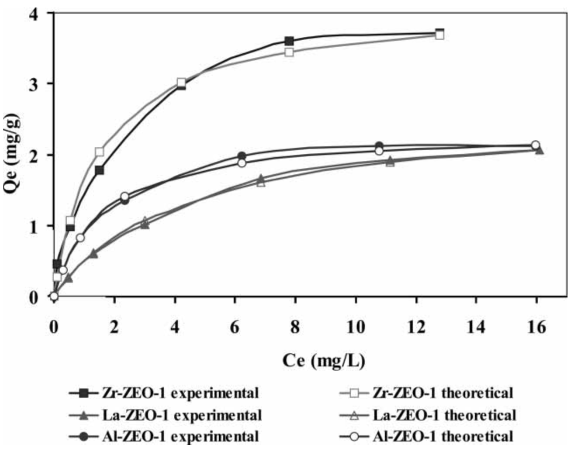

Figure 2. Equilibrium isotherm for loading fluoride onto metal ions loaded ZEO-1.

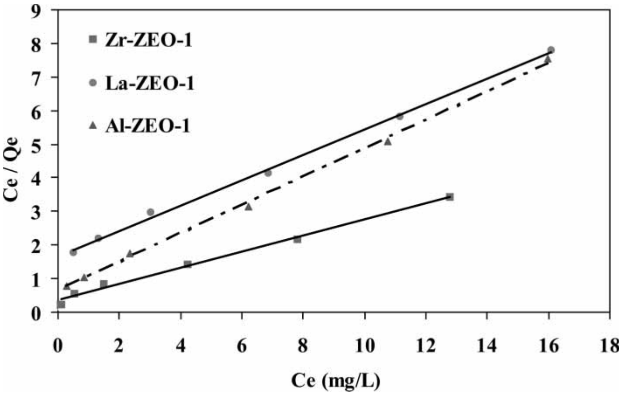

Figure 3. Linearized form of Langmuir isotherm for metal ions loaded ZEO-1.

The Freundlich model, which is indicative of surface heterogeneity of the sorbent, is given by Eq. (3).

$$Q_e = K_f C_e^{(1/n)} \tag{3}$$

The Freundlich equation can be linearized by logarithmic transfer (Eq. (4));

$$\log Qe = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

where K_f and $1/n$ are Freundlich constants related to adsorption capacity and adsorption intensity respectively. The constant of Freundlich, K_f and $1/n$ were calculated from the slope and the intercept of the linear plots log Q_e versus log C_e (Fig. 4). The correlation coefficients for the linear regression fit of Freundlich isotherm equation are given in Table 6. The data related to Freundlich adsorption isotherm explain the surface heterogeneity of the sorbent. The obtained data fit the Freundlich adsorption isotherm. This explains altering

Table 5. Langmuir isotherm constants and correlation coefficient

Zeolite	Q (mg/g)	b	R^2
Zr-ZEO-1	4.13	0.65	0.9936
Zr-ZEO-2	3.68	0.86	0.9964
Zr-ZEO-3	3.37	0.9	0.9968
La-ZEO-1	2.63	0.23	0.9978
La-ZEO-2	2.37	0.27	0.9831
La-ZEO-3	2.55	0.22	0.9878
Al-ZEO-1	2.35	0.64	0.9955
Al-ZEO-2	2.04	0.63	0.9964
Al-ZEO-3	2.33	0.5	0.9944

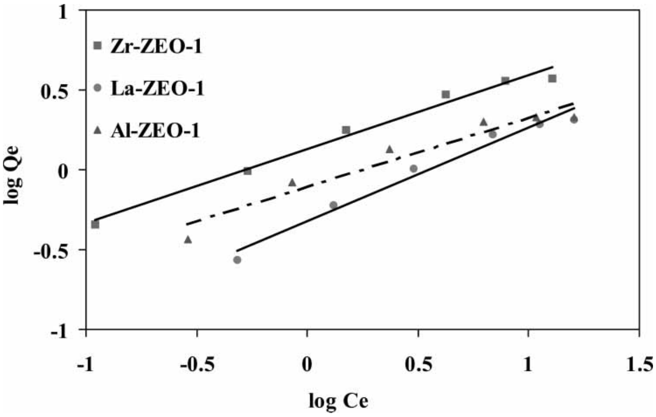

Figure 4. Linearized form of Freundlich isotherm for metal ions loaded ZEO-1.

the probability of adsorption to vacant sites. The Freundlich constant K_f for Zr-ZEO-1, Zr-ZEO-2, Zr-ZEO-3 (ZrO^{2+}-exchanged zeolite) were 1.34, 1.34, 1.24, respectively. However, the adsorption intensity was less for La^{3+}-exchanged zeolite than those of ZrO^{2+} and Al^{3+}-exchanged zeolites. Lesser values imply lesser heterogeneity (26).

To distinguish the mechanisms involved in fluoride uptake by metal-ion-exchanged zeolite, it was applied the Dubinin–Radushkevich (DR) isotherm model, which is based on the Polanyi theory. In its widely used form, it relates the fractional coverage to the Polanyi potential (ε) as given (27):

$$\frac{C_{ads}}{X_m} = e^{(-k\varepsilon^2)} \tag{5}$$

and its linear form $\ln C_{ads} = \ln X_m - k\varepsilon^2$

Table 6. Freundlich isotherm constants and correlation coefficient

Zeolite	K_f (mg/g)	n	R^2
Zr-ZEO-1	1.34	2.18	0.9825
Zr-ZEO-2	1.34	2.25	0.9477
Zr-ZEO-3	1.24	2.25	0.9404
La-ZEO-1	0.47	1.7	0.9713
La-ZEO-2	0.51	1.91	0.9668
La-ZEO-3	0.43	1.61	0.9519
Al-ZEO-1	0.77	2.25	0.9317
Al-ZEO-2	0.84	3.06	0.9083
Al-ZEO-3	0.89	2.94	0.8834

where C_{ads} is the number of fluoride ions adsorbed per unit weight of adsorbent (mol/g), X_m is the maximum sorption capacity (mol/g).

For liquid-phase adsorption,

$$\varepsilon = RT \ln(1 + 1/C_e) \tag{6}$$

where C_e is the equilibrium concentration of fluoride, R is the gas constant (kJ/mol · K), and T is the temperature (K). The slope of the plot of ln C_{ads} versus ε gives k ($\mathrm{mol}^2/\mathrm{kJ}^2$) and the intercept yields the sorption capacity, X_m (mol/g).

To evaluate the nature of interaction between fluoride and the binding sites, mean free energy of sorption per mole of the adsorbate, which is the energy required to transfer one mole of a adsorbate to the surface from infinity in solution, was determined (Eq. (7)).

$$E = 1/\sqrt{-2k} \tag{7}$$

The plot of ln C_{ads} against ε^2 for fluoride ion sorption on metal ion loaded zeolite types is shown in Fig. 5. The DR parameters are calculated from the slope of the line in Fig. 5 and listed in Table 7. As shown in Table 7, the *E* values for fluoride sorption on metal ions loaded zeolite types are in the range of 9.28 – 11.62 kJ/mol. Since E value are between 8 and 16 kJ/mol, the adsorption process proceeds by ion exchange as follows (27);

$$\text{ZEO-MeOH}_2^+ + \text{F}^- \leftrightarrows \text{ZEO-MeF} + \text{H}_2\text{O} \tag{8}$$

$$\text{ZEO-MeOH} + \text{F}^- \leftrightarrows \text{ZEO-MeF} + \text{OH}^- \tag{9}$$

The sorption energy E determined in the DR equation revealed the nature of the ion-exchange mechanism in this system.

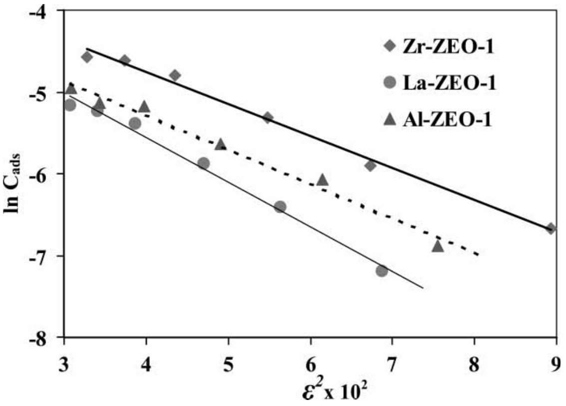

Figure 5. DR plots of fluoride ions on metal ions loaded zeolite at constant temperature.

Table 7. Parameter obtained in the DR equation

	R^2	X_m (mol/g)	$-k$ (mol^2/kJ^2) × 10^{-3}	$-E$ (kJ/mol)
Zr-ZEO-1	0.9921	0.041	3.9	11.32
Zr-ZEO-2	0.9875	0.035	3.7	11.62
Zr-ZEO-3	0.9710	0.035	3.8	11.47
La-ZEO-1	0.9892	0.034	5.5	9.53
La-ZEO-2	0.9763	0.026	4.8	10.21
La-ZEO-3	0.9762	0.038	5.8	9.28
Al-ZEO-1	0.9642	0.024	4.0	11.18
Al-ZEO-2	0.9484	0.022	4.1	11.04
Al-ZEO-3	0.9694	0.025	4.5	10.54

Removal of Fluoride from Tap Water by Metal Hydroxide Loaded (ZEO-1)

As defined in Table 8, the metal amounts loaded on zeolite by ion exchange are determined as 21.25, 12.23, 2.44 mg/g-adsorbent for Zr, La, Al respectively, by measuring the amount of metal ions remained in the supernatant after loading excess amount of metal onto ZEO-1 samples (see 2.2). The amount of metal ions loaded on ZEO-1 samples found according to mass

Table 8. Determined metal amounts in these zeolites

Metal	Sample no	mg-metal/g-zeolite	mg-metal/g-metal loaded zeolite
		21.25[a]	21.03
Zr	1	25.00	24.58
	2	50.00	47.14
	3	75.00	67.91
	4	100.00	87.11
		12.23[a]	12.16
La	5	25.00	24.42
	6	50.00	47.27
	7	75.00	68.68
	8	100.00	88.79
		2.44[a]	2.44
Al	9	20.00	19.10
	10	30.00	27.88
	11	40.00	36.21
	12	50.00	44.10

[a] Adsorption of metal ions on zeolite by ion exchange (See 2.2).

Table 9. Removal rate of fluoride from tap water by Me-ZEO-1 zeolites

Zeolite sample (Me-ZEO-1)	Removal (%)
Zr-ZEO-1	91.05
La-ZEO-1	90.36
Al-ZEO-1	89.67

Table 10. Removal rate of fluoride from tap water by $Me(OH)_x$-ZEO-1 zeolites

Zeolite sample (Me(OH)-ZEO-1)	Removal (%)
(4)[a] Zr(OH)-ZEO-1	85.58
(8)[a] La(OH)-ZEO-1	85.12
(12)[a] Al(OH)-ZEO-1	84.68

[a] See Table 8. (4) = 100 mg Zr/g-zeolite; (8) = 100 mg La/g-zeolite; (12) = 50 mg Al/g-zeolite.

change after loading of metal ion were also listed. As seen in Table 8, the difference was negligible. The samples 1–12 given in Table 8 represent the samples prepared by loading metal ions through ion exchange and precipitation with NH_3 (see 2.2). The amounts of metal ions loaded on ZEO-1 as ($Me(OH)_x$-ZEO-1) by precipitation with NH_3 following the ion exchange were calculated according to mass change. As summarized in Table 8, the amount of metal ions loaded on ZEO-1 increase with an increase in the amount of metal concentration used.

The sorption capabilities of these prepared zeolite adsorbents were tested for removal of fluoride from tap water samples obtained from Isparta, Turkey. The results are given in Tables 9 and 10. It was seen that about 85% of fluoride from water could be removed by Me(OH)-ZEO-1 type zeolite adsorbent while metal loaded ZEO-1 has 90% of the removal. These results show that metal loaded zeolite can be used effectively for the removal of fluoride from tap water.

CONCLUSIONS

In this study, removal of fluoride from aqueous solutions and tap water was investigated by using metal ion loaded natural zeolite. The removal of fluoride increased with an increasing amount of metal ion loaded zeolite. The adsorption process obeys the Langmuir and Freundlich isotherm. The metal ion loaded natural zeolite can be used for removing fluoride from water.

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