

Adsorption behaviour of calcined layered double hydroxides towards removal of fluoride from aqueous solution

Liang Lv

ABSTRACT

Removal of fluoride from aqueous solution by calcined layered double hydroxides (CLDHs) was investigated in batch mode. The influences of calcined temperature, Mg/Al molar ratio of CLDHs, pH of aqueous solution, temperature and co-existing anions on the removal of fluoride have been discussed in detail. It was found that the LDHs with an Mg/Al ratio of 2 calcined at 500°C had the highest capacity to remove fluoride and the maximum percentage removal of fluoride takes place at pH 6.0. The adsorption capacity of CLDHs decreases with a rise in temperature, indicating that the removal process is exothermic in nature. The data from isotherms fitted well to the linearly transformed Langmuir equation. The negative values of ΔG° and ΔH° calculated using the Langmuir constant, confirm the spontaneous and exothermic nature of the removal of fluoride.

Key words | adsorption, calcined, defluorination, fluoride, layered double hydroxides, removal

Liang Lv

The West Branch of Zhejiang University of Technology,
Zhejiang 324006,
China
Tel.: +86 570 8510552
Fax: +86 570 8026668
E-mail: lianglv_qzxy@126.com

INTRODUCTION

Fluorine, usually in combined fluoride forms, is naturally present in varying amounts in the atmosphere, water and soils (Mahramanlioglu *et al.* 2002). Fluoride in appropriate quantity is an essential component for normal mineralization of bones and formation of dental enamel (Bell & Ludwig 1970). However, long-term drinking of water that contains more than a suitable level of fluoride may result in bone disease such as fluorosis and mottling of the teeth. There are more than 20 developed and developing countries including China where many provinces are endemic for fluorosis. Excess of fluoride ($>1.5 \text{ mg l}^{-1}$) in drinking water is harmful to human health (Ghorai & Pant 2005). Though drinking water is the major contributor, other sources of fluoride poisoning include food, industrial exposure, drugs and cosmetics (Meenakshi *et al.* 2004). Various technologies are being used to remove fluoride from water, such as adsorption (Chaturvedi *et al.* 1990; Zhang & Liang 1992; Sujana *et al.* 1998; Sivasamy *et al.* 2001; Ku & Chiou 2002; Ensar 2005), coagulation-precipitation (Azbar & Turkman 2000), ion exchange (Castel *et al.* 2000), membrane

processes (Meenakshi *et al.* 2004) such as nanofiltration (Simons 1993), electro dialysis and Donnan dialysis (Liu *et al.* 1987; Adhikary *et al.* 1989; Amor *et al.* 2001; Ruiz *et al.* 2003), but still the problem has not been rooted out. Among these technologies adsorption appeared to be more interesting for defluorination of water.

Layered double hydroxides (LDHs), also known as hydroxide-like compounds are a class of synthetic anionic layered clays whose structure can be described as containing brucite-like layers and positively charged sheets. The general formula is $[\text{M}_{1-x}^{\text{II}}\text{M}_x^{\text{III}}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot y\text{H}_2\text{O}$, where M^{2+} and M^{3+} represent divalent and trivalent cations in the octahedral sites within the hydroxyl layers, x is equal to the ratio of $\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$ with a value varying in the range of 0.17–0.50, and A is the exchange interlayer anion (Cavani *et al.* 1991). When calcined within a certain temperature range, layered double hydroxides afford mixed metal oxides (denoted here as CLDHs), which have been shown to reconstruct their original layered structure in the presence of aqueous solution of appropriate anions.

Therefore, the CLDHs are good adsorbents for removal of toxic anions from water (Das *et al.* 2003; Lazaridis & Asouhidou 2003; Orthman *et al.* 2003; Lv *et al.* 2006).

The purpose of this work was to investigate the removal of fluoride by CLDHs, taking into account the effects of calcined temperature, Mg/Al molar ratio of CLDHs, pH, temperature and co-existing anions in fluoride aqueous solution on removal of fluoride. The results reported here show that these factors affect the uptake of fluoride and are significant for a better understanding of the potential application of CLDHs for defluorination of fluoride-contaminated water.

MATERIALS AND METHODS

Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, NaNO₃, NaOH, NaF, trisodium citrate dehydrate (Na₃C₆H₅O₇·2H₂O), glutin and urea are analytically pure reagents. All reagents were used without purification, and deionized water was decarbonated before use. The fluoride aqueous solution used in this study was a synthetic wastewater. The standard fluoride solutions used in the experiments were prepared from anhydrous NaF.

MgAl-CO₃ LDHs were prepared using glutin-urea methods in an autoclave. The following solutions were obtained: (a) 12.58 g Mg(NO₃)₂·6H₂O and 9.19 g Al(NO₃)₃·9H₂O with Mg²⁺/Al³⁺ ratio of 2.0 were dissolved in 25 ml deionized water; (b) 20.28 g urea ([urea]/([Mg²⁺] + [Al³⁺]) = 4.59) was dissolved in 25 ml water; and (c) glutin (3 g) was dissolved in 25 ml water. Solutions (b) and (c) were mixed in 100 ml autoclave stirring for 20 min. Solution (a) was added to the mixed solution, stirring for 20 min. The mixture was held at 130°C for 6 h. The precipitate was washed thoroughly at 80°C with deionized water, and dried at 80°C for 24 h to obtain MgAl-CO₃ LDHs (Mg/Al molar ratio of 2). Calcined MgAl-CO₃ LDHs (CLDHs) were obtained by calcining LDHs in a muffle furnace at a certain temperature for 2 h.

CLDHs samples (0.2 g) and fluoride solution (180 ml) were agitated in a series of 250 ml conical flasks for 6 h at a rate of 200 rpm, at a designated temperature (30, 40, 50, 60°C) under N₂ atmosphere. The pH of the solution was adjusted using dilute nitric acid and/or NaOH. After

shaking for 6 h, the mixture was then filtered. Fluoride ions were measured in the solution using a selective electrode for fluoride ions (Diaz-Nava *et al.* 2003), whose linear range is from 10⁻⁶ M to saturated solution. TISAB II (total ionic strength adjustment buffer) was added to the solutions to reduce the variation of the ionic strength in the samples that could interfere in the determinations.

RESULTS AND DISCUSSION

Effect of CLDHs structure

The uptake capacity of LDHs with calcination at various temperatures is shown in Figure 1. It can be seen that the uptake capacity by CLDHs increases along with calcination temperature between 200°C and 500°C from 65.46 mg g⁻¹ to 80.12 mg g⁻¹, but decreased between 500°C and 800°C from 80.12 mg g⁻¹ to 49.87 mg g⁻¹. This is consistent with the structure of LDHs transformed at a certain temperature range. Specific surface areas of calcined LDHs are 76.2, 122.2, 240.6, 213.6 and 39.9 mg g⁻¹ and the pore diameters are 2.35, 2.66, 3.72, 2.45, 2.27 nm with calcination temperature 200, 400, 500, 600, 800°C, respectively. When LDHs calcined at 200°C, it lost the H₂O of the interlayer but kept the original layered structure. LDHs are gradually transformed to aluminium and magnesium oxides (LDO), which have the property of reconstruction, by losing or decomposing interlayer anions (CO₃²⁻) in the temperature

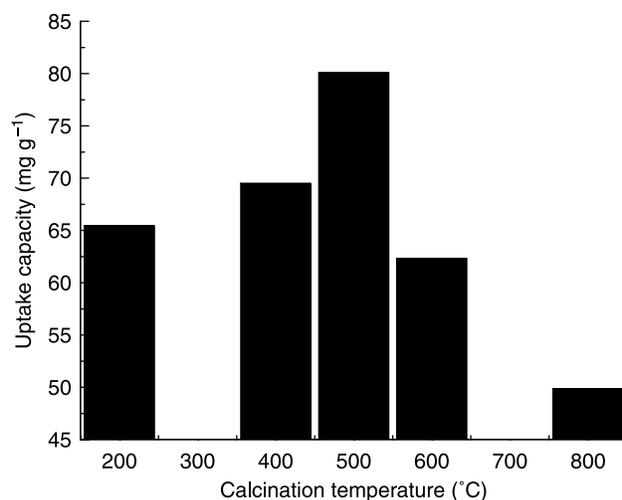


Figure 1 | Effect of calcination temperature on the removal of fluoride ([F⁻]₀ = 100 mg l⁻¹, [CLDH] = 2.0 g/1.8 l, T = 30°C, pH = 6.0).

range 400–600°C. While the calcination temperature is above 800°C, mixed metal oxides changed into spinel, which has no property of reconstruction (Ren *et al.* 2002), and the specific surface and pore diameter decreased. The LDHs calcined at 500°C had the highest surface area and pore diameter, which accounts for the highest uptake capacity of LDHs calcined at 500°C for fluoride.

The effects of Mg/Al molar ratio on removal of fluoride have also been investigated. The uptake capacity of CLDHs with a Mg/Al molar ratio of 2 is the best of all, reaching 80.12 mg g⁻¹, higher than that of CLDHs with Mg/Al ratios of 3 and 4, 64.60 mg g⁻¹ and 63.60 mg g⁻¹, respectively. Due to the charge density in the layers, CLDHs with an Mg/Al ratio of 2 have a higher uptake capacity than those of 3 and 4. On the other hand, the specific surface areas of CLDHs are 240.6, 205.9 and 190.3 m²g⁻¹ and the pore diameters of CLDHs are 2.66, 2.41, 2.15 nm with Mg/Al ratio 2, 3 and 4, respectively, showing that the retention of fluoride is related to the surface of CLDHs and the pore size.

Effect of pH

Generally, the pH is an important variable that controls adsorption at water-adsorbent interfaces (José dos Reis *et al.* 2004). Therefore, the uptake of fluoride by CLDHs was examined at different pH values ranging from 5.0 to 10.0 and the amount of F⁻ adsorbed by CLDHs is presented in Figure 2. The amount of F⁻ adsorbed by CLDHs increases

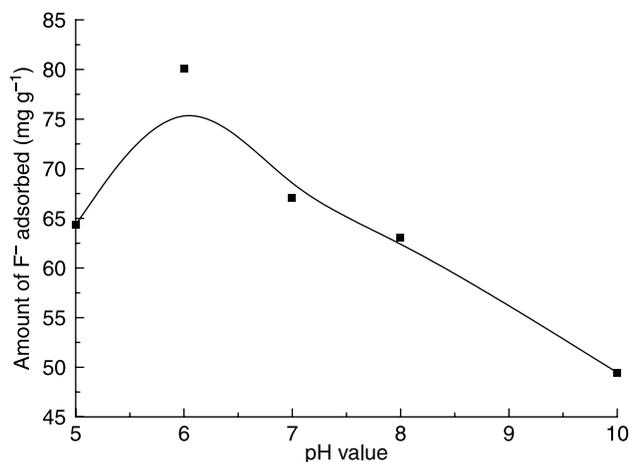


Figure 2 | Effect of pH on the removal of fluoride ($[F^-]_0 = 100 \text{ mg l}^{-1}$, [CLDH] = 2.0 g/1.8 l, T = 30°C).

with the decrease in the pH from 10.0 to 6.0, reaching 80.12 mg g⁻¹ from 49.47 mg g⁻¹. This result can be attributed to the increase of concentration of competing anions OH⁻, with higher pH. But with the pH further decreased to 5.0, the layered metal was partly dissolved, leading to a decrease in the amount of F⁻ adsorbed.

Effect of temperature and calculation of thermodynamic parameters

Figure 3 shows that the amount of F⁻ adsorbed decreases with a rise in temperature. The observation shows that the interaction between adsorbate and adsorbent is exothermic

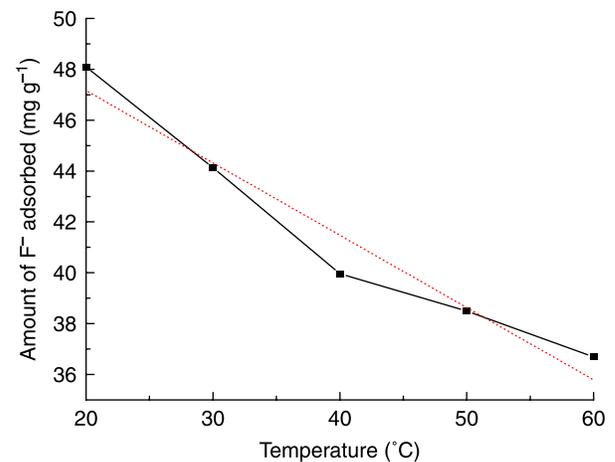


Figure 3 | Effect of temperature on the removal of fluoride ($[F^-]_0 = 50 \text{ mg l}^{-1}$, [CLDH] = 2.0 g/1.8 l, pH = 6.0).

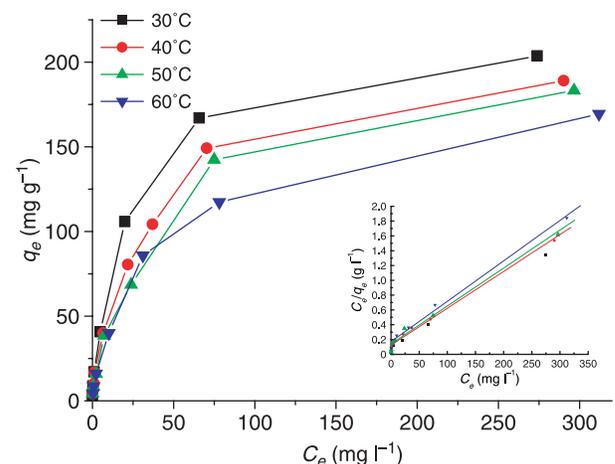


Figure 4 | Adsorption isotherms (inset is the Langmuir plot).

Table 1 | Langmuir constants and thermodynamic parameters associated with fluoride removal by CLDHs

Temp (°C)	Q(mg g ⁻¹)	b(l mol ⁻¹)	ln b	Ka	ΔG ⁰ (KJ mol ⁻¹)	ΔH ⁰ (KJ mol ⁻¹)	ΔS ⁰ (KJ mol ⁻¹)
30	213.2	910.0	6.813	10.21	-17.18	-11.67	18.40
40	201.6	845.3	6.740	8.97	-17.55		
50	194.9	699.1	6.550	7.17	-17.60		
60	183.2	609.2	6.412	5.87	-17.76		

in nature. Even the change in temperature does not influence the equilibrium time and the removal curve is smooth and continuous.

The temperature dependence of the removal of fluoride process is associated with several thermodynamic parameters. The data obtained from the equilibrium of the fluoride removal process are shown in the adsorption isotherms (see Figure 4). The data fitted well to the linearly transformed Langmuir equation ($R^2 > 0.97$).

$$C_e/q_e = 1/Qb + C_e/Q \quad (1)$$

Where C_e is the equilibrium concentration (mg l⁻¹), q_e the defluorination capacity of CLDHs at equilibrium (mg g⁻¹), and Q and b are the Langmuir constants related to the capacity and energy of adsorption, respectively. The values of Q and b were calculated from the slope and the intercept of the linear plots C_e/q_e versus C_e . The decrease in the values of both b and Q with increased temperature suggests that the removal of fluoride is exothermic.

There is a decrease in Ka (apparent equilibrium constant) values with an increase in temperature, which suggests a reduction in affinity with increasing temperature as shown in Table 1.

Thermodynamic parameters such as Gibbs free energy (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) for the process were calculated using the following equations (Das *et al.* 2003):

$$\Delta G^0 = -RT \ln b \quad (2)$$

$$\ln b = \Delta S^0/R - \Delta H^0/(RT) \quad (3)$$

Where R is the universal gas constant, T is temperature (K), and b is the Langmuir constant. The values of ΔG^0 , ΔH^0 and ΔS^0 are also listed in Table 1. The negative ΔG^0 value

indicates the spontaneity of the removal of fluoride process. ΔH^0 and ΔS^0 were calculated from a Vant' Hoff plot (not shown here) using the slope and intercept by regression method, respectively. The negative value of ΔH^0 confirms the exothermic nature of defluorination which was predicted earlier from Figure 5 and Ka values (Table 1). The positive value of ΔS^0 suggests the increased randomness at the solid/solution interface for the removal of fluoride on CLDHs.

Co-existing anions in fluoride aqueous solution

A variety of other anions such as sulphate, phosphate and chloride are generally present in fluoride-containing water. They will compete with fluoride to be adsorbed onto CLDH. As is shown in Figure 5, the co-existing anions in solution lead to a decrease in the amount of F⁻ adsorbed by CLDH in the order PO₄³⁻ > SO₄²⁻ ≈ Cl⁻. The phosphate

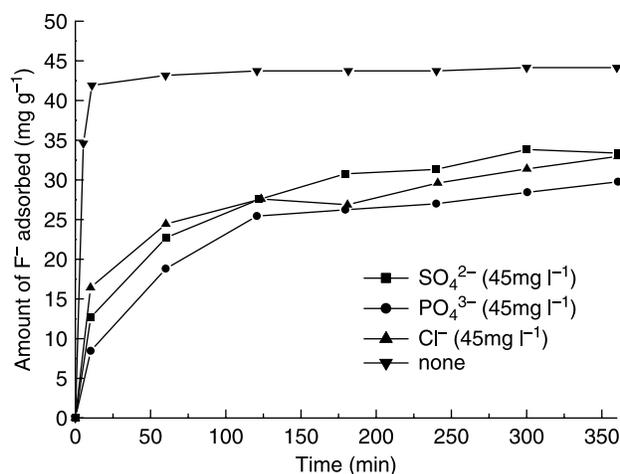


Figure 5 | Effect of co-existing anions on the removal of fluoride ($[F^-]_0 = 50 \text{ mg l}^{-1}$, $[CLDH] = 2.0 \text{ g/1.8 l}$, $[Anion] = 45 \text{ mg l}^{-1}$, $T = 30^\circ\text{C}$, $\text{pH} = 6.0$).

ions have the most significant effect on fluoride removal by CLDH. The effect of chloride ions on removal of fluoride is less important than that of sulphate during the first 120 min, but more significant after 120 min. The effect of these anions on defluorination may be due to their affinity to CLDH. CLDH has greater affinities for anions with a higher charge density; that is, multicharge anions get adsorbed more easily than monovalent anions. But the chloride influencing on fluoride removal in this system is especially because the molar concentration of chloride ions is higher than that of other additive anions.

CONCLUSIONS

The calcined MgAl-CO₃ LDHs can be used as an effective material to remove fluoride from aqueous solution. The results show that defluorination capacity of CLDHs at 500°C is higher than that calcined at other temperatures, and CLDHs with an Mg/Al ratio of 2 have a marked ability to adsorb anions. It was found that maximum removal of fluoride takes place at pH 6.0. The amount adsorbed by CLDHs decreases with increasing temperature. The co-existing anions in fluoride aqueous solution influence the adsorption by CLDH of F⁻ in the order PO₄³⁻ > SO₄²⁻ ≈ Cl⁻. The negative ΔG⁰ value indicates the spontaneity of the removal of fluoride process. The negative value of ΔH⁰ confirms the exothermic nature of uptake of fluoride. The positive value of ΔS⁰ suggests the increased randomness at the solid/solution interface for the uptake of fluoride on CLDHs.

ACKNOWLEDGEMENTS

The author thanks the Education Department of Zhejiang Province, Young Faculty Fund of the Education Department of Zhejiang Province (2003) and Zhejiang Juhua Group (200246-10) for financial support.

REFERENCES

- Adhikary, S. K., Tipnis, U. K., Harkare, W. P. & Govindan, K. P. 1989 Defluoridation during desalination of brackish water by electro dialysis. *Desalination*, **71**, 301–312.
- Amor, Z., Barioub, B., Mameri, N., Taky, M., Nicolas, S. & Elmidaoui, A. 2001 Fluoride removal from brackish water by electro dialysis. *Desalination*, **133**(3), 215–223.
- Azbar, N. & Turkman, A. 2000 Defluorination in drinking waters. *Wat. Sci. Technol.* **42**(1–2), 403–407.
- Bell, M. C. & Ludwig, T. G. 1970 The supply of fluoride to man: Ingestion from water. *Fluorides and Human Health*, World Health Organization, Geneva WHO Monograph Series 59.
- Castel, C., Schweizer, M., Simonnot, M. O. & Sardin, M. 2000 Selective removal of fluoride ions by a two-way ion-exchange cyclic process. *Chem. Eng. Sci.* **55**(17), 3341–3352.
- Cavani, F., Trifiro, F. & Vaccari, A. 1991 Hydrotalcite-type anionic clays: Preparation, properties and applications. *Catalysis Today*, **11**(2), 173–301.
- Chaturvedi, A. K., Yadav, K. P., Pathak, K. C. & Singh, V. N. 1990 Defluoridation of water by adsorption on flyash. *Wat. Air Soil Pollut.* **49**(1), 51–61.
- Das, D. P., Das, J. & Parida, K. 2003 Physicochemical characterization and adsorption behavior of calcined Zn/Al hydrotalcite compound (HTlc) towards removal of fluoride from aqueous solution. *J. Colloid Interface Sci.* **261**(2), 213–220.
- Diaz-Nava, C., Solache-Rios, M. & Olguin, M. T. 2003 Sorption of fluoride ions from aqueous solutions and well drinking water by thermally treated hydrotalcite. *Sep. Sci. Technol.* **38**(1), 131–147.
- Ensar, O. 2005 Adsorption of fluoride on gas concrete materials. *J. Hazard. Mater.* **117**(2–3), 227–233.
- Ghorai, S. & Pant, K. K. 2005 Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina. *Sep. Purif. Technol.* **42**, 265–271.
- José dos Reis, M., Silvério, F., Tronto, J. & Valim, J. B. 2004 Effects of pH, temperature, and ionic strength on adsorption of sodium dodecylbenzenesulfonate into MgAl-CO₃ layered double hydroxides. *J. Phys. Chem. Solids*, **65**(2–3), 487–492.
- Ku, Y. & Chiou, H.-M. 2002 The adsorption of fluoride ion from aqueous solution by activated alumina. *Wat. Air Soil Pollut.* **133**, 349–360.
- Lazaridis, N. K. & Asouhidou, D. D. 2003 Kinetics of sorption removal of chromium (VI) from aqueous solutions by calcined MgAl-CO₃ hydrotalcite. *Wat. Res.* **37**(12), 2875–2882.
- Liu, M., Sun, R. Y., Zhang, J. H., Bina, Y., Wei, L., Liu, P. & Kei, C. F. 1987 Elimination of excess fluoride in potable water with coacervation by electrolysis using aluminium anode. *Fluoride*, **20**(2), 54–63.
- Lv, L., He, J., Wei, M., Evans, D. G. & Duan, X. 2006 Uptake of chloride ion from aqueous solution by calcined layered double hydroxides: Equilibrium and kinetics studies. *Wat. Res.* **40**(2), 735–743.
- Mahramanlioglu, M., Kizilcikli, I. & Bicer, I. O. 2002 Adsorption of fluoride from aqueous solution by acid treated spent bleaching earth. *J. Fluorine Chem.* **115**(1), 41–47.

- Meenakshi, Garg, V. K., Kavita, Renuka, & Malik, A. 2004 Ground water quality in some villages of Haryana, India: focus on fluoride and fluorosis. *J. Hazard. Mater.* **106**(1), 85–97.
- Orthman, J., Zhu, H. Y. & Lu, G. Q. 2003 Use of anion clay hydrotalcite to remove coloured organics from aqueous solution. *Sep. Purif. Technol.* **31**(1), 53–59.
- Ren, Z. F., He, J., Zhang, C. Q. & Duan, X. 2002 Removal of chloride anion by calcined layered double hydroxides. *Fine Chemicals*, **19**(6), 339–342.
- Ruiz, T., Persin, F., Hichour, M. & Sandeaux, J. 2003 Modelisation of fluoride removal in Donnan dialysis. *J. Membrane Sci.* **212**, 113–121.
- Simons, R. 1993 Trace element removal from ash dam waters by nanofiltration and diffusion dialysis. *Desalination*, **89**, 325–341.
- Sivasamy, A., Singh, K. P., Mohan, D. & Maruthamuthu, M. 2001 Studies on defluoridation of water by coal-based sorbents. *J. Chem. Technol. Biotechnol.* **76**(7), 717–722.
- Sujana, M. G., Thakur, R. S. & Rao, S. B. 1998 Removal of fluoride from aqueous solution by using alum sludge. *J. Colloid Interface Sci.* **206**(1), 94–101.
- Zhang, Q. & Liang, H. 1992 Aluminium phosphate for the defluorination of potable water. *Environ. Int.* **18**(3), 307–310.

First received 18 July 2005; accepted in revised form 20 April 2006