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Research Article

Adsorption of Fluoride on the Raw and Modified Cement Clay

Adsorption of fluoride (F) on the raw and modified local cement clay was investigated by batch method. Modified clays were prepared through calcination, using the Na and Mg saturated (C-Na, C-Mg) clay at 500 and 850°C (C-500, C-850) and calcination of Mg incorporated clay at 500°C (C-Mg-500). The equilibration time was attained in 5 h. Adsorption of F increased with increasing adsorbent dose. Decrease of the initial F concentration resulted in an increasing amount of F adsorption. F adsorption isotherms fitted well with both Freundlich and Langmuir models. Low F adsorption was obtained on the raw, incorporated or calcined clays. However maximum F adsorption was found for C-Mg-500, with K_f and Q_0 values of 0.27 and 1.69, respectively. This work indicated that the calcination of incorporated clay with Mg increased the F adsorption significantly, due to increased and stabilized positive sites.

1 Introduction

Fluoride (F) in nature exists in minerals and naturally contaminates the ground water resources. Surface waters are also polluted by F through various anthropogenic activities [1]. The permissible limit of F concentration in drinking water is 1 mg L^{-1} according to the World Health Organization [2]. Presence of F >1.5 mg L^{-1} in drinking water can result in multidimensional health problems, such as dental and skeletal fluorosis. However, F is beneficial for dental enamels when present within the permissible limit of 1.0–1.5 mg L^{-1} in groundwater [3, 4]. Fluorosis is a chronic disease manifested by mottling of teeth in mild cases and softening of bones, ossification of tendons and ligaments, and neurological damage in severe cases. Severe forms of the disease typically develop only when the F concentration of drinking water is >5–10 mg L^{-1}. However, symptoms can develop when drinking water F concentrations are within the range of 1–2 mg L^{-1}. Endemic fluorosis affects many millions of people worldwide [5]. Fluorosis arising from the consumption of high fluorine water was observed also in some parts of Turkey with volcanic rocks and geothermal resources, especially when the range is between 1.5 and 13.7 mg L^{-1}.

Research on water defluoridation, the removal of F from drinking-water, has attracted significant interest in the world particularly in F endemic areas [4]. Several defluoridation methods proposed and tested worldwide are mostly based on the principles of precipitation, adsorption, and ion exchange [6]. Among the above technologies, adsorption is a common technique used for F removal from aqueous solution, mainly because it is relatively low in cost, robust, environmental friendly, and simple [7]. Adsorption process is regarded appropriate for the endemic areas of the developing world

and takes care of the problem of sludge generation in conventional method of precipitation.

A wide range of adsorbents have been used for F removal such as alumina, metal oxide, clays, chitin–chitosan, cement [8], activated carbon, bone charcoal, coconut shell carbon, natural zeolites, and lime [7]. Clay size substrates were commonly used in the adsorption studies; such as, phosphorus [9–11], nitrate [12, 13] and various heavy metals [14–18], and several adsorbent materials to remove F [19] from aqueous solutions.

The aims of the study are to: investigate the F adsorption capacity of a natural cement clay which is locally available, cost-effective, simple, and common adsorbents in the region and study on the variation of adsorption capacity of modified clay that were treated using various processes.

2 Materials and methods

2.1 Raw (natural) adsorbent

Natural clay (CR) used in the present study were local materials procured from Yaylak village of Şanlıurfa is currently used in cement production. Chemical composition of raw clay (CR) is presented in Tab. 1. Air-dried and sieved (<2 mm) CR were processed for adsorption or modification studies.

X-ray diffraction pattern of CR is presented in Fig. 1. As can be seen in this figure, clay is crystalline in nature. Calcite ($CaCO_3$) is the most distinct component in the CR and this was followed by quartz, montmorillonit, and kaolinit phases. Mineralogical composition of CR was exhibited as; calcite-$CaCO_3$ (42.6%), quartz low-SiO_2 (27.3%), montmorillonit (13.1%), and kaolinite (10.9%) contents.

2.2 Preparation of homoionic clays with magnesium (Mg) and sodium (Na)

Ten grams of natural clay was mixed with 100 mL of 1.25 M $MgCl_2$ solution and the mixture was agitated for 6 h. Mass was kept in a

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Abbreviation: CR, raw clay

Table 1. Chemical composition of raw and modified cement clay

Chemical composition	CR % concentration	C-500 % concentration	C-850 % concentration	C-Mg-500 % concentration
SiO_2	31.756	31.650	35.491	33.354
Al_2O_3	8.209	8.250	8.511	8.445
Fe_2O_3	4.467	4.605	4.965	4.125
MgO	3.133	3.117	3.181	9.311
CaO	27.501	27.190	31.395	20.369
Na_2O	0.093	0.097	0.138	0.103
K_2O	0.846	0.848	0.933	0.808
TiO_2	0.549	0.547	0.578	0.509
P_2O_5	0.164	0.162	0.170	0.153
MnO	0.086	0.090	0.101	0.082
Cr_2O_3	0.038	0.034	0.039	0.031
Loss on ignition	23.160	23.410	14.500	22.710
Total	100	100	100	100

water bath in 60°C for 1 h and then at room temperature for 24 h. Mixture was washed twice with distilled water in 1:20 ratio to remove excessive magnesium from media. Mixture was centrifuged and aqueous supernatant was removed in each washing. The mixture was transferred into glass petri dish and dried at 150°C in an oven. Dried mass was then ground to fine powder and appointed as "incorporated with Mg" clay [20]. Homoionic Na clay followed the same experimental procedures that were used for the preparation of homoionic Mg clay. They were designated as:

Incorporated clay with NaCl: C-Na.
Incorporated clay with $MgCl_2$: C-Mg.

2.3 Activation of adsorbents by heating

Clays were heated for 4 h in porcelain crucibles at 500 and 850°C in muffle furnace. About 10 g of heated clays were mixed with 100 mL of 1.25 M $MgCl_2$ solution and the mixture was agitated for 6 h. After shaking, the mass was oven dried at 150°C. Dried mass was then ground to obtain fine powder and calcined at 500°C for 4 h in muffle furnace. The calcined powder was cooled to room temperature and washed twice with distilled water in 1:20 ratio. The material was finally dried at 70°C for 6 h and entitled as "incorporated with Mg and calcined" clay [3]. Heat activated clays were entitled as:

Calcined CR at 500°C: C-500.
Calcined CR at 850°C: C-850.
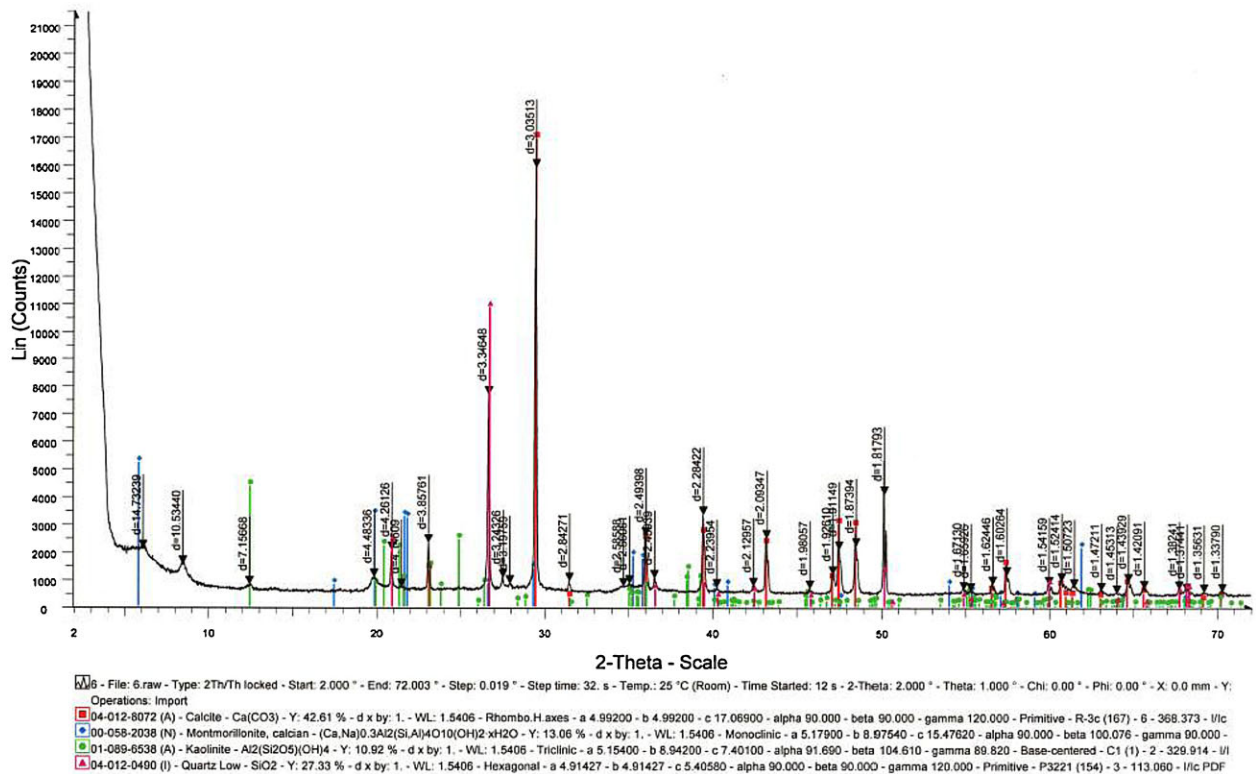Incorporated clay with Mg and calcined at 500 °C: C-Mg-500.

Figure 1. X-Ray diffraction of raw clay.

Chemical compositions of C-500, C-850, and C-Mg-500 are presented in Tab. 1. The MgO contents of C-500 and C-850 were close to each other (3%); however, MgO content of C-Mg-500 was increased to 9% by incorporation process.

2.4 Adsorption studies

Stock solution (100 mg L^{-1}) was prepared by dissolving 0.221 g anhydrous sodium F (Merck) to 1 L of deionized water. This was further diluted to get desired concentration for the experiment. Adsorption tests were carried out by Batch method for the "raw", "calcined at 500°C", "calcined at 850 °C", "incorporated with Mg", "incorporated with Na", and "incorporated with Mg and calcined at 500°C" clay adsorbents. Adsorption kinetics, optimum adsorbent dosage, and adsorption isotherms were determined by adsorption tests at natural pH and room temperature.

A preliminary kinetic experiment was carried out to establish the equilibration time for F adsorption. Tests were conducted in duplicate samples in 50 mL polypropylene test tubes. CR samples (0.2 g) were shaken with 40 mL of F solutions (5 mg L^{-1}) on a reciprocating shaker (150 rpm) for 1, 2, 3, 4, 5, 11, and 24 h to attain the equilibration time at room temperature and then supernatant, which was percolated from syringe filtrate, was decanted carefully and analyzed for the residual F. All reported results constituted the mean of duplicate measurements. The specific amount of F adsorbed and % F adsorption was calculated using the following equation:

$$C_s = \frac{(C_0 - C_e)V}{W} \quad \% \text{ adsorption} = \frac{(C_0 - C_e)100}{C_e} \qquad (1)$$

where C_s is the adsorption capacity (mg g^{-1}) in the solid at equilibrium; C_0, C_e are initial and equilibrium concentrations of F (mg L^{-1}), respectively. V is the volume of the aqueous solution and W is the mass (g) of adsorbent used in the experiments. Adsorption isotherms were obtained after the optimum adsorbent dosage and equilibration time studies. All the experiments were conducted with controls-with only F in tube (no adsorbents) and blanks-with the same amount of adsorbent in tube (without F).

2.5 Sampling and analysis

All solution samples were taken through 0.45 μm syringe filters. F analyses were performed by Hach mark Fluoride Meter (product code: 2589 99) by TISAB method.

2.6 Data analysis

Adsorption data were analyzed using linearized form of the Langmuir (Eq. (2)) and Freundlich isotherms (Eq. (3)):

$$\frac{C_e}{C_s} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \qquad (2)$$

$$\log C_s = \log K_f + \frac{1}{n_f} \log C_e \qquad (3)$$

where b is the Langmuir constant and Q_0 is the maximum amount of adsorbent that can be adsorbed. Plotting C_e/C_s versus C_e, the slope is $1/Q_0$ and the intercept is $1/Q_0 b$. K_f and $1/n_f$ are the empirical Freundlich constants. By plotting $\log C_s$ (amount adsorbed to adsorbent, mg g^{-1})

versus $\log C_e$ (amount of F in solution, mg L^{-1}), $1/n_f$ is calculated as the slope of the curve and the intercept is equal to $\log K_f$ [21].

3 Results and discussion

3.1 Effect of contact time

Figure 2 shows the effect of contact time on the adsorption of F on the CR. As contact time was increased, initially, adsorbed F also increased, but after some time, it gradually approached an almost constant value indicating equilibrium in 5 h. Increase of equilibration time was due to negative charge of F ion and the possible positive charge on the CR. However clays are predominantly negatively charged. Repulsion of negatively charged F from the negatively charged sites on the CR particles made the adsorption difficult on the vacant sites. The high sorption in 5 h was followed by a slower sorption of F throughout 24 h.

The changes in the rate of adsorption might be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high. Later, the F uptake rate by adsorbent had decreased significantly due to the decrease in number of adsorption sites [22]. Because the changes in solution concentration were rather small after equilibration period of F, equilibration times were used in the remaining adsorption studies. It was also mentioned by other researchers that, the changes in solution concentration were quite small after equilibration time [7].
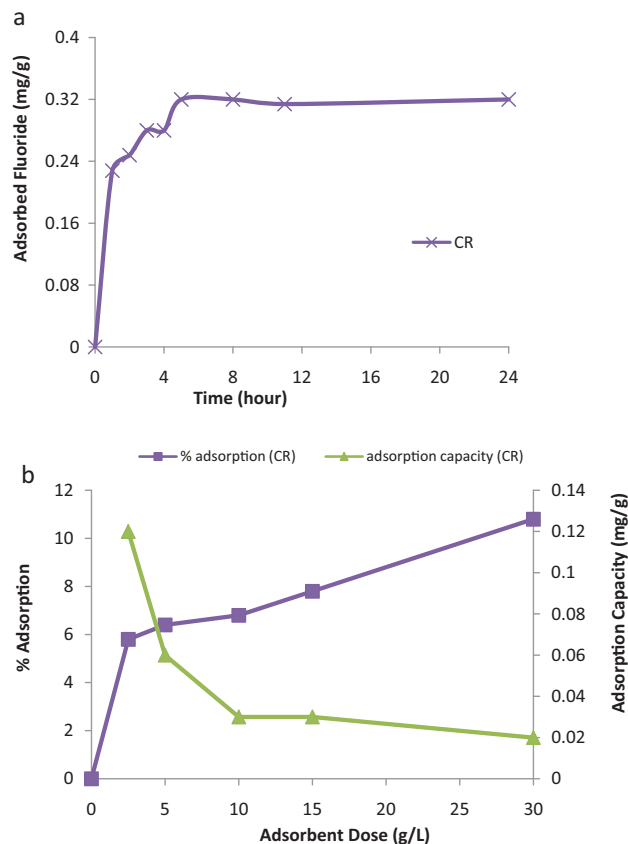

Figure 2. Effect of (a) contact time and (b) adsorbent dose on the fluoride adsorption of raw clay.
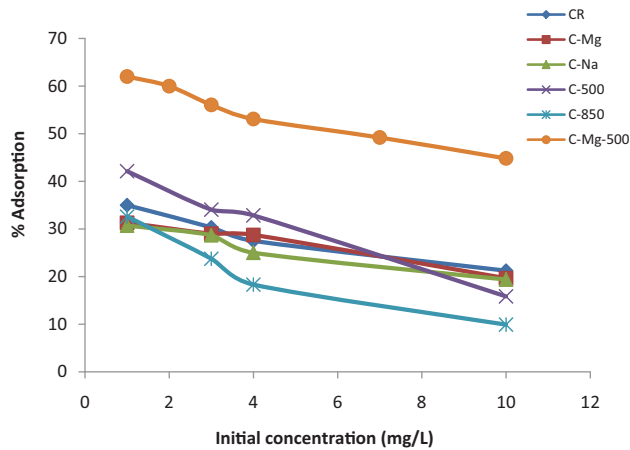
Figure 3. Effect of initial fluoride concentration on the fluoride adsorption by raw and modified clays.

3.2 Effect of adsorbent concentration

The effect of adsorbent concentration on F adsorption was studied for CR at room temperature (25°C) and natural pH for initial F concentration of 5 mg L^{-1} and contact time of 5 h. The effect of adsorbent dose on the F adsorption is shown in Fig. 2. It was observed that the amount (mg g^{-1}) of F adsorbed is decreased with the increase in concentration. The maximum adsorption capacity was found to be 0.36 mg g^{-1} at a dose of 0.2 g/40 mL (2.5 g L^{-1}). The percentage F adsorption increased with the increase in the concentration of the clay and it was obviously due to the enhanced active sites with an increase in the amount of adsorbent [23, 24]. A dose of 5 g L^{-1} was fixed as optimum dosage and it was used in the remaining adsorption studies.

3.3 Effect of initial concentration

Effect of initial concentration on the adsorption of F was studied at different initial F concentrations by keeping other parameters constant such as adsorbent dose 5 g L^{-1}, speed 150 rpm, contact time 5 h, natural pH (7.6), and temperature (25°C). The effect of initial concentration on F adsorption is shown in Fig. 3. Results indicated that higher adsorption of F was found on C-Mg-500 with positively charged sites. The decrease of the adsorption percentage could be attributed to the insufficient active sites of the adsorbents, which was caused by the occupation of the F ions, as the more F ions were

occupied the active sites and then the lower adsorption percentage represented [7].

3.4 Adsorption isotherms and F adsorption on raw and modified clays

The values of the Freundlich and Langmuir adsorption constants are given in Tab. 2. F adsorption isotherms fitted well with both Freundlich and Langmuir models. Freundlich and Langmuir correlation coefficients ranged between 0.94 and 0.99 and 0.99–0.99, respectively.

According to the Giles classification [25], F isotherm was type L for raw, incorporated and calcined clays, which is typical isotherm of an adsorbent with affinity for the adsorbate (Fig. 4). The values of $1/n_f$ for all adsorbents were <1.0 implying the L type isotherm. Langmuir equation also showed a good fit to experimental data for F, as indicating L type isotherm. Gupta et al. [1], Jagtap et al. [8], Sundaram et al. [23], Karthikeyan and Elango [26], Karthikeyan et al. [27], and Mandal and Mayadevi [28] also found that the experimental data for F adsorption in various adsorbents fitted well with both Langmuir and Freundlich equations.

A smaller value of $1/n$ (<1) indicates a weaker bond (physical bonding) between adsorbate and adsorbent and also it indicates the heterogeneous adsorbent surface while a lower value for K_f indicates that the rate of adsorbate adsorption is low [29]. Low F adsorption on the CR can be accounted by negatively charged sites on the clays, which makes the material inefficient adsorbent for anionic species such as F. This means that negatively charged pollutants usually exhibit very little sorption [30]. Generally, positively charged ions were attracted to the negatively charged sites on the clay particles by incorporation of Na and Mg with the expectation of F ions retaining on the positively charged (with Na or Mg) sites. However incorporation of CR with Mg and Na did not exhibit an enhancement in its F adsorption capacity (Fig. 4a). The reason for this is not clear but this fact is thought to have arisen from desorption or exchanging of adsorbed cations on the incorporated clays. Therefore Mg incorporated clay was heated at 500°C to entail a strong retention between sorption sites and Mg ions.

Adsorbed F ions on the calcined clays increased with equilibrium concentration up to 3 mg L^{-1}, more increase in F concentration did not alter the F ion uptake. Adsorption of F on C-500 was higher than on C-850 with K_f values of 0.13 and 0.09, respectively (Fig. 4b and Tab. 2). Therefore calcination heat was assigned to 500°C for the incorporated clay with Mg (C-Mg-500). The data set for the calcined soil confirms earlier results by Wang and Reardon [5] and Wang et al. [31] that heating to 400–500°C appears to improve the various

Table 2. Freundlich and Langmuir constants for the fluoride adsorption on raw and modified clays

Isotherms	Isotherm constants	CR	C-Na	C-Mg	C-500	C-850	C-Mg-500
Freundlich isotherm	K_f	0.10	0.09	0.09	0.13	0.09	0.27
	$1/n_f$	0.72	0.75	0.75	0.50	0.43	0.73
	n_f	1.39	1.33	1.33	1.99	2.33	1.37
	r	0.99	0.99	0.99	0.94	0.96	0.99
Langmuir isotherm	$1/Q_0b$	8.90	10.33	9.42	4.52	7.39	3.02
	$1/Q_0$	1.25	1.31	1.34	2.58	4.23	0.59
	b	0.14	0.13	0.14	0.57	0.57	0.20
	Q_0	0.80	0.76	0.75	0.39	0.24	1.69
	r	0.99	0.99	0.99	0.99	0.99	0.99

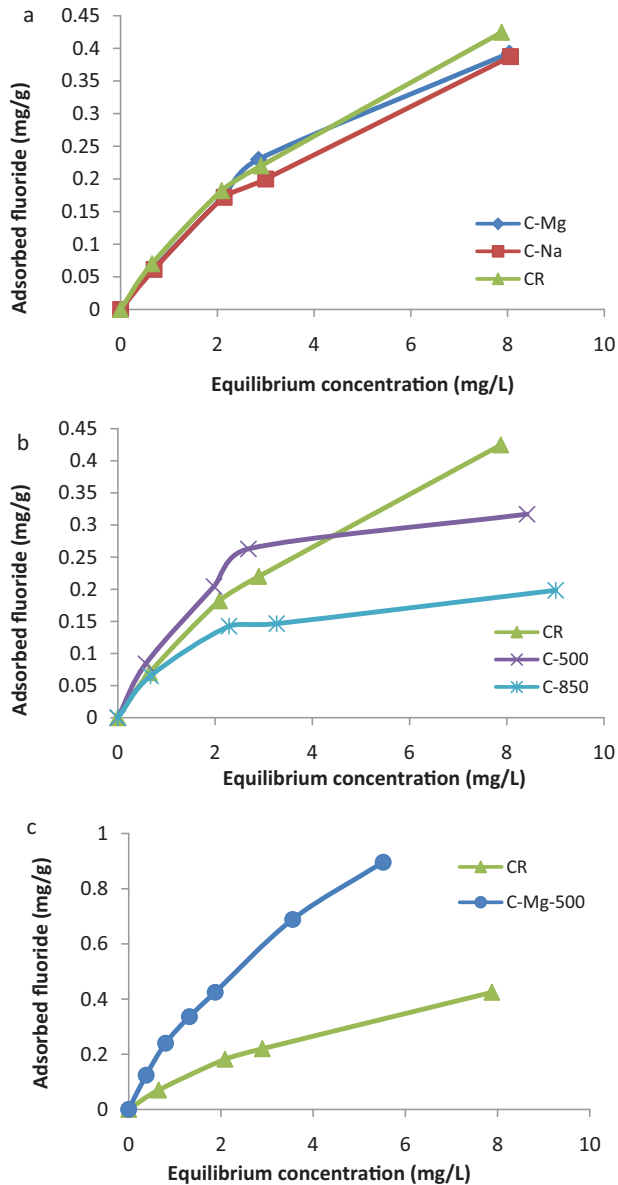**Figure 4.** Adsorption isotherms of (a) raw and incorporated clays (b) raw and calcined clays (c) raw and incorporated-calcined clays.

increased the F adsorption of C-Mg-500. C-Mg clay exhibited a low F adsorption. However, calcination of incorporated clay at 500°C disclosed strongly adsorbed Mg ions on the vacant or adsorption sites and increased F adsorption.

4 Concluding remarks

The following conclusions can be drawn from the present study.

(1) Experimental data for F adsorption in raw and modified clays fitted well with both Langmuir and Freundlich equations.

(2) Low F adsorption (max. 0.43 mg g^{-1}) was found on the CR. Negatively charged sites on the CR made the material an inefficient adsorbent for F.

(3) Incorporation of Na or Mg into CRs did not significantly change the amount of F adsorption. Maximum F adsorption was 35% on the CR and 31% on the C-Na and C-Mg. Perhaps cations were weakly bonded on CR and desorption phenomena took place with time.

(4) Adsorption of F on C-500 (K_f: 0.13) was higher than C-850 (K_f: 0.09) and CR (K_f: 0.10). F adsorption increased a little on the calcined clay at 500°C. However calcination alone did not show higher F adsorption on the clay.

(5) Saturation of CR with Mg and then calcination at 500°C increased the F adsorption, significantly. Maximum F adsorption was found for C-Mg-500, with K_f and Q_0 values of 0.27 and 1.69, respectively. Calcination resulted in the strong retention of cations on the clay particulates and this phenomenon increased the F adsorption due to possibly creation of positive sites.

References

[1] V. K. Gupta, I. Ali, V. K. Saini, Defluoridation of Wastewaters Using Waste Carbon Slurry, *Water Res.* **2007**, *41*, 3307–3316.

[2] WHO, Technical Report Series, *Fluorides and Oral Health Report of a WHO Expert Committee on Oral Health Status and Fluoride Use*, WHO, Geneva, Switzerland **1994**.

[3] D. Thakre, S. Rayalu, R. Kawade, S. Meshram, J. Subrt, N. Labhsetwar, Magnesium Incorporated Bentonite Clay for Defluoridation of Drinking Water, *J. Hazard. Mater.* **2010**, *180*, 122–130.

[4] B. Thole, F. Mtalo, W. Masamba, Groundwater Defluoridation with Raw Bauxite, Gypsum, Magnesite, and Their Composites, *Clean – Soil Air Water* **2012**, *40* (11), 1222–1228.

[5] Y. Wang, E. J. Reardon, Activation and Regeneration of a Soil Sorbent for Defluoridation of Drinking Water, *Appl. Geochem.* **2001**, *16*, 531–539.

[6] M. Agarwal, K. Rai, R. Shrivastas, S. Dass, Defluoridation of Water Using Amended Clay, *J. Cleaner Prod.* **2003**, *11*, 439–444.

[7] S. Gao, R. Sun, Z. Wei, H. Zhao, H. Li, F. Hu, Size-Dependent Defluoridation Properties of Synthetic Hydroxyapatite, *J. Fluorine Chem.* **2009**, *130*, 550–556.

soils' F removal capacity. The apparent gain in F adsorption capacity with temperature is related to some volatilization or mineralization of F already present on sorption sites during the heating period. Although differing in detail, heating 850°C appears to result in a progressive loss of sorption capacity as shown in Fig. 4b.

The maximum F adsorption was found for C-Mg-500, with K_f (Freundlich adsorption coefficient) and Q_0 (Langmuir constant) values of 0.27 and 1.69, respectively, while incorporation or calcination processing alone did not change the F adsorption significantly. Based on our unpublished data, F adsorption on the incorporated with Mg and then calcined bauxite at 500°C was higher than the raw bauxite. Increased adsorption capacity of modified clay is related to the increased positively charged sites due to stronger retention of Mg ions on the clay by calcination. Volatilization or mineralization during the heating period and retaining of Mg on the sorption sites

[8] S. Jagtap, M. K. N. Yenkie, N. Labhsetwar, S. Rayalu, Defluoridation of Drinking Water Using Chitosan Based Mesoporous Alumina, *Microporous Mesoporous Mater.* **2011**, *142*, 454–463.

[9] M. W. Kamiyango, S. M. I. Sajidu, W. R. L. Masamba, Removal of Phosphate Ions from Aqueous Solutions Using Bauxite Obtained from Mulanje, Malawi, *Afr. J. Biotechnol.* **2011**, *10*, (*56*), 11972–11983.

[10] A. D. Karathanasis, P. D. Shumaker, Organic and Inorganic Phosphate Interactions with Soil Hydroxy-Interlayered Minerals, *J. Soils Sediments* **2009**, *9*, 501–510.

[11] H. Liang, J. Liu, Y. Wei, X. Guo, Evaluation of Phosphorus Removal from Wastewater by Soils in Rural Areas in China, *J. Environ. Sci.* **2010**, *22* (*1*), 15–22.

[12] N. Öztürk, T. E. Bektaş, Nitrate Removal from Aqueous Solution by Adsorption onto Various Materials, *J. Hazard. Mater.* **2004**, *B112*, 155–162.

[13] C. J. Mena-Duran, M. R. Sun Kou, T. Lopez, J. A. Azamar-Barrios, D. H. Aguilar, M. I. Domínguez, J. A. Odriozola, P. Qintana, Nitrate Removal Using Natural Clays Modified by Acid Thermoactivation, *Appl. Surf. Sci.* **2007**, *253*, 5762–5766.

[14] M. Park, C. L. Choi, Y. J. Seo, S. K. Yeo, J. Choi, S. Komarneni, J. H. Lee, Reactions of Cu^{2+} and Pb^{2+} with Mg/Al Layered Double Hydroxide, *Appl. Clay Sci.* **2007**, *37*, 143–148.

[15] M. Sprynskyy, Solid–Liquid–Solid Extraction of Heavy Metals (Cr, Cu, Cd, Ni and Pb) in Aqueous Systems of Zeolite–Sewage Sludge, *J. Hazard. Mater.* **2009**, *161*, 1377–1383.

[16] C. Volzone, L. B. Garrido, Use of Modified Hydroxy-Aluminum Bentonites for Chromium(III) Removal from Solutions, *J. Environ. Manage.* **2008**, *88*, 1640–1648.

[17] W. Yuhua, L. Ye, H. Yuehua, Adsorption Mechanisms of Cr(VI) on the Modified Bauxite Tailings, *Miner. Eng.* **2008**, *21*, 12–14.

[18] K. L. Wasewar, P. Kumar, S. Chand, B. N. Padmini, T. T. Teng, Adsorption of Cadmium Ions from Aqueous Solution Using Granular Activated Carbon and Activated Clay, *Clean – Soil Air Water* **2010**, *38* (*7*), 649–656.

[19] S. Vasudevan, J. Lakshmi, G. Sozhan, Studies on a Mg–Al–Zn Alloy as an Anode for the Removal of Fluoride from Drinking Water in an Electrocoagulation Process, *Clean – Soil Air Water* **2009**, *37* (*4–5*), 372–378.

[20] A. Mumcu, *MSc Thesis*, İnönü Üniversity, Graduate School of Natural and Applied Sciences, Malatya **2006**.

[21] D. L. Sparks, *Environmental Soil Chemistry*, Academic Press, San Diego, CA **1995**.

[22] A. K. Yadav, C. P. Kaushik, A. K. Haritash, A. Kansal, N. Rani, Defluoridation of Groundwater Using Brick Powder as an Adsorbent, *J. Hazard. Mater.* **2006**, *B128*, 289–293.

[23] C. S. Sundaram, N. Viswanathan, S. Meenakshi, Defluoridation of Water Using Magnesia/Chitosan Composite, *J. Hazard. Mater.* **2009**, *163*, 618–624.

[24] E. W. Wambu, C. O. Onindo, W. Ambusso, G. K. Muthakia, Removal of Fluoride from Aqueous Solutions by Adsorption Using a Siliceous Mineral of a Kenyan Origin, *Clean – Soil Air Water* **2013**, *41* (*4*), 340–348.

[25] C. H. Giles, T. H. Macewan, S. N. Nakhava, Studies in Adsorption, Part XI. A System of Classification of Solution Adsorption Isotherms and Its Use in Diagnosis of Adsorption Mechanism and in Measurement of Specific Surface Areas of Solids, *J. Chem. Soc.* **1960**, *111*, 3973–3993.

[26] M. Karthikeyan, P. Elango, Removal of Fluoride from Water Using Aluminium Containing Compounds, *J. Environ. Sci.* **2009**, *21*, 513–1518.

[27] M. Karthikeyan, K. K. Satheeshkumar, K. P. Elango, Defluoridation of Water via Doping of Polyanilines, *J. Hazard. Mater.* **2009**, *163*, 1026–1032.

[28] S. Mandal, S. Mayadevi, Defluoridation of Water Using As-Synthesized Zn/Al/Cl Anionic Clay Adsorbent: Equilibrium and Regeneration Studies, *J. Hazard. Mater.* **2009**, *167*, 873–878.

[29] M. G. Sujana, H. K. Pradhan, S. Anand, Studies on Sorption of Some Geomaterials for Fluoride Removal from Aqueous Solutions, *J. Hazard. Mater.* **2009**, *161*, 120–125.

[30] I. L. Pepper, C. P. Gerba, M. L. Brusseau, J. W. Brendecke, *Pollution Science*, Academic Press, San Diego, CA **1996**, pp. 259–263.

[31] Y. Wang, X. Yuan, H. Gou, Remediation of high fluoride groundwaters from arid regions using heat-treated soils: a column experiment study in Xinzhou China, in *Proceedings of the 9th International Symposium on Water–Rock Interactions* (Eds.: G. B. Arehart, J. R. Hulston) A.A. Balkema, Rotterdam **1998**, pp. 189–192.