ADSORPTION OF FLUORIDE BY CLAYS FROM THE POTENTIAL SITES FOR ACID WASTE STORAGE

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ABSTRACT

The aim of this work, consists to evaluate the potential effectiveness of clays coming from three sites (MK, H and ZB) intended for the storage of acid industrial waste Charged by F^-. The interaction between fluoride and clays is affected by some parameters: pH, contact time, type of clays and initial fluoride ion concentration. Firstly, we examined the adsorption of fluoride from NaF solution at various concentrations and pHs (3, 4, 5.5 and 6.5). We concluded that for each sample the maximum fluoride sorption capacity was found at pH 3. In the second step, the study of fluoride adsorption on clay is carried out by the solution of accompanying waste (pH between 2-3 and F^- concentration is 2360 mg/l). MK palygorskitic clay was showed to be a superior fluoride sorbent than other samples.

1. INTRODUCTION

Within the framework of storage of high acidic waste charged by fluoride ion, the protection of groundwaters is of primary importance to avoid the risk of fluorosis associated to the using of water for human consumption. In this context, it exist many studies on F^- sorption in soils (Peek and Volk, 1983; Robbins, 1986).

Clay soils retain fluoride better than others soils, and calcium in the soil tends to increase retention. Fluoride is adsorbed onto clays (gibbsite, smectite, palygorskite, illite, kaolinite) in ion-exchange reactions where the fluoride ion competes with hydroxyl ions (OH^-), but the primary exchange reaction appears to be with iron and aluminium hydroxides, at low fluoride levels. High levels of fluoride will result in exchange of F^- by OH^- in clay minerals themselves (Bower and Hatcher, 1967; Flühler et al., 1982). On the other hand, several methods have been tried to remove fluorides from water, namely adsorption (Kau et al., 1997 and 1998; Azbar and Turkman, 2000; Oguz, 2005), precipitation (Reardon and Wang, 2000), electrodialysis (Amor et al., 2001) and electrochemical methods (Shen et al., 2003; Mameri et al., 1998). However, adsorption is still one of the most extensively used methods for defluoridation of wastewater.

The aim of this work is to test the ability of fluoride adsorption by three clay samples coming from three sites intended for the storage of the acidic industrial waste in south of Tunisia. This waste is accompanied by lixiviate solution, where the fluoride concentration is about 2360 mg/L and pH≈3. Considering that doesn't have any information on the fluoride removal capacity of Tunisian clays and soils are currently available. We started our study by

determining the F⁻ adsorption capacity of these clays by a synthesized solution of NaF and varying the pH from 3 to 6.5. Then, we interested to the determined of adsorption isotherm of the three sample by synthesized and waste solution at pH≈3. Moreover, the adsorption equilibrium is well correlated by Freundlich and Langmuir models.

2. EXPERIMENTAL MATERIALS AND METHODS

2.1 Materials.

The samples used in this study were collected from three locations of acidic waste storage in Gabes from the South-East of Tunisia. The physico-chemical characterization of three raw clays has been presented in the Table 1.

TABLE 1.   Mineralogical composition, specific surface areas and cation exchange capacities of clay samples.

Sample	Mineralogical composition of clay samples (%)							S_{BET} (m²/g)	CEC (meq/100g)
	Paly	Smec	Kao	Il	Q	Ca	Do		
MK	35.39	1.69	14.9	-	28.07	18.94	-	35.43	16.54
H	-	56.26	6.51	-	12,94	26.62	-	57.12	49.82
ZB	-	-	22.9	62.7	8,69	-	4,73	91.51	24.67

Paly: palygorskite, Smec: Smectite, Kao: Kaolinite, Il: Illite, Q: Quartz, Ca: Calcite, Do: Dolomite

For all samples, the powder was sieved to get a particle sizes under 106 μm and were dried at 90°C for a minimum of 24 hours before sorption studies.

2.2 Instruments and procedure of sorption studies.

The fluoride concentrations were measured using a Metrohm 781 pH/Ion Meter with fluoride crystal membrane electrodes. The pH measurements were made using an HI 9321 Microprocessor pH meter (HANNA Instruments) combination electrode. The calibration curve for fluoride measurements was obtained using NaF standard solutions with different F⁻ concentrations from 1 to 50 mg/L. During the experimental F⁻ measurements, the dilution is necessary if the F⁻ concentration of the solution exceeds the range of the apparatus.

2.2.1 Kinetic studies.

Adsorption capacities for the different samples were determined at different pH values (3, 4, 5.5, and 6.5) by shaking 1g of sieved and dried clay with 10 ml of 500 mg/L NaF solution in polyethylene bottles at 25°C. Small amounts of (5 10⁻¹ or 5 10⁻² M HNO₃) were also added initially to provide the solutions with final pH values, then the solute was made up to a volume of 30 mL with deionised water. The bottles were mixed in a rotary agitator for periods ranging from 2 hours to 8 days before being centrifuged at 3000 rpm for 10 min. After centrifugation, total F⁻ concentrations in the recovered solution were measured after addition of TISAB buffer (Harwood, 1969) which reduces the variation of the ionic strength in the solutions and it's the decomplexing agent that releases all complexed F⁻ into free fluoride ions.

2.2.2   Adsorption Isotherms.

Fluoride sorption isotherms were determined by a procedure similar to that described above, 1 g of clay and 10 mL of NaF solution at various concentrations 50 to 10000 mg/L were pH has adjusted to 3 and the solute was made up to a volume of 30 mL with deionised water, also has been mixed in polyethylene bottles at 25°C.

2.2.3   Adsorption Isotherms using waste solution.

Clay adsorbent (1g) was suspended in 30 mL of waste solution where F^- concentration (2360 mg/L) and at pH≈3. Moreover, this solution contains many others ions such as Cl^-, Ca^{2+} and Na^+. The variations of the concentrations has made by dilution of the initial solution were using a range of (23.6 to 2360 mg/L) preserving even pH.

3. RESULTS AND DISCUSSION

3.1   Equilibrium time and pH effect

The pH of the solution is a controlling factor in the adsorption process. The equilibrium time for the fluoride sorption reaction is defined as the agitation period necessary for the F^- concentration in solution to achieve a steady state. It is found that the removal of fluoride ions increases with increasing of contact time to some extent. Further increase in contact time does not increase the uptake due to deposition of fluoride ions on the available adsorption sites on adsorbent material. First observations on the uptake of fluoride ions on the adsorbent samples at their optimum pH values indicate that the processes are quite rapid. On average, more than 60% of the adsorption occurs within the second hours of the contact of initial solution with raw clays sorbents see (Fig. 1, 2 and 3). Kau et al., 1998 observed similar results using kaolinite and Bentonite clay as adsorbent.
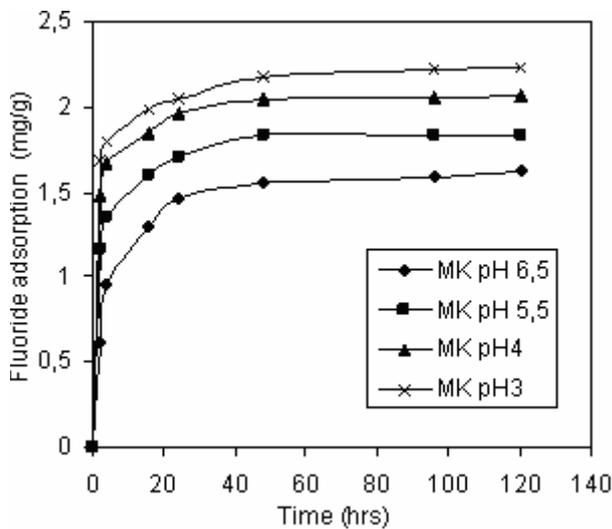

FIGURE 1. Effects of reaction time on sorbed fluoride at pH values between 3 and 6.5 for MK clay.
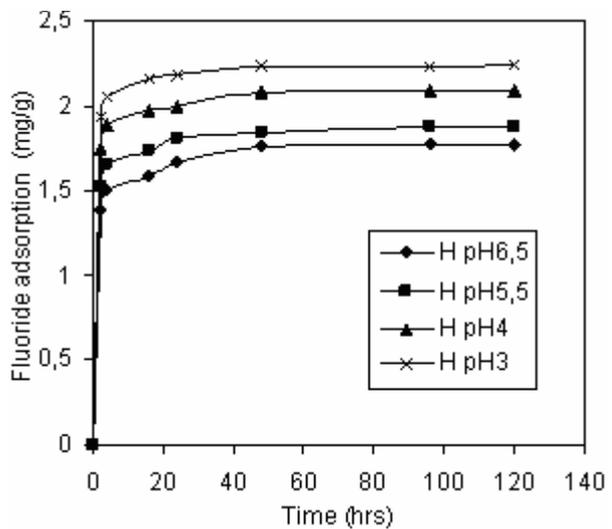
FIGURE 2. Effects of reaction time on sorbed fluoride at pH values between 3 and 6.5 for H clay.

This initial rapid adsorption subsequently gives way to a very slow approach to equilibrium but saturation is reached in 24 hrs for ZB and 48 hrs for H and MK samples. This contact time was considered as the equilibrium time for the remains of adsorption study. In the other hand, we have observed a decrease in the fluoride adsorption with increase in the pH of the solution. In the case of H and Mk sorbents, the percentage of adsorption increased almost linearly as function of pH between 3 and 6.5, attaining a maximum F⁻ removal at pH 3.

Figure 4 shows that two samples (MK and H) have a very high F⁻ adsorption capacity even with pH 6.5, but in the case of ZB the adsorption capacity is weak, considering that the essentially fraction is the illite which has a low F⁻ adsorption capacity (Coetzee et al, 2003). Then, the higher adsorption capacity is due firstly to the structure of the clay (for MK composed essentially of the palygorskite, for H the principal fraction is the smectite) which have a higher F⁻ adsorption capacity in agreement with (Coetzee et al, 2003) and (Kau et al, 1998) respectively. Secondary, the important amount of calcite fraction in MK and H played a very significant role in fluoride removal from solution. According to Brett et al, 2006 the calcite helps well to fluoride removal.
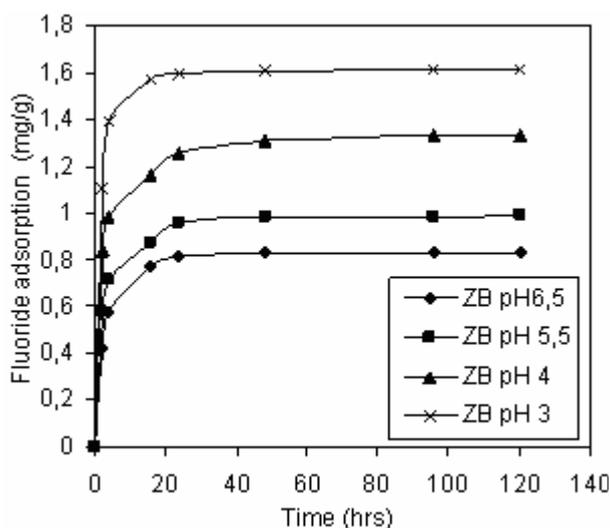

FIGURE 3. Effects of reaction time on sorbed fluoride at pH values between 3 and 6.5 for ZB clay.
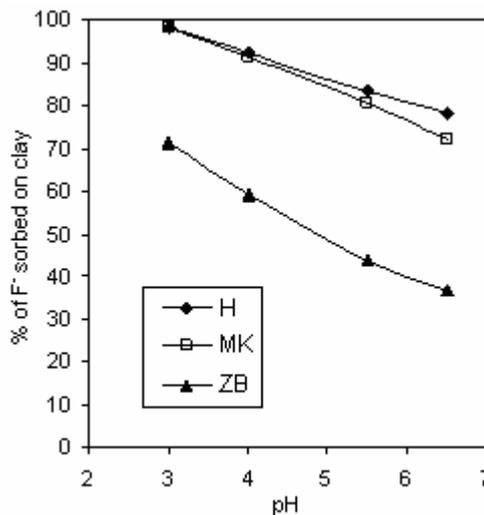
FIGURE 4. Effects of pH on the percentage removal of fluoride.

3.2 Fluoride sorption isotherms

Equilibrium studies were carried out to determine the optimum conditions for maximum fluoride removal by these three samples. The experimental sorption isotherm is to plot the amount of F⁻ sorbed, expressed in milligrams of F⁻ per gram of clay, vs the equilibrium F⁻ concentration (mg/l). The adsorption isotherm, using NaF solution of all samples has been study at pH 3 to approach the waste solution condition. The experimental sorption data for the removal of fluoride ions at pH 3 have been correlated with Langmuir (Eq. 1) and Freundlich (Eq. 2) models.

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \qquad\qquad (1)$$

$$q_e = K_F C_e^{1/n} \qquad\qquad (2)$$

Where q_e is the amount of ions adsorbed per unit weight of adsorbents (mg/g), C_e is the equilibrium concentration (mg/l), Q_o and b are the Langmuir constants related to capacity and energy of adsorption, respectively. K_F and $1/n$ are the Freundlich constants.

Figure 5 present the experimental sorption isotherms with NaF solution and the correlation using the two models for the three clays at pH 3. We observed that the sorptivity gradients for MK and H clays are very similar, as predicted by the modelled bonding constants, but the MK sample has slightly higher sorption capacities.
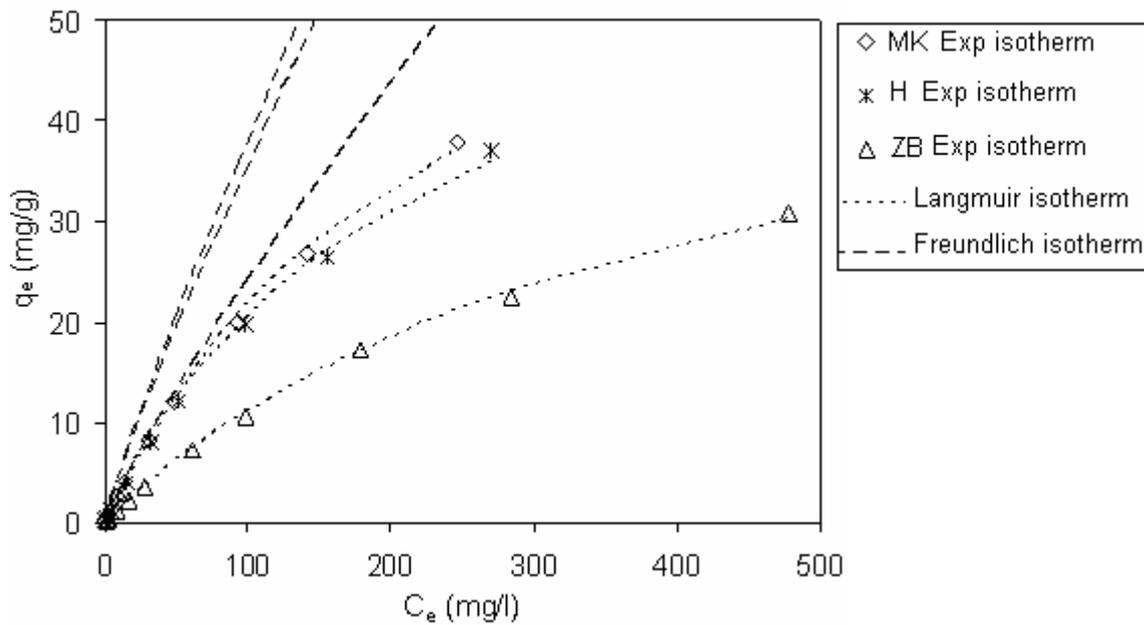

FIGURE 5. Experimental sorption of fluoride by the three samples (NaF solution) with fitted Langmuir, and Freundlich isotherms.

Table 2 shows that for all samples, the Langmuir sorption isotherm provided a slightly better approximation than the Freundlich isotherm and this is very clear in the case of ZB clay where ($r_F^2 = 0.947$, $r_L^2 = 0.994$). Also, we note that the Freundlich constant ($1/n$) is in the range of 0.1–1 which indicates it can be a favourable adsorption process. Then, the maximum adsorption capacity is 73 mg/g for MK clay, is relatively higher than reported on other adsorbents for fluoride removal.

TABLE 2.   Summary of optimised isotherm parameters (NaF solution).

Sample	Isotherm type	Q_0 (mg/g)	b (l/mg)	K_F	1/n	r^2
MK	Langmuir	73	$4.25\ 10^{-3}$	-	-	0.991
	Freundlich	-	-	0.64	0.89	0.965
H	Langmuir	64.32	$4.83\ 10^{-3}$	-	-	0.992
	Freundlich	-	-	0.62	0.88	0.979
ZB	Langmuir	54.94	$2.56\ 10^{-3}$	-	-	0.994
	Freundlich	-	-	0.46	0.86	0.947

Figure 6 shows the sorption isotherm of the three clay samples using the lixiviat solution at pH 3. We remarked a decrease of adsorption capacity of fluoride by ZB sample. This is due to the attack of the kaolinite under this acidic condition (Hamdi et al., 2005) which can explain the consumption of F^- within the dissolution reaction.
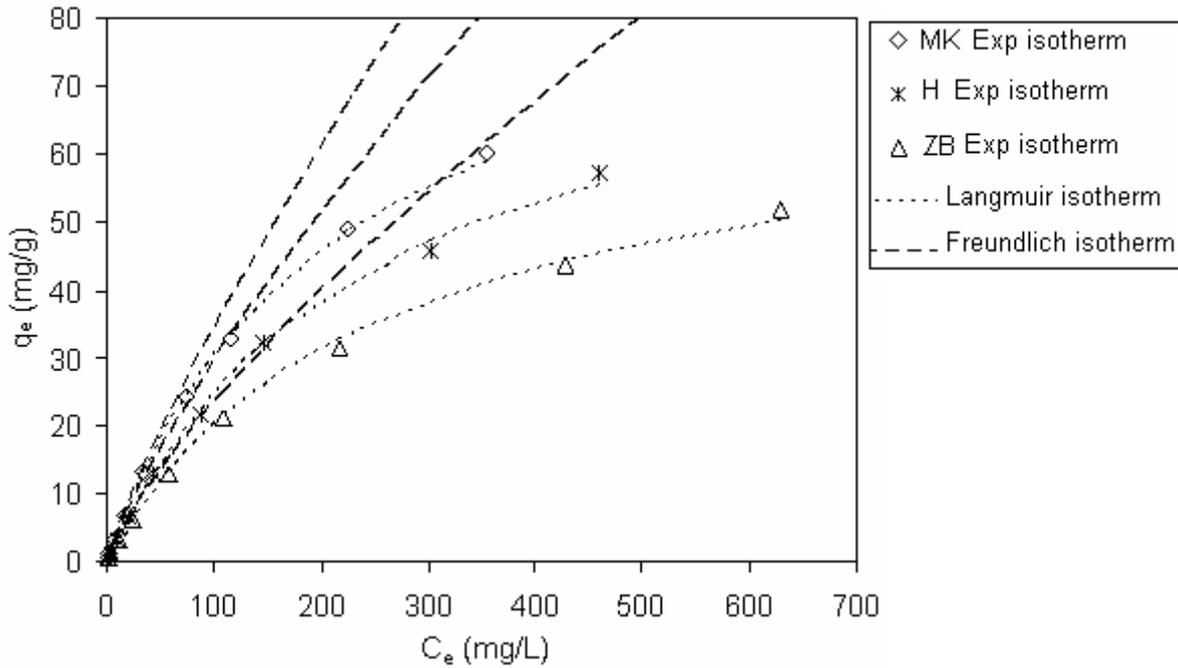

FIGURE 6. Experimental sorption of fluoride by the three samples (waste solution) with fitted Langmuir, and Freundlich isotherms.

The optimised parameters of Freundlich and Langmuir isotherm for each sample and the coefficient of regression r^2 are summarised in Table 3. The values of r^2 for both models of adsorption show that very similar, but the Langmuir model remains the best. The higher

sorption capacity of the MK and H clays may be partially attributed to the clay type and to its comparatively greater amount of calcite than ZB sample. Calcium in these samples (MK and H) also assists in F immobilisation through precipitation. Although, the solubility of carbonate minerals, such as calcite or dolomite, makes the application of adsorption theory difficult. For that it's not easy to differentiate adsorption from precipitation. However, at high fluoride concentration, we notice that the capacity of F^- adsorption of the sample H became lower comparing to MK clays this is due probably to the interaction with others ions (Cl^-, Na^+, Ca^{2+}) existing in the waste solution that influences the fluoride adsorption because H clay has a high exchange capacity. In addition, this best fluoride adsorption by MK sample has confirmed by (Hamdi and Srasra, 2005) using the EDS/SEM analysis which shows an amount of fluoride in MK solid sample after treatment by acidic lixiviat.

TABLE 3.   Summary of optimised isotherm parameters (waste solution).

Sample	Isotherm type	Q_0 (mg/g)	b (l/mg)	K_F	1/n	r^2
MK	Langmuir	93.45	4.91 10^{-3}	-	-	0.994
	Freundlich	-	-	0.82	0.84	0.991
H	Langmuir	84.03	4.29 10^{-3}	-	-	0.982
	Freundlich	-	-	0.75	0.8	0.981
ZB	Langmuir	69.44	4.22 10^{-3}	-	-	0.986
	Freundlich	-	-	0.72	0.76	0.983

4. CONCLUSION

The study of fluoride adsorption behaviour by clay soil shows clearly that the adsorption capacity depends to the clay structure, the percentage of carbonate in the sample and the pH of medium which is responsible to the charge distribution on the surface of adsorbent. For this reason the pH solution governs the amount of variable charge on the clay and also the extent to which hydroxyl groups may be removed to facilitate F^- sorption. For that, the results of the kinetic studies show a maximum of F^- adsorption capacity for all samples at pH 3. In addition, in this pH the carbonate (calcite or dolomite) in samples are attacked and the free calcium in solution can also play an important role in F^- immobilisation by precipitation to CaF_2. The experimental sorption isotherm results indicate that MK and H clay is a favorable adsorbent for removal of fluoride of waste solution. However, for characterising the experimental sorption isotherm, the utilisation of a suitable model of sorption isotherm is most important. In this context, Langmuir isotherm was found to provide a more accurate approximation than the Freundlich isotherm, mainly because of the asymptotic nature of the isotherm and this is confirmed by a better approximation r^2. Following these results, the maximum of F^- adsorption capacity Q_0 obtained for MK clay is equal 73 mg/g using NaF synthesis solution

and 93.45 mg/g with the waste solution. For H sample we observed again a high F⁻ adsorption capacity equal 84.03 mg/g with the waste solution, but in the case of ZB, the illito-kaolinitic fraction and poor amount of dolomite are responsible to the low F⁻ adsorption capacity.

REFERENCES

Amor, Z., B. Bernard, N. Mameri, M. Taky, S. Nicolas, A. Elmidaoui (2001), Fluoride removal corn brackish water by electrodialysis, *Desalination, 133,* 215-223.
Azbar, N., and A. Turkman (2000), Defluorination in drinking waters, *Water Sci. Tech., 42,* 403-407.
Bower, C.A., and J.T. Hatcher (1967), Adsorption of fluoride by soils and minerals, *Soil Sci. 103,* 151-164.
Brett, D. T., P. J. Binning, and S .L. S. Stipp., (2006), Fluoride removal by calcite: vidence for fluorite precipitation and surface adsorption, *Environ. Sci. and Technol.,* doi:10.1021/es0505090, in press.
Coetzee, P. P., L. L. Coetzee, R. Puka and S. Mubenga (2003), Characterisation of selected South African clays for defluoridation of natural waters. *Water S. A. 29,* 331-338.
Flühler, H.J., J. Polomski, and P. Blaser (1982), Retention and movement of fluoride in *soils. J. Environ. Qual. 11,* 461-468.
Hamdi, N., and E. Srasra, (2005), Textural and structural evolution of clays from three potentials sites for acid effluents storage: Effect of the acid attack, *Materials science, An Indian journal, 1,* (1-2).
Hamdi, N., M. Della, and E. Srasra (2005), Experimental study of the permeability of clays from the potential sites for acid effluent storage, *Desalination, 185,* 523-534.
Harwood, J. E., (1969), The use of an ion-selective electrode for routine fluoride analyses on water samples, *Water Res., 3,* 273.
Kau, P. M. H., D. W Smith, and P. J. Binning (1997), The dissolution of kaolin by acidic fluoride wastes, *Soil Sci., 162 ,* 12, 896-911.
Kau, P. M. H., D. W Smith, and P. J. Binning (1998), Experimental sorption of fluoride by kaolinite and Bentonite, *Geoderma, 84,* 89-108.
Mameri, N., A. R. Yeddou, H. Lounici, D. Belhocine, H. Grib, and B. Bariou (1998), Defluorination of septentrional Sahara water of north Africa by electrocoagulation process using bipolar aluminium electrodes, *Water Res., 32,* 1604-1612.
Oguz, E. (2005), Adsorption of fluoride on gas concrete materials, *J. Hazard. Mater., 117,* 227-233.
Peek, D.C., V.V. Volk (1983), Fluoride sorption by Oregon soils. *Agron. Abstr.* 1983, 149.
Reardon, E. I., and Y. X. Wang (2000), A limestone reactor for fluoride removal from wastewater, *Environ. Sci. Tech., 34,* 3247-3253.
Robbins, C.W., (1986), Fluoride adsorption by a saline sodic soil irrigated with a high fluoridex water. *Irrig. Sci. 7,* 107.
Shen, F. X. Chen, P. Gao, and G. Chen (2003), Electrochemical removal of fluoride ions from industrial wastewater, *Chem. Eng. Sci., 58,* 3341-3352.