

## RETENTION OF FLUORIDE FROM INDUSTRIAL ACIDIC WASTEWATER AND NaF SOLUTION BY THREE TUNISIAN CLAYEY SOILS

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**SUMMARY:** Clayey soil samples, Sebkhath El Malah-El Mkhacherma (MK), Jebel Haidoudi (H), and Zemlet El Beidha (ZB), from three regions in Southeast Tunisia were evaluated for their effectiveness to remove fluoride (F) from acidic industrial waste water with pH 2.75–3.0 and [F] = 2360 mg/L. F removal by these soils from solutions containing 50 to 10,000 mg/ NaF/L at pH 3.0, 4.0, 5.5, and 6.5 with a contact time > 24 hr and pH = 3.0 was optimal for treating the acidic wastewater. For the three soils the sorption capacity was found to be in the order of 50–60 mg F/g, and it reached to 85% of the fluoride removal from the wastewater in the case of the MK soil. Fitting the results to the Langmuir isotherm adsorption model gave correlation coefficients ( $r^2$ ) ranging from 0.982 to 0.994 and a better fit than with the Freundlich model. The MK soil containing palygorskite clay and calcite was superior as a F sorbent (MK>H>ZB) where the adsorption capacities ( $Q_0$ ) calculated from the Langmuir isotherms were, respectively, 71.94, 66.62, and 55.80 mg F/g soil from the NaF solution and 93.45, 84.03, and 69.44 mg F/g soil from the acidic wastewater.

Keywords: Acidic wastewater; Clayey soil; Fluoride removal; Freundlich isotherm model; Industrial wastewater; Langmuir isotherm models; Tunisian clayey soils.

### INTRODUCTION

For the storage of highly acidic waste charged with fluoride (F), the protection of groundwater from F contamination for human consumption is of primary importance to avoid the risk of fluorosis. In this context, several methods have been proposed to remove F from aqueous solution, namely adsorption,<sup>1-4</sup> precipitation,<sup>5,6</sup> electrodialysis<sup>7</sup> and electrochemical methods.<sup>8,9</sup> However, adsorption is still one of the most extensively used methods for defluoridation of wastewater. Clayey soils retain F better than others soils,<sup>10,11</sup> and calcium in the soil tends to increase retention. F is adsorbed onto clays (smectite, palygorskite, illite, and kaolinite) in ion-exchange reactions where the F ion ( $F^-$ ) competes with hydroxyl ions ( $OH^-$ ), but the primary exchange reaction appears to be with iron and aluminium hydroxides at low F levels. High levels of F will result in exchange of  $F^-$  by  $OH^-$  in clay minerals themselves.<sup>12,13</sup> Therefore, the adsorption concept for the kaolinite presented by Kau et al.,<sup>1</sup> may be viewed in terms of a chemical reaction, where the sorption process is defined as an equilibrium reaction (Eq. 1).



Here we report on F adsorption from acidic industrial waste by three clayey soils in southern Tunisia. This waste is an aqueous solution containing ca. 2360 mg F/L at pH~3. At present there is no information available on the F removal capacity of Tunisian soils and clays. The F adsorption capacity of these clayey soils was tested using a synthesized solution of NaF at pH 3–6.5. Adsorption isotherms of three

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samples were determined for waste solution at pH~3. Adsorption equilibrium was compared to Freundlich and Langmuir models.

### MATERIALS AND METHODS

*Materials:* The samples used in this study were collected from three locations designed for acidic waste storage in Gabes from South-East Tunisia. The samples were MK (Sebkhat El Malah-El Mkhacherma), H (Jebel Haidoudi), and ZB (Zemlet El Beidha) and were generally formed by clay-silt melange coloured light brown, light green, and dark grey, respectively. The geology of these regions can be simplified into three main stratigraphic units: Segui formation from Mio-Pliocene (MK), Aleg formation from Coniacian/Santonian (H) and Intercalated Continental formation from Lower Cretaceous (ZB). The physico-chemical characterization of the three soils is presented in Table 1.

**Table 1.** Mineralogical composition, specific surface areas, and cationic exchange capacities of samples according to Hamdi et al.<sup>14</sup>

| Sample | Mineralogical composition of clay samples (%) |      |     |    |      |    |    | S <sub>BET</sub><br>(m <sup>2</sup> /g) | CEC<br>(meq/100g) |
|--------|---|------|-----|----|------|----|----|---|-------------------|
|        | Paly  | Smec | Kao | Il | Q    | Ca | Do |   |                   |
| MK     | 35.5  | 2    | 15  | -  | 28.5 | 19 | -  | 35.4                                    | 16.5              |
| H      | -   | 56   | 6   | -  | 12   | 26 | -  | 57.1                                    | 49.8              |
| ZB     | -   | -    | 23  | 63 | 9    | -  | 5  | 91.5                                    | 24.6              |

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

S<sub>BET</sub>: Specific surface areas by application of the BET (Brunauer-Emmett-Teller) method.<sup>15</sup>

CEC: Cationic exchange capacities.<sup>16</sup>

The initial F content in all clays does not exceed 0.02% of the hydrated sample. For all samples, the powder was sieved to particle sizes <106 µm, and the samples were dried at 90°C for a minimum of 24 hr before sorption studies.

*Instruments and procedure:* The F concentrations and pH were measured using a Metrohm 781 pH/Ion Meter and an HI9321 pH meter (HANNA Instruments), respectively.

*Kinetic studies:* Adsorption capacities for the different samples were determined at different pH values (3, 4, 5.5, and 6.5) by shaking 1.0 g of sieved and dried soil in 10 mL of 500 mg/L of aqueous NaF solution in capped polyethylene bottles at 25°C. Small amounts of 0.5 or 0.05 M of HNO<sub>3</sub> were also added initially to adjust to the desired final pH values. The volume was then made up to 30 mL with deionised water. The bottles were agitated in a rotary agitator for periods ranging from 2 hr to 5 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.<sup>17</sup>

*Adsorption Isotherm using NaF solutions:* F sorption isotherms were determined by a procedure similar to that described above. One gram of soil sample and 10 mL of NaF solution at various concentrations (50 to 10000 mg/L) were adjusted to pH 3, and the solute was made up to a volume of 30 mL with deionised water mixed in polyethylene bottles at 25°C.

*Adsorption Isotherms using F waste solution:* Sample adsorbent (1g) was suspended in 30 mL of waste solution containing ca. 2360 mg F ion/L at pH~3. This solution was also found to contain ca. 880 mg Cl<sup>-</sup>/L, 850 mg Ca<sup>2+</sup>/L, and 1410 mg Na<sup>+</sup>/L. Solutions of the wastewater with F concentrations ranging from

23.6 to 2360 mg F/L were prepared by dilution with deionized water while maintaining pH 3 with 0.5M HNO<sub>3</sub>.

### RESULTS AND DISCUSSION

#### *Equilibrium time and pH effect:*

The pH of the solution is a controlling factor in the adsorption process. The equilibrium time for the F sorption reaction is defined as the agitation period necessary for the F<sup>-</sup> concentration in solution to achieve a steady state. In this study, in order to evaluate the effect of the complex composition of wastewater on the sorption speed compared to a single solution (500 mg/L of NaF), the kinetic adsorption experiments were carried out using both solutions. It is found in the case of NaF solution that the removal of F ions increases to some extent with increasing of contact time. Initial observations on the uptake of F 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 a few hr of the initial contact of the NaF solution with raw clays sorbents (Figures 1–3). Kau et al.<sup>2</sup> observed similar results using kaolinite and bentonite clay as the adsorbent.

This initial rapid adsorption subsequently gives way to a very slow approach to equilibrium. Saturation is reached in 24 hr for ZB and 48 hr for MK and H. This contact time was considered as the equilibrium time for the rest of the adsorption studies using NaF solution.

On the other hand, we observed a decrease in the F adsorption with increase in the pH of the solution. In the case of MK and H sorbents, the percentage of adsorption increased almost linearly between pH 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

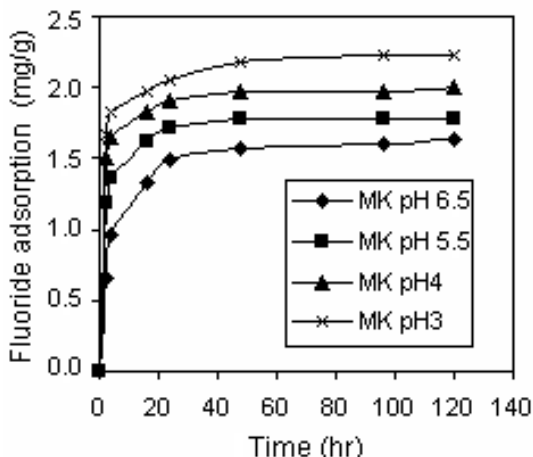


Figure 1. Effects of reaction time on sorbed fluoride at pH values between 3 and 6.5 for MK soil.

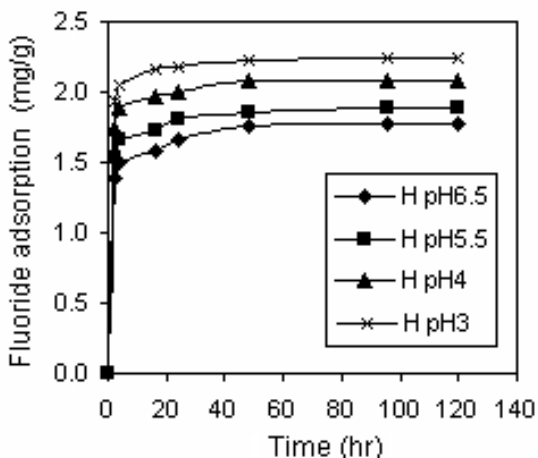


Figure 2. Effects of reaction time on sorbed fluoride at pH values between 3 and 6.5 for H soil.

F adsorption capacity even at pH 6.5, but in the case of soil ZB the adsorption capacity is weak, which is probably due to the high fraction of the illite having a low F adsorption capacity.<sup>18</sup> The higher adsorption capacity is related, firstly, to the composition of the clayey soils (sample MK is composed of palygorskite and soil H is mostly composed of smectite), which have a higher F adsorption capacity.<sup>2,18</sup> Secondly, the important amount of calcite fraction in MK and H soils is very significant for F removal from solution. According to Brett et al.,<sup>19</sup> the calcite promotes F removal.

The kinetic test of adsorption of F from wastewater solution was carried out using 1 g of powdered soil in 30 mL of solution. The results for all three samples are shown in Figure 5. It can be seen that the adsorption kinetics varies from one sample to another, whereas the longer adsorption time (96 hr) is observed for the H sample due to the swelling character of smectite. This contact time was used as the equilibrium time for the subsequent adsorption study with the waste water. This delay of F adsorption compared to the case of a single-component solution is probably caused by competition with the other ions available in the waste solution. In addition, the adsorption capacity was found to be in the order of 50–60 mg/g for all adsorbents (Table 2), and it reached 85% of the F removal from the wastewater in the case of the MK soil.

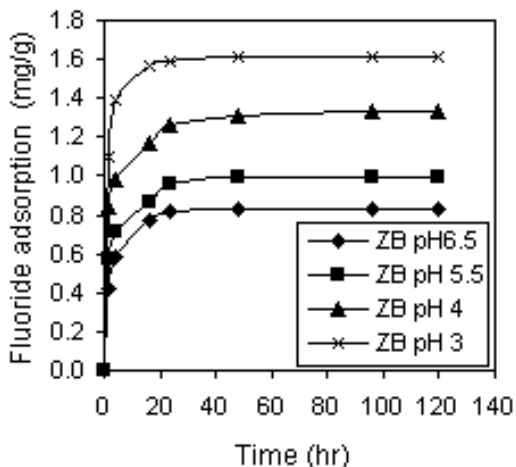


Figure 3. Effects of reaction time on sorbed fluoride at pH values between 3 and 6.5 for soil ZB.

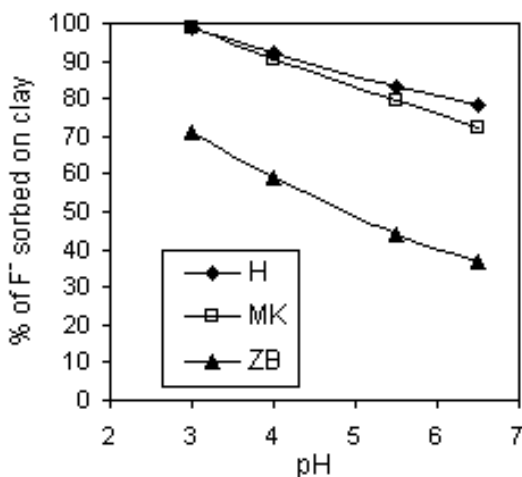
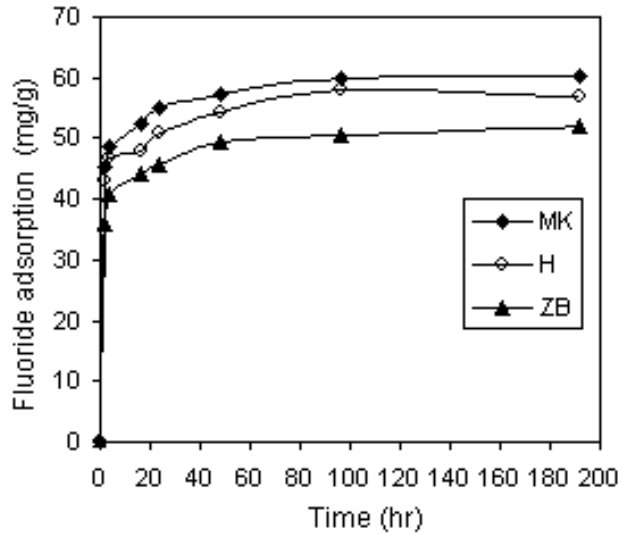


Figure 4. Effects of pH on the percentage removal of fluoride.

Table 2. Summary of kinetics of adsorption by three soils using waste solution

| Soil sample | Q <sub>eq</sub> (mgF/g) | % of F removed | t <sub>c</sub> (hours) |
|-------------|-------------------------|----------------|------------------------|
| MK          | 60.18                   | 85             | 72                     |
| H           | 57.93                   | 81.82          | 96                     |
| ZB          | 51.91                   | 70.31          | 48                     |

**Figure 5.** Effects of reaction time on sorbed fluoride using waste solution for the three soils.



*Fluoride sorption isotherms:* This sorption study was an attempt to evaluate the F removal potential of these three Tunisian soils. The experimental sorption isotherm is used to plot the amount of F adsorbed, expressed in milligrams of F per gram of sample against the equilibrium F<sup>-</sup> concentration (mg/L). The experimental sorption data for the removal of F ions at pH =3 was then compared to plot that would be obtained assuming either the Langmuir (Eq. 2) or Freundlich (Eq. 3) adsorption isotherm model.

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (\text{Eq. 2}) \quad q_e = K_F C_e^{1/n} \quad (\text{Eq. 3})$$

Where  $q_e$  is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g);  $C_e$ , the equilibrium concentration (mg/L);  $Q_0$  and  $b$ , the Langmuir constants related to monolayer capacity and energy of adsorption, respectively; and  $K_F$  and  $1/n$ , the Freundlich constants.

Figure 6 presents the experimental sorption isotherms with NaF solution and the correlation using both models for three soils at pH 3. Note that the sorptivity gradients for the MK and H soils were very similar, as predicted by the modelled bonding constants, with sorption capacity slightly higher for the MK sample. Isotherms of F sorption fit the Langmuir model well, with a correlation coefficient of 0.99. The maximum sorption capacity calculated from this model and reported in Table 3 is 71.94 mg/g for the MK sample, which value is greater than for other clay minerals reported in the literature.<sup>2,20</sup>

Figure 7 shows the sorption isotherm of the three clay samples using the F waste solution at pH~3. The maximum sorption capacity found by experiment for the three samples was 60.18, 57.93 and 51.91mg F/g respectively for MK, H and ZB. The results of modelling of adsorption isotherms by Langmuir and Freundlich models are summarized in Table 4. Both models fit the experiment isotherms well,

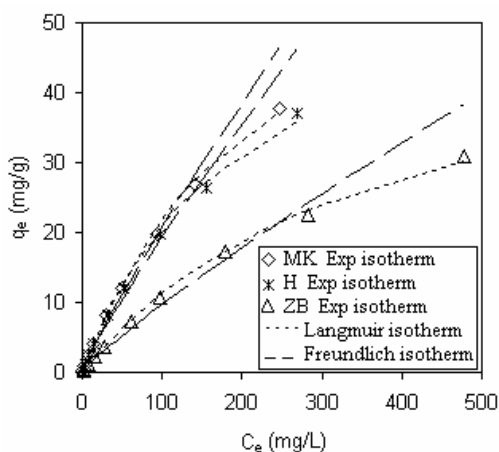
with a correlation coefficient of 0.98-0.99. The higher sorption capacity of the MK and H soils may be partially attributed to the prevailing clay type and to their comparatively higher amount of calcite compared to ZB soil. Free calcium from carbonate dissolved in case of the MK and H samples also assists in F immobilisation through  $\text{CaF}_2$  precipitation.<sup>6</sup> Although, the solubility of carbonate minerals such as calcite or dolomite, makes the application of adsorption theory difficult. For that reason it is not easy to differentiate adsorption from precipitation. Moreover, the presence of  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Al}^{3+}$ , and  $\text{Fe}^{3+}$  in waste solution can form precipitates with F ( $\text{CaF}_2$ ,<sup>6</sup> fluoroaluminate,<sup>21</sup> etc.), which are apparently responsible for the higher removal capacity found by using the wastewater compared to the synthetic solution.

**Table 3.** Summary of optimized isotherm parameters (NaF solution)

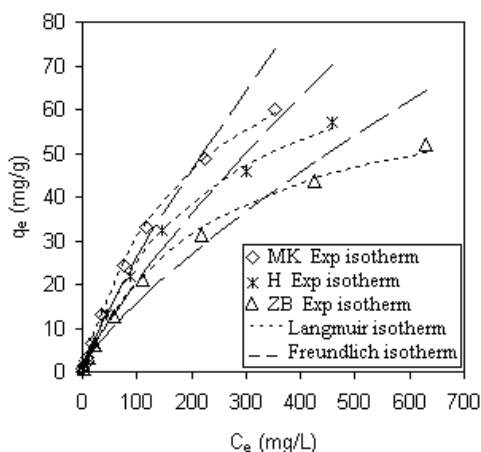
| Soil sample | Isotherm type |                      |       |            |       |       |
|-------------|---------------|----------------------|-------|------------|-------|-------|
|             | Langmuir      |                      |       | Freundlich |       |       |
|             | $Q_0$ (mg/g)  | $b$ (L/mg)           | $r^2$ | $K_F$      | $1/n$ | $r^2$ |
| MK          | 71.94         | $4.28 \cdot 10^{-3}$ | 0.991 | 0.34       | 0.89  | 0.985 |
| H           | 66.62         | $4.44 \cdot 10^{-3}$ | 0.992 | 0.33       | 0.88  | 0.989 |
| ZB          | 55.80         | $2.49 \cdot 10^{-3}$ | 0.994 | 0.18       | 0.86  | 0.977 |

**Table 4.** Summary of optimized isotherm parameters (waste solution)

| Samples | Isotherm type |                      |       |            |       |       |
|---------|---------------|----------------------|-------|------------|-------|-------|
|         | Langmuir      |                      |       | Freundlich |       |       |
|         | $Q_0$ (mg/g)  | $b$ (L/mg)           | $r^2$ | $K_F$      | $1/n$ | $r^2$ |
| MK      | 93.45         | $4.91 \cdot 10^{-3}$ | 0.994 | 0.60       | 0.83  | 0.991 |
| H       | 84.03         | $4.29 \cdot 10^{-3}$ | 0.982 | 0.52       | 0.80  | 0.981 |
| ZB      | 69.44         | $4.22 \cdot 10^{-3}$ | 0.986 | 0.48       | 0.76  | 0.983 |



**Figure 6.** Experimental sorption of fluoride (NaF solution) by three samples with fitted Langmuir, and Freundlich isotherms at pH=3.



**Figure 7.** Experimental sorption of fluoride (waste solution) by the three samples with fitted Langmuir and Freundlich isotherms.

## CONCLUSION

This study of F adsorption behaviour by clayey soils shows clearly that the adsorption capacity depends on the clay structure, the percentage of carbonate in the sample, and the pH of the medium, which is responsible for the charge distribution on the surface of adsorbent. The results of the kinetic studies show a maximum of F adsorption capacity for all samples at pH 3. The experimental adsorption isotherm results indicate that the MK and H soils are favourable adsorbents for removal of F<sup>-</sup> from the waste solution (60.18 and 57.93 mg F/g respectively). However, for characterising the experimental sorption isotherm, the utilisation of a suitable model of sorption isotherm is most important. In this context, the 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 of r<sup>2</sup>. Following these results, the maximum of F<sup>-</sup> adsorption capacity Q<sub>0</sub> obtained for the MK soil is equal to 71.94 mg/g using NaF solution and 93.45 mg/g with the waste solution. For the H soil we also observed a high F adsorption capacity equal to 84.03 mg/g with the waste solution, but in the case of the ZB soil, the illito-kaolinitic fraction and small amount of dolomite are responsible to the low F adsorption capacity.

## REFERENCES

- 1 Kau PMH, Smith DW, Binning PJ. Fluoride retention by kaolin, *J Contam Hydrol* 1997;28:267-88.
- 2 Kau PMH, Smith DW, Binning PJ. Experimental sorption of fluoride by kaolinite and bentonite. *Geoderma* 1998;84:89-08.
- 3 Azbar N, Turkman A. Defluorination in drinking waters. *Water Sci Tech* 2000;42:403-7.
- 4 Oguz E. Adsorption of fluoride on gas concrete materials. *J Hazard Mater* 2005;117:227-33.
- 5 Reardon EI, Wang YX. A limestone reactor for fluoride removal from wastewater. *Environ Sci Tech*. 2000;34:3247-53.
- 6 Grzmil B, Wronkowski J. Removal of phosphates and fluorides from industrial wastewater. *Desalination* 2006;189:261-8.
- 7 Amor Z, Bernard B, Mameri N, Taky M, Nicolas, S, Elmidaoui A. Fluoride removal from brackish water by electrodialysis. *Desalination* 2001;133:215-23.
- 8 Shen FX, Gao P, Chen G. Electrochemical removal of fluoride ions from industrial wastewater. *Chem Eng Sci* 2003;58:3341-52.
- 9 Mameri N, Yeddou AR, Lounici H, Belhocine D, Grib H, Bariou B. Defluorination of septentrional Sahara water of North Africa by electrocoagulation process using bipolar aluminium electrodes. *Water Res* 1998;32:1604-12.
- 10 Peek DC, Volk VV. Fluoride sorption by Oregon soils. *Agron Abstr* 1983;149.
- 11 Robbins CW. Fluoride adsorption by a saline sodic soil irrigated with a high fluoridex water. *Irrig Sci* 1986;7:107-15.
- 12 Bower CA, Hatcher JT. Adsorption of fluoride by soils and minerals. *Soil Sci* 1967; 103:151-64.
- 13 Flühler HJ, Polomski J, Blaser P. Retention and movement of fluoride in soils. *J Environ Qual* 1982;11:461-68.
- 14 Hamdi N, Della M, Srasra E. Experimental study of the permeability of clays from the potential sites for acid effluent storage. *Desalination* 2005;185:523-34.
- 15 Sing KSW, Everett DH, Haul RAW, Moscou L, Pierotti RA, Rouquerol J, et al. Reporting physisorption data for gas/solid system. *Pure & Appl. Chem.*, 1985, 57:603-19.
- 16 Bergaya F, Vayer M. CEC of clays: measurement by adsorption of a copper ethylenediamine complex, *Appl Clay Sci* 1997;12:275-80.
- 17 Harwood JE. The use of an ion-selective electrode for routine fluoride analyses on water samples. *Water Res* 1969;3:273-82.
- 18 Coetzee PP, Coetzee L L, Puka R, Mubenga S. Characterisation of selected South African clays for defluorination of natural waters. *Water SA* 2003;29:331-38.
- 19 Brett DT, Binning PJ, Stipp SLS. Fluoride removal by calcite: evidence for fluorite precipitation and surface adsorption. *Environ Sci Technol* 2005;39(24):956-68.
- 20 Chaturvedi AK, Pathak KC, Singh VN. Fluoride removal from water by adsorption on china clay. *Appl Clay Sci* 1988;3: 337-46.
- 21 Kau PMH, Smith DW, Binning PJ. The dissolution of kaolin by acidic fluoride wastes. *Soil Sci* 1997;162(12):896-911.