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Design and operation of fixed bed laterite column for the removal of fluoride from water

Mitali Sarkar*, Aparna Banerjee, Partha Pratim Pramanick, Asit Ranjan Sarkar

Department of Chemistry, University of Kalyani, Kalyani 741235, West Bengal, India

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Abstract

Laterite, the geomaterial, is used as an adsorbent for the removal of fluoride from drinking water. The equilibrium data obtained through batch study is fitted to the Langmuir and Freundlich isotherm. The values of thermodynamic constants and the separation factor indicate that fluoride removal on laterite is feasible. The solution movement through the laterite column bed was predicted from the mass balance concept. The nature of breakthrough curve was found to be influenced by several operational parameters, adsorption capacity and adsorption rate. The governing influence of primary adsorption zone formation was characterized by different secondary parameters. The laterite bed capacity under dynamic condition was determined from the breakthrough curve and is higher compared to that evaluated from static mode. Sharp breakthrough curve was obtained at higher feed fluoride concentration and lesser bed height. Column capacity does not change up to a flow rate of 6.5 $\text{cm}^3\,\text{min}^{-1}$ even for the highest concentration studied. It is found that a maximum of 80.4% of retained fluoride was eluted at pH $\geq$ 9.8. In a typical set with initial fluoride concentration of 20 $\text{mg}\,\text{dm}^{-3}$ and bed height 20 cm the retention–elution process was repeated for a number of times. It is found that the capacity though decrease with the cycle number, it remains within 68% after five cycles.

Keywords: Laterite; Fluoride; Column behavior; BTC; Elution; Efficiency

1. Introduction

It is found that long-term ingestion of fluoride rich drinking water leads to serious health disorder, the fluorosis [1]. Release of fluoride in ground water occurs due to both natural dissolution of minerals from subterranean strata and the industrial discharge. Fluorosis results in molting of teeth, softening of bones, ossification of tendons and ligaments and also the neurological damage in severe situation. It is alarming to note that fluorosis is endemic in many parts of world, particularly in mid-latitude regions. In India, it is estimated that about 62 million people are affected with fluorosis. Our study on the water quality survey on the Rampurhat block, Birbhum district, West Bengal, India, reveals that ground water of a large area is contaminated with moderate to high concentration of fluoride [2] considering WHO guidelines [3]. Rural populations consuming contaminated water in the study area develop fluoride related health complaints; such irreversible health damage is a real cause of concern to the scientists and health professionals. It is suggested that the solution lies only in prevention; the fluoride should be removed from its source of entry.

The popular technologies for fluoride removal from water are (a) the coagulation followed by precipitation and (b) the adsorption. In coagulation trace amounts of fluoride ion tend to remain in solution due to the solubility restriction of the salts. In addition a large amount of wet bulky sludge is generated. Further major shortcoming of liming is the resulting high pH of the treated water [4]. The Nalgonda technique, based on precipitation process is the most commonly used defluoridation technique [5]. The major limitations are frequent addition of chemicals, large amount of sludge production, less effectiveness with water having high total dissolved solids and hardness. Further, increase of residual aluminium was also reported, which is dangerous to human health as concentration of aluminum, a neurotoxin, as low as 8.0×10^{-2} $\text{mg}\,\text{dm}^{-3}$ in drinking water has been reported to cause Alzheimer's disease. A good number of reports dealing with the removal techniques of fluoride include electrochemical degradation [6,7], ion exchange separation [8,9] and adsorption using different kinds of adsorbent both natural and synthetic [10–17] as well as of biomaterials [18].

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* Corresponding author. Tel.: +91 33 2582 3883; fax: +91 33 2582 8282.
E-mail address: mitali_ku@yahoo.com (M. Sarkar).

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Our study indicates that laterite, the red soil, available in plenty in different parts of India has the potential of removing fluoride from aqueous solution [19]. The kinetics and activation energy parameters via batch operation suggest that the process is diffusion controlled and the alumina, silica and iron oxide phase act as the probable main sites for adsorption [20]. However, the batch study fails to simulate the dynamics in a continuous mode and so the column study seems essential to model the flow dynamics of a solution front through a fixed bed. The present communication aims at to evaluate the performance of fixed bed laterite column for fluoride removal. The efficiency of the process was tested following a series of retention–elution cycles.

2. Materials and methods

2.1. Materials

In the present study laterite, the geomaterial, obtained from Bankura District, West Bengal, India, is used as a low cost adsorbent [19]. The physico-chemical and surface characteristics of laterite are presented in Table 1. Stock solution of sodium fluoride (NaF) of desired concentration was prepared by dissolving appropriate quantity of sodium fluoride in ultra pure water. The fluoride concentration in the filtrate was measured with an ion meter (model no. pH 340/ion set, WTW, Germany) using fluoride ion selective electrode following standard methodology [21].

Table 1
Characterization of laterite sample

Constituent	Amount (%)
Chemical characteristics	
SiO_2	72.90
Fe_2O_3	3.70
K_2O/Na_2O	1.81
CaO	2.00
MgO	0.80
P_2O_5	2.35
TiO_2	1.49
Al_2O_3	14.51
SO_3	0.55
Parameter	**Value (%)**
General characteristics	
Ash	76.32
Loss on ignition	8.99
Volatile matter	4.22
Organic carbon	9.89
Moisture	1.12
Parameter	**Value**
Surface characteristics	
Particle size (mm)	0.5
Total porosity (%)	48.53
Water holding capacity (%)	1.09
Sp. surface area (cm^2)	12.97
Bulk density ($g\,cm^{-3}$)	0.92
Particle density ($g\,cm^{-3}$)	1.79
pH_{ZPC}	3.98
Volume expansion (%)	20.03

2.2. Batch study

In the batch adsorption process fluoride solution of known concentration was agitated with laterite in an incubator till equilibrium is reached. The process was optimized for initial fluoride concentration (10–50 mg dm^{-3}), dose (1.0 g) and size of laterite particle (+0.50 to −0.25 mm), shaking period (195 min) and speed (400 rpm), pH (6.8) and temperature (303 K) of working solution [19]. The solution was filtered using micro filter (Satorious, A.G. Goettingen, Germany, 0.45 μm) and the fluoride concentration in the filtrate was measured.

2.3. Column study

Column experiment was performed in a perspex column (i.d. 0.6 cm, length 60.0 cm) packed with laterite of uniform size following the procedure of Hutchins [22]. A flow controller was used to control the inlet flow rate. The process was optimized for the feed fluoride concentration (20–50 mg dm^{-3}), flow rate (5.0 cm^3 min^{-1}) and laterite bed height (20–40 cm) with particle size of +0.75 to −0.50 mm in the column. The finer particles used for batch study, although the preferred choice in terms of the higher capacity, is avoided in column packing in order to overcome the possibility of chocking of the column bed with progress of solution movement. The effluent was collected from the column end at regular time intervals and fluoride concentration was measured.

3. Results and discussion

3.1. Characterization of laterite sample

The air-dried laterite sample is characterized through physico-chemical analysis. The weight percentage of the chemical constituents, general and surface characteristics are presented in Table 1. The morphological and the mineralogical patterns are characterized through SEM (indicating porous structure) and XRD analysis (indicating presence of crystalline iron oxides such as goethite, hematite, lepidocrocite as well as amorphous iron oxides together with α-quartz and γ-alumina) [20].

3.2. Evaluation of adsorption isotherm and thermodynamic parameters

The adsorption isotherm in a batch equilibrium test is performed to determine suitability of adsorption treatment for a given application. The equilibrium data was fitted to linear form of Langmuir (Eq. (1)) and Freundlich isotherm (Eq. (2)) and the best fit model is evaluated through regression.

$$\frac{1}{q_e} = \frac{1}{QbC_e} + \frac{1}{Q} \qquad (1)$$

$$\ln q_\mathrm{e} = \ln K_f + \left(\frac{1}{n}\right) \ln C_\mathrm{e} \qquad (2)$$

where C_e is the equilibrium fluoride concentration (mg dm^{-3}); q_e the equilibrium amount of fluoride on laterite (mg g^{-1}); Q (mg g^{-1}) and b (dm^3 mg^{-1}) are the Langmuir isotherm constants related to the capacity and the energy, respectively, may be obtained from the plot of $1/q_\mathrm{e}$ against $1/C_\mathrm{e}$. Similarly, K_f (dm^3 g^{-1}) and $1/n$, the Freundlich constants, signifying the capacity and the intensity, respectively, may be obtained from the plot of $\ln q_\mathrm{e}$ against $\ln C_\mathrm{e}$. The isotherm constants at different temperatures together with regression coefficient (R^2) are given in Table 2. It is found that Q value decreases with increasing temperature, while no definite trend for b is observed. Further, as indicated from the regression coefficient values (R^2) either Langmuir or Freundlich model may sufficiently describe the fluoride–laterite adsorption. The isotherm criteria is described by a dimensionless quantity 'r', the constant separation factor [23], defined as,

$$r = 1/(1 + bC_0) \qquad (3)$$

The calculated 'r' values (between 0.0960 and 0.3681) in the studied fluoride concentration indicate favorable case of adsorption at the selected operational conditions.In order to test the feasibility of fluoride–laterite interaction, the thermodynamic parameters like free energy change (ΔG), enthalpy change (ΔH), and the entropy change (ΔS) are evaluated following the Eqs. (4) and (5) as:

$$\Delta G = -RT \ln K_\mathrm{c} \qquad (4)$$

$$-R \ln K_\mathrm{c} = \frac{\Delta H}{T} - \Delta S \qquad (5)$$

where T is the absolute temperature, R the universal gas constant and K_c is the equilibrium constant. Negative values of ΔG at all temperatures (Table 3) indicate spontaneous nature. Negative values of the enthalpy change (ΔH) and the entropy change (ΔS) of the process were obtained (Table 3) from the slope and the intercept, respectively, of van't Hoff plot (Fig. 1) following Eq. (5). Generally, adsorption process is associated with positive value of ΔS. In contrary, negative value of ΔS for adsorption on some heterogeneous material is reported [24]. The negative value of ΔH indicates exothermic nature of interaction for the present system.

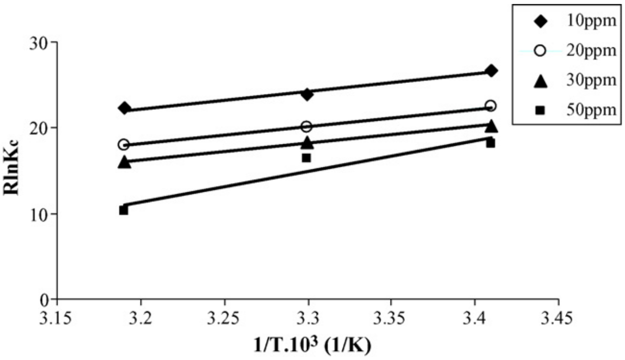

Fig. 1. van't Hoff equation plot.

3.3. Parametric design of single solute retention in a fixed bed laterite column

Adsorption isotherm, being a batch equilibrium test, however, fails to simulate or predict dynamic performance during continuous flow movement. The most important deficiency is the lack of a predictable contact time necessary to achieve the equilibrium capacity in a granular bed. In order to design the operation in a fixed bed column as well as to dictate the flow dynamics the breakthrough curve is constructed.

For the retention fluoride solution of known concentration and pH was continuously fed at the top of the column bed at a fixed flow rate. A plot of fluoride concentration (C) against the volume of effluent (V) yielded the breakthrough curve (BTC). It is assumed that during solute retention on the laterite bed fluoride mass transfer occurs by convection only, no radial and axial dispersions occur, the flow pattern is ideal plug flow and no chemical reaction occurs in the column [25].

Retention of fluoride in the column occurs as equilibrium is established. With progress of time (t) the upper part of the column becomes saturated with incoming fluoride, in the intermediate zone fluoride is found in solution as well as on laterite surface with any fluoride still to reach the lower part of the column. In the intermediate zone, known as the interaction zone, the concentration (C) of fluoride retained is different at different layers of the bed or the distance (d) from the top of the column bed. The ratio C/C_0 is, therefore, a function of d at a given t (or a function of t at a known d). The interaction zone moves downwards as segment or primary adsorption zone following the mass balance concept and the effluent from the column is free from fluoride until an amount of solution just sufficient for the

Table 2
Equilibrium and isotherm parameters

Temperature (K)	Q (mg g^{-1})	b (dm^3 mg^{-1})	r	$1/n$	K_f (dm^3 g^{-1})
293	0.8565	0.1882 (0.9784, 0.22762)[a]	0.3469	0.5636	0.1534 (0.9985, 0.0277)[a]
303	0.8461	0.1358 (0.9698, 0.27829)[a]	0.4240	0.5897	0.1328 (0.9976, 0.0269)[a]
313	0.6051	0.1761 (0.9901, 0.14666)[a]	0.3681	0.4261	0.1319 (0.9603, 0.1054)[a]

[a] Values in parenthesis represents R^2 and S.E.

Table 3
Thermodynamic parameters

C_0 (mg dm^{-3})	K_c	ΔG (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})	$-\Delta S$ (J mol^{-1}K^{-1})	R^2
10	17.73	−7.2397	2.0583	43.697	0.9830
20	11.24	−6.0921	2.0227	46.627	0.9999
30	9.08	−5.5547	1.9634	46.637	0.9952
50	7.17	−4.9601	3.5591	102.652	0.8989

interaction zone to reach end of the column has been run through the column. This is the breakthrough point when fluoride is first detected in the effluent. At the exhaustion point of BTC the total bed is thought to be exhausted and fluoride finds no place for retention. Theoretical considerations show that shape of BTC is largely dependent on the type of adsorption isotherm governing the static equilibrium [25]. The performance is expressed as the capacity and was compared with that from batch operation. The efficiency of the column bed is determined from the percent saturation (S), that is the function of δ (depth of primary adsorption zone) and f (fractional capacity of adsorbent in the adsorption zone). The total time t_x required the primary adsorption zone to establish itself; move down the length of the column and out of bed is calculated as,

$$t_x = \frac{v_1}{F_m} \tag{6}$$

where F_m is the mass flow rate (mg min^{-1} cm^{-2}) corresponding to the experimental flow rate F (cm^3 min^{-1}). The time t_δ required for movement of primary adsorption zone downwards in the column is given by,

$$t_\delta = \frac{v_1 - v_2}{F_m} \tag{7}$$

where v_2 and v_1 are the mass unit volume (mg cm^{-2}) corresponding to the breakthrough volume V_2 and exhaustion volume V_1, respectively.

Thus, for a column bed depth D, the correlation between depth and time can be made [25] as,

$$\frac{\delta}{D} = \frac{t_\delta}{t_x - t_f} = \frac{t_\delta}{t_x - t_\delta\,(1-f)} = \frac{v_1 - v_2}{v_2 + f(v_1 - v_2)} \tag{8}$$

where t_f is the time required for initial formation of primary adsorption zone. The fractional capacity, f of adsorbent in the adsorption zone at break point to continue to remove solute from solution under the limiting conditions is given by,

$$f = \frac{M}{C_0(V_1 - V_2)} = 1 - \left(\frac{t_f}{t_\delta}\right) \tag{9}$$

where M is the amount adsorbed in the primary adsorption zone between V_2 and V_1.

The percent saturation of column bed is given by,

$$S\,(\%) = \left[1 - \frac{\delta(1-f)}{D}\right] \times 100 \tag{10}$$

The study was conducted with (i) three different fluoride concentrations, viz. 20, 30 and 50 mg dm^{-3} at a fixed column bed length of 20 cm and (ii) three different column bed lengths, viz. 20, 30 and 40 cm for a fixed fluoride concentration of 20 mg dm^{-3}. The characteristic parameters are presented in Table 4.

3.4. Optimization of operational parameters during column study

The operation and performance of a column as is influenced by several operational parameters like the bed height, volume, concentration and flow rate of the feed solution, the optimization of such variables was made.

3.4.1. Effect of concentration and volume of feed solution

Fluoride retention on the laterite column was investigated with different fluoride concentrations, viz. 20, 30 and 50 mg dm^{-3}. The characteristic shape and position of BTC on the volume axis for different concentrations are shown in Fig. 2. Sharp breakthrough curve was obtained at higher feed fluoride concentration. The breakthrough time decreases as the feed fluoride concentration increases. The percent saturation lies in the range between 73 and 78% and found to increase with feed fluoride concentration. The column capacity per unit weight of laterite remains almost the same. The value of secondary parameters, viz. δ, t_x, t_δ and t_f were found to decrease as the feed fluoride concentration increases.

3.4.2. Effect of flow rate of feed fluoride solution

The effect of flow rate of the feed fluoride solution was studied for a fixed fluoride concentration (20 mg dm^{-3}) and laterite bed height (20 cm). It is found that the column capacity does not change up to a flow rate of 6.5 cm^3 min^{-1} even for the highest concentration studied (Fig. 3). However, in subsequent studies a flow rate of 5.0 cm^3 min^{-1} was maintained to ascertain the equilibrium mass transfer through the bed. It is expected that at a lower flow rate due to adequate interaction time adsorption

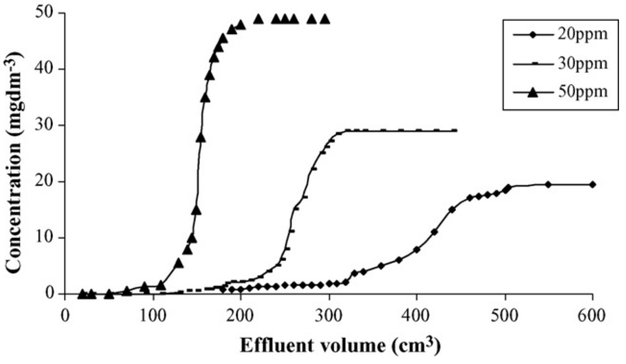

Fig. 2. BTC with different feed concentration.

Table 4
Evaluation of characteristic and operational parameters for fixed bed column

C_0 (mg dm^{-3})	D (cm)	v_1 (mg cm^{-2})	v_2 (mg cm^{-2})	$v_1 - v_2$ (mg cm^{-2})	t_x (min)	t_δ (min)	t_f (min)	f (min)	δ (cm)	S (%)
20	20	41.40	14.86	26.54	168	98	35	0.64	14.79	73.37
20	30	51.31	15.99	35.11	242	166	42	0.75	24.94	74.22
20	40	61.00	17.34	43.66	287	206	21	0.90	30.84	92.29
30	20	32.91	18.05	14.86	103	47	19	0.56	11.14	76.59
50	20	33.08	21.58	11.50	62	22	11	0.48	8.48	77.94

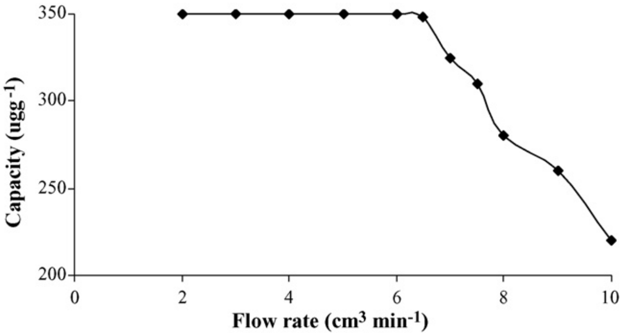

Fig. 3. Influence of flow rate.

was very efficient, at least in the initial step of process. With gradual occupancy of the sites extent of fluoride retention gradually decreases. Even after breakthrough occurs the column is still capable of accumulating fluoride, although at a lower efficiency. As the flow rate is increased, the breakthrough curve becomes steeper. The breakthrough time and adsorbed fluoride concentration decreases. This is due to the shorter residence time of fluoride in column.

3.4.3. *Effect of laterite bed height*

In order to study the effect of bed height on fluoride retention, laterite column of three different bed depths, viz. 20, 30 and 40 cm were taken. Fluoride solution of fixed concentration (20 mg dm^{-3}) was passed through the individual column at a fixed flow rate of 5.0 cm^3 min^{-1}. The typical curves are shown in Fig. 4. It is seen that with increase in bed height the breakthrough curve becomes gentler. The column capacity and the percent saturation increase. All the secondary parameters, viz. δ, t_x, t_δ and t_f evaluated were found to increase as the bed depth increases.

3.5. *BDST model*

Breakthrough service time (BDST) model is used to predict the column performance for any bed length, if that for some other depth is known. According to Bohart and Adams [26] the service time (t) was related to process conditions and operating parameters as,

$$\ln\left[\left(\frac{C_0}{C_t}\right)-1\right] = \ln(\mathrm{e}^{\mathrm{kND}/F}-1) - kC_0t \tag{11}$$

where N is the adsorption capacity, k the rate constant and D is the depth of column bed. A plot of $\ln[(C_0/C_t)-1]$ against time, yields k from the slope. Hutchins [22] proposed a linear relationship between bed depth and service time as follows,

$$t = \left[\frac{N}{C_0F}\right]D - \left(\frac{1}{kC_0}\right)\ln\left[\left(\frac{C_0}{C_t}\right)-1\right] \tag{12}$$

i.e.,

$$t = m_xD - C_x \tag{13}$$

A plot of service time against bed depth, following the above model of Hutchins gives a straight line (Fig. 5) [slope = N/C_0F, intercept = $(1/kC_0)\ln\{(C_0/C_t)-1)\}$]. The high regression value ($R^2 = 0.9796$) of the linear plotindicates the validity of BDST equation.

3.6. *Performance evaluation in batch and column mode*

Adsorption capacity of fluoride in the batch mode and column mode is calculated to be 0.1854 and 0.3586 mg g^{-1}, respectively,

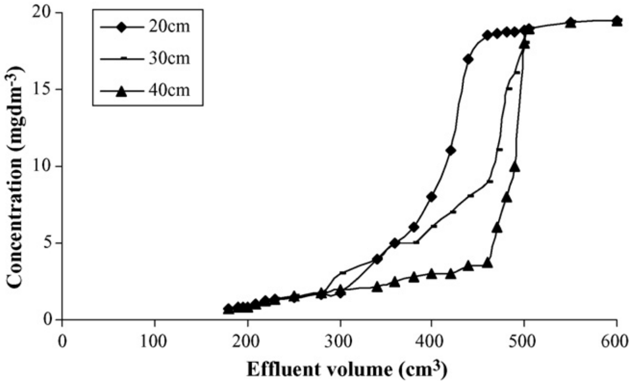

Fig. 4. BTC with variation of bed depth.

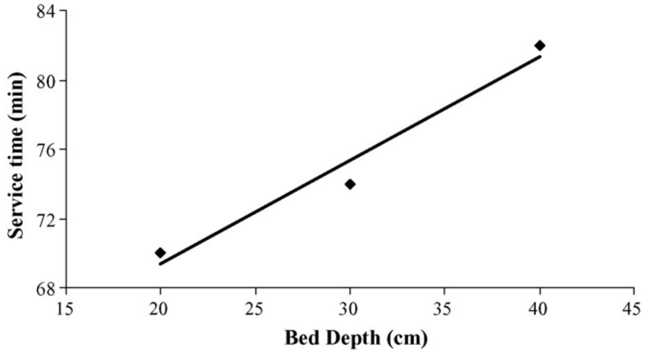

Fig. 5. Plot of BDST equation.

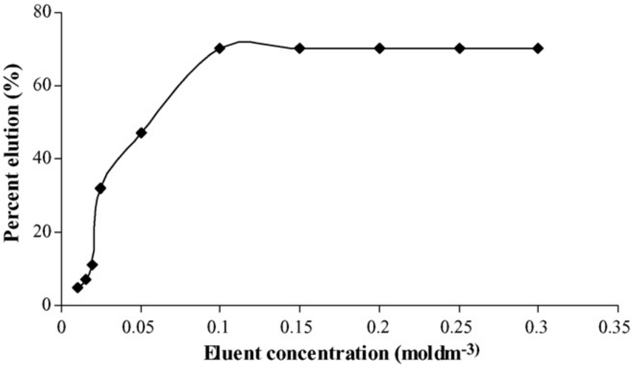

Fig. 6. Elution of retained fluoride.

indicating that column capacity is higher than the batch capacity for the fluoride–laterite system. Thus, column operation is preferred to the batch operation.

3.7. Elution study

Elution of the retained fluoride from the laterite phase was made with sodium hydroxide solution of different concentrations (Fig. 6). A constant flow rate of $3.0\,\mathrm{cm}^3\,\mathrm{min}^{-1}$ was maintained throughout the operation. It is found that a maximum of 80.4% of retained fluoride was eluted with $1.0 \times 10^{-1}\,\mathrm{mol\,dm}^{-3}$ NaOH solution. The elution pattern and volume were evaluated from Fig. 7.

3.8. Effectiveness of the column operation

In order to find the effectiveness of the column bed the operation is repeated for a number of times and the capacity after each cycle was evaluated. In a typical set with initial fluoride concentration of $20\,\mathrm{mg\,dm}^{-3}$ and bed height 20 cm the retention–elution process was repeated for five times. It is found that column capacity though decreases with cycle number it remains within 68% (Fig. 8). The experimental column capacity ($0.3473\,\mathrm{mg\,g}^{-1}$) is compared with theoretical breakthrough capacity ($0.3586\,\mathrm{mg\,g}^{-1}$) as well as the fluoride recovery ($0.2792\,\mathrm{mg\,g}^{-1}$) through elution.

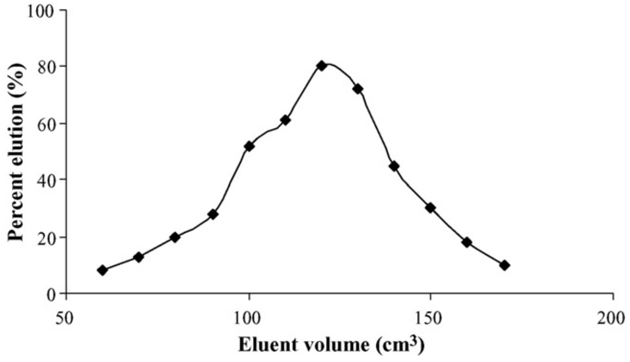

Fig. 7. Elution pattern.

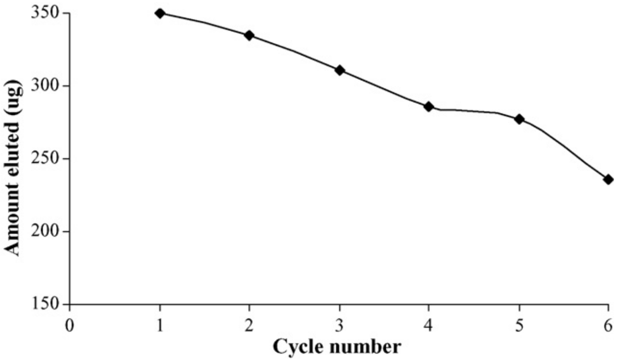

Fig. 8. Variation of column capacity.

4. Conclusions

Laterite, the geomaterial is found to be a suitable adsorbent for the removal of fluoride from aqueous sample. The equilibrium behavior of the adsorption was represented by Langmuir and Freundlich isotherms. From the value thermodynamic constants and the separation factor it is stated that fluoride removal on laterite is feasible and spontaneous.

The mass balance concept is applied to predict the behavior of solution movement through the column. The nature of breakthrough curve is influenced by the flow rate, column bed height, adsorption capacity and adsorption rate. The formation of primary adsorption zone is predicted and characterized by different secondary parameters. The breakthrough capacity is found higher compared to the batch capacity. With increased fluoride concentration sharp breakthrough curve is obtained. On the other hand, the breakthrough curve becomes gentler as the bed height increases. The retained fluoride can be eluted with NaOH solution ($1.0 \times 10^{-1}\,\mathrm{mol\,dm}^{-3}$). On repetition of the retention–elution cycles for five times column capacity remains within 68%.

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