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A FIXED BED SORPTION SYSTEM FOR DEFLUORIDATION OF GROUND WATER

Ayoob Sulaiman[1*] , Ashok K. Gupta[2] and Abi B. Basheer[3]

[1,3]*Department of Built and Natural Environment, Caledonian College of Engineering, Seeb, Sulanate of Oman*

[2]*Department of Civil Engineering, Environmental Engineering Division, Indian Institute of Technology, Kharagpur, India*

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Abstract: The presence of excess fluoride in ground water has become a global threat with as many as 200 million people affected in more than 35 countries in all the continents. Of late, there have been significant advances in the knowledge base regarding the effects of excess fluoride on human health. As a result, defluoridation of ground water is regarded as one of the key areas of attention among the universal water community triggering global research. This study describes the sorptive responses of a newly developed adsorbent, alumina cement granules (ALC), in its real-life application in fixed beds, for removing fluoride from the ground waters of a rural Indian village. ALC exhibited almost consistent scavenging capacity at various bed depths in column studies with an enhanced adsorption potential of 0.818 mg/g at a flow rate of 4 ml/min. The Thomas model was examined to describe the sorption process. The process design parameters of the column were obtained by linear regression of the model. In all the conditions examined, the Thomas model could consistently predict its characteristic parameters and describe the breakthrough sorption profiles in the whole range of sorption process.

Keywords: Adsorption; breakthrough curve; column study; fluoride; modeling

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[*] Correspondence to: S. Ayoob, Tel.: 00968-95738249. E-mail: ayoobtkm@gmail.com

INTRODUCTION

Water serves as a life-line to the entire biota. But, the world is in a water crisis as more than 1.1 billion people are having no access to safe drinking water. The presence of geogenic pollutants like fluoride in ground water exacerbates the gravity of this issue and poses hindrance to the global onward march of humanity towards a ‘water secure world’. Of late, excess fluoride in drinking water wreaks havoc in more than 35 nations across the globe; forcing hundreds of million people live under the shadows of fluorosis (Ayoob & Gupta 2006; Ayoob *et al*., 2008). Blame it on different forms of fluorosis, in countries like India where 66.64 million people in more than 20 states (**Fig. 1**) were estimated already under ‘risk’(Susheela, 2003), its excess presence in water is prioritized as a major impediment to the sustainable drinking water supply.

Among the various available techniques, adsorption is most widely used for excess fluoride removal from aqueous solution, especially at the fluoride endemic areas of the developing world. In this process, a packed bed of adsorbent in fixed columns is continuously used for cyclic sorption and/or desorption of pollutants by effectively utilizing the capacity of an adsorbent bed. From a relatively bulk liquid volume, the pollutant gets concentrated and confined onto a small adsorbent mass which can invariably be regenerated, reused, or safely disposed under control (Ayoob *et al*., 2008). Though many adsorbents like bone char, activated alumina, activated bauxite, ion exchange resins, clays and soils, and synthetic zeolites had been developed for defluoridation, activated alumina has become popular in field applications (Daw, 2004; WHO, 2006). However, the poor sorption kinetics due to slow intraparticle diffusion, and the low pH range for optimum removal may be viewed as its limitations.

An in-depth analysis of defluoridation research reveals that most of the reported works are confined to batch studies, that too in synthetic systems. Batch studies only suggest the feasibility of an adsorbent for sorption, and render its adsorption capacity through best-fitting isotherms and some kinetic models. Since the nature and characteristics of water to be treated, and presence of coexisting ions are decisive factors in sorption, the adsorption capacity derived from column studies of natural ground water, would be a most reliable indicator for its field use. Though, the inherent unsteady situation prevailing in the fixed bed makes accurate prediction of the dynamic sorption responses a difficult task (Aksu & Gönen, 2004)**,** simple numerical models which had have been used to predict the dynamic behavior of adsorption columns could as well be used for fluoride sorption (Ko *et al*., 2000; Ayoob & Gupta, 2007). Nonetheless, full-fledged fixed bed studies suggesting the field applicability of adsorbents in natural fluoride rich ground waters describing its sorption profile are only very rarely reported.

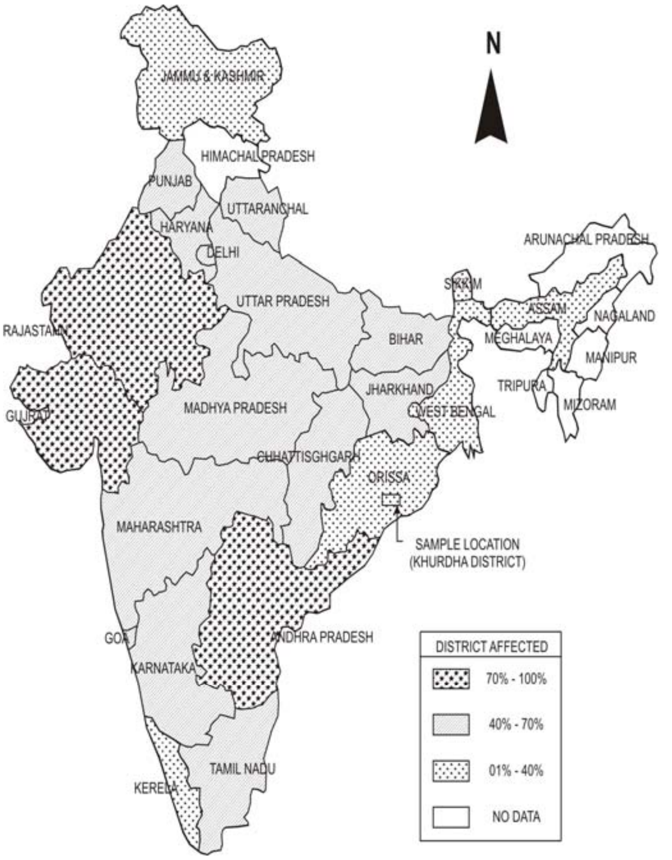

Fig. 1 Fluoride map of India showing the percentages of districts affected in various states and the tentative location of ground water sample collection.

Based on the spirit of literature cited above, this study depicts the synthesis and responses of a real-life fixed bed sorption system, a rare of its kind, in defluoridation research. The objective is focused on evaluating the sorption profile of an adsorbent alumina cement granules (ALC) in a fixed bed continuous flow system, in defluoridating natural ground waters of a fluoride endemic rural Indian village. Attempts have also been made in analyzing various factors affecting breakthrough sorption profile, and in describing the sorptive responses through modeling.

MATERIALS AND METHODS

Adsorbent and Adsorbate

The adsorbent (ALC), used in the present research, was prepared from a commercially available high alumina cement. It was suggested that, due to high electro-negativity and small ionic size, fluoride ion is classified as a hard base having strong affinity towards trivalent metals and oxides like alumina (Wu *et al*., 2007). The rich presence of alumina and calcium, whose (established) potential for fluoride scavenging was instrumental in selecting this adsorbent. Initially, a slurry was prepared by adding distilled water to 1 kg of high alumina cement at a water-cement ratio of ~ 0.3.

The slurry was kept at ambient temperature for two days for setting, drying and hardening. This hardened paste was cured in water for five days. After curing, it was broken, granulated, sieved to geometric mean size of ~ 0.212 mm, and kept in airtight containers for use. The elemental composition of ALC (combined with oxygen) obtained from EDX showed the presence of Al_2O_3 (78.49%), CaO (15.82%), SiO_2 (5.39%), and Fe_2O_3 (0.30%). The bulk density and pH of zero point charge (pHzpc) were 2.33 g/cm^3 and 11.32 respectively.

The natural fluoride rich ground water was collected from Baliasingh Patna, a fluoride endemic village (Kurda district, Orissa state) in India (**Fig. 1**). Only plastic wares were used for handling this ground water and were not experimented in glass containers. All plastic wares were washed in dilute HNO_3 acid bath and rinsed thoroughly with deionized water prior to use. The characteristics of the ground water under study are shown in **Table 1**.

Analysis

Expandable ionAnalyzer EA 940 with Orion ionplus (96–09) fluoride electrode (Thermo Electron Corporation, USA), using TISAB III buffer was used for fluoride measurement. The pH measurement was done by a Cyber Scan 510 pH meter (Oakton Instruments, USA). A high precision electrical balance (Mettler Toledo, Model AG135) was used for weight measurement. The elemental composition of ALC combined with oxygen was determined by Energy Dispersive X-ray (EDX) analysis (Oxford ISIS-300 model) by quantitative method in two iterations using ZAF correction, at a system resolution of 65 eV, and results were normalized stoichiometrically.

Sorption Studies in Fixed Bed System

The sorptive characteristics ALC on fluoride were investigated under continuous flow fixed bed experiments using glass columns of length 550 mm and internal diameter 20 mm. The column was packed with desired depth of ALC between two layers of glass wool at the top and bottom ends to prevent absorbent from floating. Then the column was fed continuously with fluoride rich ground water at a desired volumetric flow rate by using peristaltic pumps (Miclins, India). The effluent samples were collected at pre-determined time intervals and analyzed for the remaining fluoride concentration. All studies were performed at a constant temperature of 300 K to be representative of the prevailing environmental conditions. During sorption experiments, it was observed that the flow rate remained more or less constant indicating the absence of clogging of pores and that the sorption sites of ALC were easily accessible through the interparticle pore network.

Table 1. Characteristics of natural ground water (collected from Baliasingh Patna, Kurda district, Orissa State, India)

Characteristic parameter	Quantitative value (mg/l)
Fluoride	8.65
pH	6.9 ± 0.4
TDS	463
Acidity	1.5
Alkalinity	260
Chloride	165
Total Hardness	145
Total Organic Carbon	59.08
Total phosphorous	0.032
Silicate as SiO_2	39.22
Boron	0.33
Sodium	14.00
Pottasium	2.00
Ammonia Nitrogen	0.328
Salinity	0.30*

*Salinity is expressed in PSS (practical salinity scale).

* Minimum detection limit of salinity- 0.1 PSS

MATHEMATICAL DESCRIPTIONS

Adsorption Capacity of ALC in Fixed Bed

In the fixed bed studies, the dynamic responses of the adsorbent during sorption, was documented by a 'breakthrough curve'. The point on this curve at which effluent fluoride concentration (C_t) crosses the permissible limit of 1 mg/l is taken as 'breakthrough point' and that corresponding to 90% of influent fluoride concentration (C_t/C_0 = 0.90) as the 'exhaust point'. Capacity of column upto breakthrough will be representing the minimum capacity of ALC in single column operation ($q_{min,col}$) and will be of use in its application in domestic defluoridation units. In pilot scale and field scale community applications involving series of columns, the capacity of column up to exhaust (q_{col}) will be useful. The total quantity of fluoride adsorbed (F_{tot}) in the column for a given feed concentration (C_0) and flow rate (Q) can be found by calculating the area above breakthrough curve by integrating the adsorbed fluoride concentration ($Cad = C_0 - C_t$) versus time t (h) plot as:

$$F_{tot} = Q \int_{t=0}^{t=et} Cad\ dt \tag{1}$$

similarly, the quantity of fluoride adsorbed up to breakthrough (F_b) as:

$$F_b = Q \int_{t=0}^{t=bt} Cad\ dt \tag{2}$$

The minimum and maximum adsorption capacity of ALC in the sorptive filtration system can be calculated as:

$$q_{\min,col} = \frac{F_b}{M} \tag{3}$$

$$q_{col} = \frac{F_{tot}}{M} \qquad (4)$$

where, M represents the mass of ALC in the column.

Modeling of Breakthrough Profile

For a given bed depth, the service times of a unit plant are correlated with initial sorbate concentration, flow rate, and adsorption capacity of adsorbent to be used. So, obtaining a meaningful and reliable loading capacity of the adsorbent turns crucial in efficient process design and operation. This necessitates a careful evaluation and analysis of the experimental data, to predict the effect of variations in operational parameters of sorption process, through modeling.

Thomas model (Thomas, 1944) is one of the most widely used models in column performance theory. This model is derived by assuming Langmuir kinetics of adsorption-desorption with no axial dispersion and that the rate driving force obeys second-order reversible reaction kinetics. The data obtained in fixed bed column studies are used to calculate maximum solid phase concentration of sorbate on the sorbent and the adsorption rate constant. The expression by Thomas for an adsorption column is given as:

$$\frac{C_t}{C_0} = \frac{1}{1+\exp\left(\frac{k_{Th} q_{Th} M}{Q} - k_{Th} C_0 t\right)} \qquad (5)$$

where, C_0 indicates the initial concentration of fluoride in solution (mg/L), C_t the concentration of fluoride in the solution at any time t (mg/L), Q the volumetric flow rate (L/h), M the mass of ALC bed in the column (g), t the service (sampling) time of the fixed bed (h), k_{Th} Thomas rate constant (L/h mg) and q_{Th} the equilibrium sorbent uptake of the adsorbent (mg/g).

The linearized form of the model is:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_{\mathrm{Th}} q_{Th} M}{Q} - k_{\mathrm{Th}} C_0 t \qquad (6)$$

The kinetic coefficient k_{Th} and adsorption capacity of column q_{Th} can be determined from a plot of $\ln[(C_0/C_t) - 1]$ against t at a given flow rate.

RESULTS AND DISCUSSION

Effect of Process Parameters on breakthrough

The fluoride sorption breakthrough curves obtained by varying the depth of ALC bed and flow rates in ground water are shown in **Figs 2** and **3**, with its quantitative evaluation of parameters in **Table 2.**

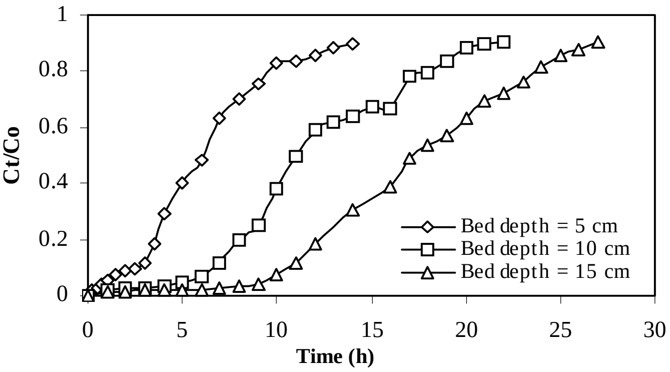

Fig. 2 Experimental breakthrough profiles of fluoride sorption onto ALC at different bed depths in natural water (Q = 8.0 ml/min, C_0 = 8.65 mg/l).

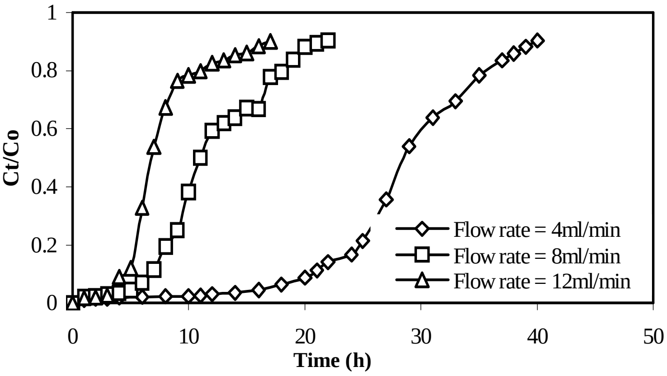

Fig. 3 Experimental breakthrough profiles of fluoride sorption onto ALC at different flow rates in natural water (C_0 = 8.65 mg/l; Z = 10 cm).

The breakthrough curves were found to be of almost the same pattern for different bed depths (5, 10 and 15 cm) under same flow rate (8 ml/min). However, a closer examination of the breakthrough curves (especially in lower C_t/C_0 ranges) indicates that the curves turns less steeper at higher bed depths. As expected, both breakthrough and exhaust times increase with corresponding volumes of water treated, with increase in bed depths. Naturally, the availability of more adsorbent at higher bed depths offers more surface area and binding sites for sorption resulting enlarged mass transfer zones. The adsorption capacity of ALC at these different bed depths for a particular flow rate of 8 ml/min does not show much variation, which may indicate its consistency and affinity for fluoride sorption.

However, the observed reduction in total adsorption capacity at higher bed depths are unexpected which may be due to some localized channelization or uneven flow patterns developed in the bed after breakthrough.

Table 2. Sorption data of fluoride onto ALC at different experimental conditions (C_0= 8.65 mg/L)

h (cm)	Q (ml/min)	bt (h)	$q_{min,col}$ (mg/g)	et (h)	q_{col} (mg/g)
5	8	3	0.3174	14	0.7503
10	8	7	0.3809	22	0.7030
15	8	11	0.4028	27	0.6660
10	4	21	0.5748	40	0.8180
10	12	5	0.4070	17	0.6800

The breakthrough curves appear steeper at higher flow rates may be due to faster movement of adsorption zone along the bed aiding its quick saturation. The increase in adsorption capacity (both up to breakthrough and exhaust) of ALC is more pronounced in the flow rate range of 8–4 ml/min; whereas the effect is almost negligible in the 12–8 ml/min. Though better diffusivity of fluoride and enhanced sorption is expected at 8 ml/min, it appears that the EBCT (volume of the bed/volumetric flow rate) corresponding to these flow rates (~6–9 min) ensures same rapid sorption features.

Application of Thomas Model

The Thomas Model was applied to investigate the breakthrough behavior of fluoride sorption onto ALC in the ground water. The respective parameters of the model obtained by linear regression of the model were used to calculate the breakthrough curve. The linear regression of the model with the experimental fluoride sorption data shows reasonably good correlations with high R^2 values (>0.95) at all bed heights and flow rates (except one at 12 ml/min). **Table 3** illustrates the model constants and regression coefficients.

The values of K_{Th} are found increasing with flow rates from 4–12 ml/min. As shown, both the parameters q_{Th} and K_{Th} of the model are found decreasing with higher bed depths. For all conditions of bed depths and flow rates, the model predicted marginally higher sorption capacity q_{Th}, than experimental values. It becomes too obvious that the Thomas model could describe the sorption of fluoride onto ALC at all these stages of sorption process. The conventional practice to compare the sorption system responses with predicted values of the model is to plot the respective curves against the same axial settings, usually C_t/C_0 versus t (**Fig. 4**). The curves show very good correlations indicating that in pilot plants and field applications involving series of columns, Thomas model would be most appropriate in describing the sorption process.

CONCLUSIONS

The synthesis of ALC sorptive system for defluoridation of ground water has been convincingly demonstrated successful, as it shows comparable and consistent fluoride adsorption potential in column applications. The adsorption capacity of ALC at different bed depths does not show much variation, for a particular flow rate indicating the consistency in fluoride scavenging. The Thomas model was found to describe the sorption of fluoride onto ALC with consistent vigour at all stages of sorption process.

Table 3. The characteristic parameters predicted by Thomas model for natural water (C_0= 8.65 mg/L)

h (cm)	Q (ml/min)	K_{Th} (L/mg h)	q_0 (mg/g)	q_{Th} (mg/g)	R^2
5	8	0.0511	0.7826	0.9044	0.9507
10	8	0.0363	0.7031	0.7461	0.9677
15	8	0.0317	0.6660	0.6944	0.9847
10	4	0.0206	0.8181	0.8419	0.9595
10	12	0.0481	0.6828	0.7770	0.8697

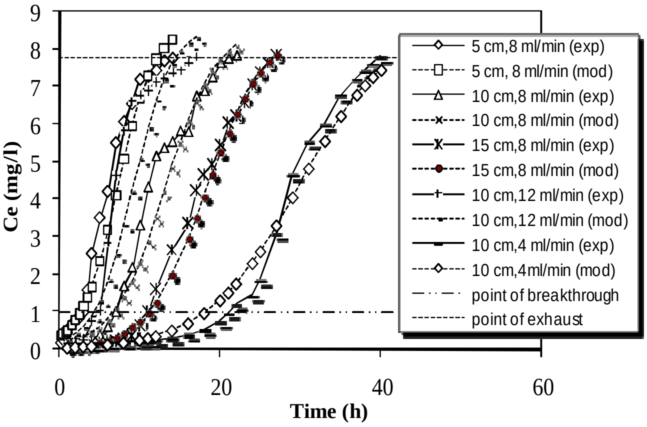

Fig. 4 Comparison of experimental breakthrough profiles against theoretical values predicted by Thomas model at different process conditions in natural water.

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REFERENCES

Aksu, Z., Gönen, F. (2004) Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves, *Process Biochem*. **39**, 599–613.

Ayoob, S. & Gupta, A.K. (2006) Fluoride in Drinking Water: A Review on the Status and Stress Effects. *Critical Rev. Environ. Sci. Technol*. **36**, 433–487.

Ayoob, S. & Gupta, A.K. (2007) Sorptive response profile of an adsorbent in the defluoridation of drinking water, *Chem. Eng. J.* **133**, 273–281.

Ayoob, S., Gupta, A.K. & Venugopal, T.B. (2008) A conceptual overview on sustainable technologies for defluoridation of drinking water, *Critical Rev. Environ. Sci. Technol*. **38**, 401–470.

Daw, R.K. (2004) Experiences with domestic defluoridation in India, Proceedings of the 30th WEDC International Conference on People-Centred Approaches to Water and Environmental Sanitation, Vientiane, Lao PDR, 467–473.

Ko, D.C.K., Porter, J.F. & McKay, G. (2000) Optimized correlations for the fixed bed adsorption of metal ions on bone char, *Chem. Eng. Sci*. **55**, 5819–5829.

Susheela, A.K. (2003) A treatise on fluorosis, Fluorosis Research and Rural Development Foundation, New Delhi, India.

Thomas, H.C. (1944) Heterogeneous ion exchange in a flowing system, *J. Am. Chem. Soc*. **66**, 1664–1666.

WHO – World Health Organization (2006) Fluoride in Drinking water, J. Fawell, K. Bailey, J. Chilton, E. Dahi, L. Fewtrell, Y. Magara, (Eds.), IWA Publishing, Alliance House, 12 Caxton Street, London SW1H 0QS, UK, 41–75.

Wu, X., Zhang, Y., Dou, X. & Yang, M. (2007) Fluoride removal performance of a novel Fe–Al–Ce trimetal oxide adsorbent, *Chemosphere,* **69**, 1758–1764.