Kinetic and Adsorption Performance of Fluoride in a Fixed-bed Column using Adsorbent: Limonite

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ABSTRACT: Drinking water containing F^- >1.5 mg/l is recognized as a major health problem. In fact, the F^- concentration <1.5 mg/l is an essential trace element for human health, but, in excessive intake may cause fluorosis. The present study used the novel adsorbent limonite for the investigation of the defluoriation capacity in aqueous condition by fixed-bed column. The potential of defluoridation of limonite was done under variable operating conditions such as pH, inlet F^- concentration, bed height and flow rates. At pH 5.02 the maximum adsorption of F^- onto the surface of the limonite observed. The column studies showed that the adsorption capacity of the bed decreased with increase of flow rate and inlet F^- concentration. The FTIR spectra of limonite shows that it contains –OH group which might be act as ion exchange for F^- ion. SEM and XRD images also give good evidence of the adsorption of F^- on the surface of limonite. The Breakthrough curve Models, Thomas Model and Yoon-Nelson Model were giving a good connection with experimental results. The column capacity for the actual high F^- water was calculated 13.4 mg/g.

Keywords: Breakthrough curve, Defluoridation, Fixed-bed, Fluorosis, Geo-material, Limonite, Optimization

1. INTRODUCTION

Fluoride is a very essential mineral for human teeth and bones when its intake concentration is < 1.5 mg/l. Excessive fluoride concentration >1.5 mg/l may cause irreversible demineralization of teeth and bone tissues, and this ill-effect called fluorosis (Grynpas et al., 2000). However, long-term exposure (>5.0 mg/l) damage the tissue of the kidney, brain and thyroid (Gazzano et al., 2010; Barbier et al., 2010).

Adsorption technology hugely applied for F⁻ removal. The effectiveness of this technique for defluoriation mostly reported under aqueous condition. Adsorption processes involve the passage of the water through a contact solid bed where F⁻ is removed by ion-exchange or surface chemical reaction. The solid bed is made from activated alumina, activated clay, charcoal, alum, ash. etc (Agarwal et al., 2003; Puka, 2004; Abe et al., 2004; Das et al., 2005; Gupta et al., 2007). Most of available materials for defluoriation are expensive and technically non-feasible in rural areas. Many bio-adsorbent also have been reported in the defluoridation process in aqueous condition such as, activated rice straw, bone char, Phyllanthus emblica, leaf of Azadirachta indica, Ficus religiosa, etc. (Jamode et al., 2004; Daifullah et al., 2007; Wei et al., 2009; Mohan et al., 2012; Mondal et al., 2013). From past few years, geomaterials are also used as adsorbent for the removal of fluoride in aqueous condition like red mud, lateritic ores, bauxite, goethite soils, Kanuma mud, soil, etc. (Wang & Reardon, 2001; Chidambaram et al., 2003; Sarkar et al., 2006; Mohan & Pittman, 2007; Eva et al., 2009; Sujana et al., 2009). Previous reported treatment technologies have several drawbacks that limit their practical applicability in the poor, undeveloped F⁻ affected regions across the world. Using of geomaterials as adsorbent for F⁻ removal in drinking water becomes popular because of easy availability and cost-effectiveness.

The present work aimed to investigate the potential of natural occurring geomaterial limonite (Iron ore) for the removal of F⁻ ion from water at a relatively low level. The objective of this research paper is to study the effect of various parameters such as pH, initial F⁻ concentration, flow rate and bed height on the adsorption of F⁻ onto limonite, experimentally as well as numerically. The various models proposed for the analysis of the breakthrough curve such as breakthrough curve models, Thomas Model and Yoon-Nelson Model were taken into account to know the kind of adsorption takes place. This paper concentrates on the investigation of the limonite as adsorbent for the removal of F⁻ ion by using fixed-bed column adsorption technique, because it is easily available, cost-effective and required minimal processing.

2. MATERIALS & METHODS

The chemical reagent is used of analytical grade. A stock solution of fluoride was prepared by dissolving 2.10 gm of NaF (Sodium Fluoride) in 1L of double distilled water. The pH of the solution was adjusted by adding 0.1M of NaOH and 0.1M HNO3 solution. F^- concentration was measured with Nova 60 spectroquant® photometer. The pH of the samples was measured by a pH meter (Elico Model 1012). The instrumental measurement was done by three instruments viz. X-ray Refraction Dispersive (Model PANalytical instrument, Germany), Fourier Transmission –IR (Model 370, Thermo scientific, USA) and Scanning Electron Microscope (Model 6390LV, Germany) respectively.

The adsorbent (Limonite) used in the present work was collected from NMDC (National Mineral Development Corporation) Chemical Laboratory, Bacheli, Chhattisgarh, India. The light yellow colour of limonite consists of FeO-43.6%, SiO_2-26.3%, Al_2O_3-18.4%, TiO_2-1.1% and P_2O_5-0.56%. The density of limonite was calculated 2.7-3.3 g/cm^3 and hardness found to be 4.5-5.1. In order to remove the earthy impurities adsorbent was washed 2-3 times with double distilled water and dried for 24 hours at 110°C. Once dried, the adsorbent grounded into small particles and followed by sieving to obtain a uniform particle size (<60 to 200 μm). Again, dried for 5-6 hours and kept in desiccators till further used (Alagumuthu et al., 2010; Chaudhari & Sasane, 2014).

Adsorption studies through the fixed - bed column were carried out in a glass column of 12 cm in height and 1.4 cm inner diameter. Before the use of adsorbent in the column it was wet with double distilled water. The wetted limonite was then packed into a column. The perforated sheet and cotton were placed in upper and bottom section of the column (2.5 cm at each end) then limonite (3.2-5.6 cm) was placed in between the column. The perforated sheet used to prevent the adsorbent from floating out of column during the continuous flow. The pH of 5.02, 7.08 and 10.01 as maintained throughout the experiment by adding 0.1 M of NaOH and 0.1 M of HNO_3 solution. The influence of various factors such as pH, fixed-bed height (B_H cm), inlet fluoride concentration (C_i mg/l) and flow

rate (F_r ml/min) were investigated. The concentration of F^- ion in the effluent sample was measured using a NOVA 60 spectroquant® photometer.

The experimental result of column fixed-bed was investigated by using various types of the breakthrough model of column study. The breakthrough curves explain the effectiveness of the column for fluoride removal in fixed-bed technique. It is expressed mathematically as:

C_o/C_i

where, C_o is the concentration of outlet F^- ion (mg/l) and C_i is the inlet concentration of F^- ion (mg/l), as a function of time (in min) after the start of the flow. The breakthrough appearance time (T_B) and exhaustion time (T_E) of the breakthrough curve were calculated by the following equation (Kavianina et al., 2012)

$$\Delta T = T_E - T_B \tag{1}$$

The total amount of F^- ion adsorbed onto limonite through a packed column can be calculated by using following equation (Kavianina et al., 2012)

$$Q_{total} = \frac{F_r A}{1000} = \frac{F_r}{1000} \int_{t=0}^{t=total} C_{ads} \, dt \tag{2}$$

Where Q_{total}, A and F_r are the total flow time until the column bed becomes saturated, total area under the breakthrough curve and F_r be the volumetric flow rate (ml/min) respectively. Mathematically, the outlet volume (V_0) or treated volume of solution could be calculated according to the following equation

$$V_0 = Q_{total} t_{total} \tag{3}$$

The equilibrium uptake capacity (Q_{eq}) of the limonite through column fixed-bed for fluoride removal was determined from the ratio of the total amount of F^- ion adsorbed (Q_{total}) to the amount adsorbent used. Mathematically, it is expressed as follows (Chen et al., 2012)

$$Q_{eq} = Q_{total} / M \tag{4}$$

Many researchers used the Thomas model to study the kinetic of fixed-bed column technique (Baek et al., 2007; Sivakumar & Palanismay 2009). This model is used to determine the maximum

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solid phase concentration of solute on the adsorbent and the adsorption rate constant of adsorption column. The linearlised form of the model is given as:

$$\ln \frac{C_i}{C_o} - = \frac{K_{TH} M q_M}{F_r} - \frac{K_{TH} V_0 C_i}{F_r} \qquad (5)$$

Where, C_i= influent concentration in mg/l, C_o= outlet concentration in mg/l, q_M= maximum adsorption capacity (mg/g), K_{TH}= Thomas rate constant (ml/min.mg), V_o= volume of outlet ml, M= amount of adsorbent in the column (gm), F_r= volumetric flow rate (ml/min).

The Yoon and Nelson (1984) model is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of an adsorbate breakthrough on the adsorbent (Tsai et al., 1999). The linearlised Yoon-Nelson model for a single component system is expressed as:

$$\ln \frac{C_o}{C_i - C_o} = K_{YN} t - \tau K_{YN} \qquad (6)$$

Where K_{YN}= rate velocity constant l/min, τ= time required for 50% adsorbate breakthrough

3. RESULTS & DISCUSSION

The spectra of FTIR were obtained to understand the nature and behaviour of the functional group present in the adsorbent (limonite). FTIR spectra (Figure 1) display a number of peaks, indicating the complex nature of the adsorbent. Band appearing at 3911-3602 cm^{-1}, 2364 cm^{-1}, 1824 cm^{-1}, 1740 cm^{-1}, 1610 cm^{-1}, 1504 cm^{-1}, 1236 cm^{-1}, 1010 cm^{-1}, 884 cm^{-1}, 668-633 cm^{-1}. It is due to–OH stretching, C=C stretching, C=O stretching of anhydrides, esters, carboxylic or amide, C-O stretching of ether, ester and amines as N-H deformation respectively. Out of these COO[-] and OH^{-} played a major role in the removal of F[-] ions through anion exchange (Bhaumik & Mondal 2011). The Scanning electron microscopy (SEM) helps us to explain the surface morphology, texture and sizes of the particles. The image of raw limonite powder consisting fine particles of irregular shape. The micro porous structure of heterogeneous rough surface with different level of porous surface seems in Fig. 2 which can promote the capturing of F[-] ion. The Fig. 2 b, shows the image of treated limonite, quite different from the previous image. No pours seem clearer, shape and sized of particles are very

irregular. Powdered limonite used to study the X-ray diffraction on the untreated and fluoride treated limonite material are given in Fig. 3 (a) and (b). The figure shows that strong adsorption of ion on the surface of the limonite. The appearance of new bands and disappearance of old bands and decrease in the transmittance percentage indicates the adsorption of F- ion onto the limonite surface (Alagumuthu et al., 2010; Veeraputhiran & Alagumuthu, 2011)

pH plays an important role in adsorption capacity on the surface of adsorbent. The effect of pH on the adsorption process of F^- ion through column method was studied in the pH range of 5.02 to 10.01. The maximum adsorption and F^- ion uptake capacity observed at pH 5.02. The effect of pH on F^- ion removal is similar to what is observed for F^- ion adsorption onto various natural adsorbent such as laterite (Gomoro et al., 2012), bio-adsorbent such as rice husk (Mondal et al., 2012) and tea residue ash (Mondal, 2010). Maximum adsorption of F^- ion at pH<5.02 is presumably due to the electrostatic attraction of F^- by the positive surface of limonite (Tchomgui-Kamga et al., 2010). The pH of the solution is an important factor and it controls the adsorption of the F^- at the limonite- solution interface. The Acid-Base dissociation at interface produces positive and negative charges ion on the surface (Kunwon et al., 2001; Chakraborty & Sharma, 2012; Yadav et al., 2013). Limonite is made up of metal oxides which are easily hydrolysed in aqueous solution. The efficiency of adsorption of F^- on its surface reflects a reduction in the quantity of the positive charges. The overall mechanism for the adsorption of F^- ion onto surface sites of limonite is explained by the following two steps protonation/ ligand-exchange mechanism (Alain, 2006) as shown below in Eq. (7), (8) and (9):

$$\equiv MOH_{(s)} \; + \; H^+ \leftrightarrow \; \equiv MOH_2^+{}_{(s)} \tag{7}$$

$$\equiv MOH_2^+{}_{(s)} + F^-{}_{(aq)} \leftrightarrow MF_{(s)} \; + H_2O \tag{8}$$

which gives the net reaction

$$\equiv MOH(s) \; + \; H^+ + F^-{}_{(aq)} \leftrightarrow MF_{(s)} + H_2O \tag{9}$$

Where M = metal surface, for limonite it may be Fe, Al, or Ti etc. It is possible because F^- ion and OH^- are similar in charge and ionic radii. On the other hand adsorption of F^- ion at higher pH level not

that extent as shown in lower pH because of increasing electrostatic repulsion between the negatively charged surface sites of the adsorbent (limonite) and F⁻ ions.

The effect of initial concentration was investigated by adding a fixed amount of adsorbent (7.1 gm) onto different F⁻ ion concentration solution such as 4.1 mg/l, 12 mg/l and 24.5 mg/l respectively at pH 5.02. Sharper breakthrough curves were obtained with 12 mg/l. The F⁻ ion removal efficiency decreased with increasing initial concentration. It is because of the capacity of the adsorbent materials getting exhausted sharply with the increase in initial fluoride concentration (Yadav et al., 2013). This is probably due to the fact that for fixed dose, the total available adsorption sited was limited which become saturated at higher concentration. A similar trend has been reported for bio-adsorbent such as neem charcoal (Chakraborty & Sharma, 2012) sugarcane charcoal (Yadav et al., 2013).

The effect of flow rate for the adsorption of F⁻ ion onto the limonite at a flow rate of 3.5 ml/min and 5.5 ml/min at an inlet F⁻ ion concentration of 12 mg/l and bed height of 5.6 cm. It is seen that the rapid uptake of F⁻ ion is noticed at initial stages, it rate decreased and finally reached saturation (Appelo & Postma, 1994). When the flow rate decreased from 5.5 to 3.5 ml/min more favourable ion exchange conditions were achieved (Shivakumar & Palanismay, 2009). This is because of the residence time of the adsorbate in the column, which is long enough for adsorption. As the flow rate increased, the breakthrough curves become steeper and reached the equilibrium quickly (Kananpanah et al., 2009) Rapid equilibrium to be reached at high flow rate. This means that the contact time between the adsorbate and the adsorbent is minimized leading to early breakthrough (Chakrabarti et al., 2008; Shivakumar & Palanismay, 2009). Increasing the flow rate gave rise to a shorter time for saturation.

The effect of bed height on F⁻ ion removal was studied. The amount of 4.4 gm, 6.2 gm, and 7.1 gm of limonite used to make the bed-height 3.4 cm, 4.2 cm and 5.6 cm respectively. The standard solution of 12 mg/l of F⁻ ion was passed through three different bed heights. From results it was

observed that with increase of bed-height adsorption capacity of adsorbent increases. It is probably due to the maximum availability of surface sites to increase of bed height in column (Shivakumar et al., 2012).

Though Thomas model, kinetic coefficient or Thomas constant K_{TH} and maximum adsorption capacity q_M of the fixed-bed were determined from the plot of ln $(C_i/C_o$ -1$)$ against t (time) with respect to various factors such as pH, flow rate, bed-height and inlet concentration of F^- ion used for defluoriation. Fig. 4 (a), (b), (c) & (d) explain the effect of various factors on the value of Thomas constant and adsorption capacity. The results of K_{TH}, q_M and R^2 are given in Table 1. From experimental data it is clearly observed that the value of K_{TH} (Thomas rate constant) is dependent on flow rate, initial F^- ion concentration and bed height. The adsorption capacity (q_M) increases with increasing bed height. This also because with increase of bed height availability of adsorption sites increases and promote the adsorption of F^- onto the surface of limonite. In Yoon-Neslon model, a plot of ln(C_o/C_i-C_o) vs t (time) gives a straight line with slope of K_{YN} and intercept τK_{YN}. Fig. 5 (a) (b) (c) and (d) are the Yoon-Nelson plot at various condition for adsorption of F^- ion onto limonite. The results show that, K_{YN} increased with increased inlet concentration of F^-ion, flow rate and bed-height. This is due to the fact that increase in initial F^- concentration increases the competition between adsorbate molecules for the adsorption site, which ultimately results in an increased uptake rate (Shivakumar et al., 2012). The time required for 50% breakthrough, τ decreased with increased in flow rate and inlet concentration of F^- ion. High values of correlation coefficient indicated that Yoon and Nelson model fitted well to the experimental data as compared with the Thomas model under all optimized conditions. The same trend observed by Tsai et al. (1999).

To investigate the efficiency of limonite for removal of F^- ion through the fixed - bed column, water having 10.5 mg/l of F^- ion used. Nearly 7.1 gm of limonite used for fixed bed and flow rate for the experimental taken 3.5 ml/min. The adsorption process was carried out at room temperature and

pH 5.11. Fig. 6 shows the breakthrough profile for an F$^-$ ion from the fixed-bed column of limonite using natural fluoride contaminated water (10.5 mg/l). From Fig. 6 it is clear that the F$^-$ ion concentration successfully reduced. According to WHO (1994) 1.5 mg/l is the permissible limit in drinking water. Inlet concentration of F$^-$ ion reduced to 1.5 mg/l for a duration of 120 min using a small amount of limonite (7.1 gm) in the fixed-bed column. It gives proof that it is an effective adsorbent for fluoride removal in aqueous condition. The column capacity for the actual fluoride contaminated water was calculated 13.4 mg/g from the area of the breakthrough curve.

There are several types of adsorbent such as natural, bio-adsorbent or resin used for fluoride removal from aqueous condition (Sinha et al., 2003; Fang et al., 2003; Tor et al., 2009; Deng et al., 2011). The adsorption capacities of various adsorbent are compared with limonite given in Table 4 provide the information about the extent of effectiveness of limonite with compared to reported adsorbent. From investigation in this paper limonite finds superior to many other adsorbents reported in the relevant literatures. It also explains about the extent of the potential for defluoridation from aqueous solution under continuous operation.

Regeneration of the column is done by permeating sufficient volume of solution of 0.2 M NaOH through exhausted bed of limonite. The volume of 0.2 M NaOH solution used is measured in terms of number of bed volume. Since the desorption of F$^-$ from the limonite bed is a slow process, the exhausted column is washed with three bed volumes of 0.2 M NaOH solution at a flow rate of 5.5 mg/min and one bed volume of 0.2 M NaOH solution is left in contact with limonite for 10 hr. The solution is then drained out and the column is washed thoroughly with double distilled water to render it free from sodium. The capacity of the regenerated limonite is determined under optimum conditions. It is observed that the adsorbent limonite has regained its original F$^-$ removal capacity, indicating that the regeneration is complete. The possible mechanism of regeneration of the limonite as shown in Eq. 10:

$$\equiv MF_{(s)} + OH^-_{(aq)} \leftrightarrow \equiv MOH_{(s)} + F^-_{(aq)} \qquad (10)$$

Where M= Fe, Al, Ti etc. From equation 10 it is very clear that by the using of 0.2 M NaOH solution effectively regeneration of the limonite happened. The cyclic defluoridation and subsequent regeneration with 0.2 M NaOH indicate the potential usefulness of the limonite for nearly 5 cycles without significant loss of sorption capacity. After 5 cycles, the limonite is withdrawn from the column, washed, air dried and weighed to find out the loss of the adsorbent. It is noticed to find there is no significant loss of the adsorbent.

4. CONCLUSIONS

The experimental data of present investigation reveal the effectiveness of the new adsorbent limonite for the removal of F^- ion in aqueous condition through fixed-bed column technique. From optimization it was found that the adsorption capacity of F^- ion through the fixed - bed column dependent on the pH of the solution, bed-height, inlet concentration and flow rate. Thomas and Yoon-Nelson model also justifies the effectiveness of limonite toward fluoride removal. Field trial of limonite also gives successful results and can be used through regeneration of limonite by 0.2 M NaOH solution. The Instrumental images justify about the adsorption of F^- ion on the surface of limonite. Proposed work is highly applicable in that area is populated with tribel's and suffered villagers are ill-literate and economically not so good. Thus, it is expectable, reasonable and eco-friendly adsorbent (limonite) and can be used for defluoridation.

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Table 1. Experimental results obtained through a fixed – bed column of limonite.

C_i (mg/l)	B_H (cm)	pH	F_r (ml/min)	T_B (min)	T_E (min)	Δt (min)	V_0 (ml)	Q_{total} (mg)	Q_{eq} (mg/g)
12	5.6	10.01	3.5	60	240	180	840	79 .73	11.2
12	5.6	5.02	3.5	90	300	210	1050	108.43	15.27
12	5.6	7.08	3.5	45	235	190	945	80.62	11.35
12	5.6	5.02	3.5	105	330	225	1207.5	149.62	21.07
12	5.6	5.02	5.5	45	285	240	1732.5	136.62	19.24
4.1	5.6	5.02	3.5	150	360	210	1312.5	208.62	29.38
12	5.6	5.02	3.5	75	390	315	1417.5	204.12	28.74
24.5	5.6	5.02	3.5	60	315	255	1365	130.77	18.41
12	3.4	5.02	3.5	45	285	240	1155	103.55	23.33
12	4.2	5.02	3.5	75	390	315	1417.5	206.38	33.28
12	5.6	5.02	3.5	120	405	285	1575	244.88	34.49

Table 2. Various parameters of the Thomas model under different condition using linear regression analysis for the adsorption of F^- ion onto limonite at 298K.

Experimental conditions					Thomas Parameters		
C_i (mg/l)	B_H (cm)	M (gm)	pH	F_r (ml/min)	K_{TH} x 10^{-4} (ml/min.mg)	q_M (mg/g)	r^2
12	5.6	7.1	10.01	3.5	10.2	85.4	0.9036
12	5.6	7.1	5.02	3.5	11.3	107.9	0.9609
12	5.6	7.1	7.08	3.5	7.2	91.1	0.7898
12	5.6	7.1	5.02	3.5	10.6	135.9	0.9519
12	5.6	7.1	5.02	5.5	8.4	164.0	0.9305
4.1	5.6	7.1	5.02	3.5	17.7	41.4	0.9572
12	5.6	7.1	5.02	3.5	6.9	121.8	0.9055
24.5	5.6	7.1	5.02	3.5	2.8	187.4	0.7645
12	3.4	4.4	5.02	3.5	7.0	125.8	0.8648
12	4.2	6.2	5.02	3.5	5.9	152.2	0.9203
12	5.6	7.1	5.02	3.5	7.8	143.3	0.9190

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Table 3. Various parameters of the Yoon-Nelson model under different condition using linear regression analysis for the adsorption of F$^-$ ion onto limonite at 298K.

Experimental conditions					Yoon-Nelson Parameters		
C_i (mg/l)	B_H (cm)	M(gm)	pH	F_r (ml/min)	$K_{YN} \times 10^{-2}$ (l/min)	τ (min)	r^2
12	5.6	7.1	10.01	3.5	4.06	116.98	0.9065
12	5.6	7.1	5.02	3.5	3.4	138.22	0.9560
12	5.6	7.1	7.08	3.5	3.3	107.40	0.9772
12	5.6	7.1	5.02	3.5	2.8	184.16	0.9314
12	5.6	7.1	5.02	5.5	3.0	138.58	0.9349
4.1	5.6	7.1	5.02	3.5	1.7	58.41	0.9500
12	5.6	7.1	5.02	3.5	1.8	195.34	0.8897
24.5	5.6	7.1	5.02	3.5	2.3	147.61	0.9318
12	3.4	4.4	5.02	3.5	2.7	140.15	0.9387
12	4.2	6.2	5.02	3.5	1.9	178.07	0.8087
12	5.6	7.1	5.02	3.5	1.5	223.20	0.9732

Table 4. A comparison of adsorption capacities of various adsorbent for fluoride removal in aqueous condition with limonite.

Adsorbents	B_H (cm)	F_r (ml/min)	C_i (mg/l)	pH	Temp .($°C$)	Q_{eq} (mg/g)	Reference
Limonite	5.6	3.5	12	5.02	25	28.74	Present method
Kanuma mud	10	5.0	20	6.9	30	1.55	(Tor et al., 2009)
Laterite	20	5.0	20	6.8	30	0.34	(Deng et al., 2011)
Granular red mud	10	5.0	20	4.7	25	0.77	(Singh et al., 2003)
Bio composite	9	-	5	4.8	25	1.70	(Fang et al., 2003)

Figure Caption

Figure 1. FTIR spectrum of Limonite at 298K.

Figure 2. (a) SEM image of raw limonite and (b) SEM image of treated limonite

Figure 3. X-ray diffraction of (a) untreated limonite (b) F- treated limonite

Figure 4 . Thomas model plot of ln (C_i/C_o -1) vs t (time) for defluoridation on to limonite at different (a) pH (b) flow rate (c) inlet conc. mg/l and (d) bed-height

Figure 5. Thomas model plot of ln (C_o/C_i-C_o) vs t (time) for defluoridation on to limonite at different (a) pH (b) flow rate (c) inlet conc. mg/l and (d) bed-height

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Fig.6. Breakthrough curve of fluoride removal through fixed-bed column of limonite (pH=5.05, F_r= 3.5 ml/min, B_H=5.6, C_i=10.5 mg/l and T=298K)
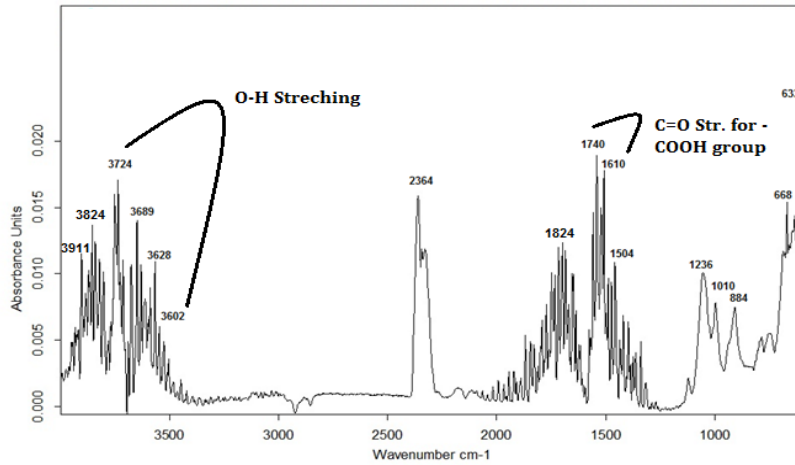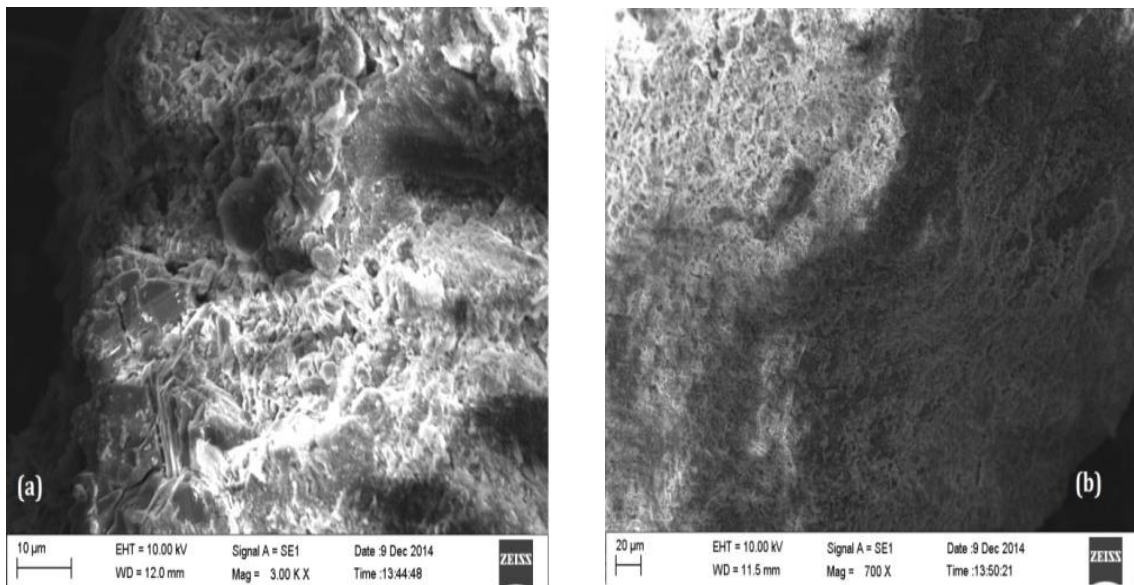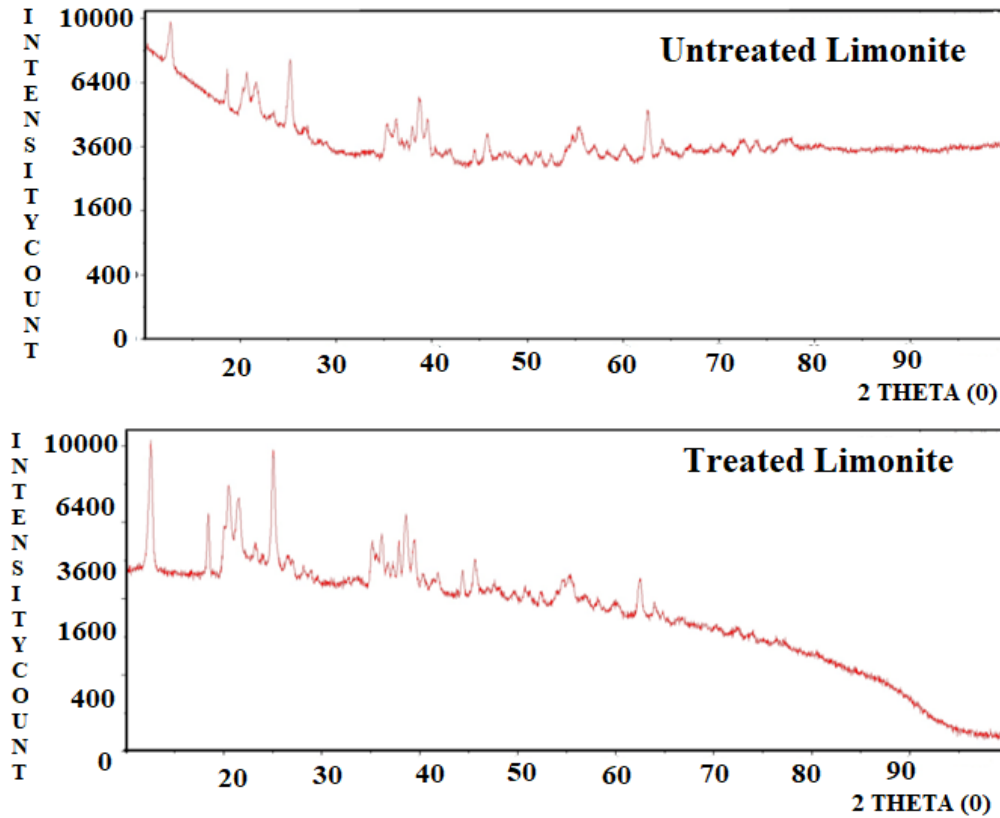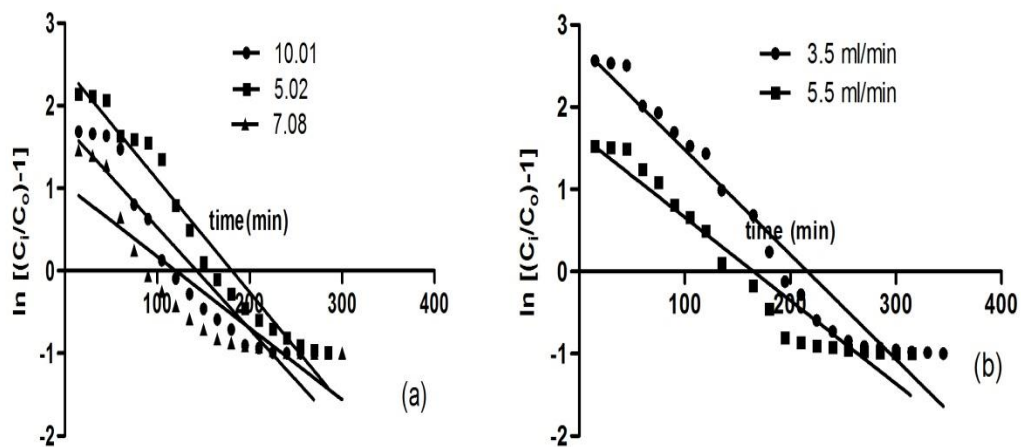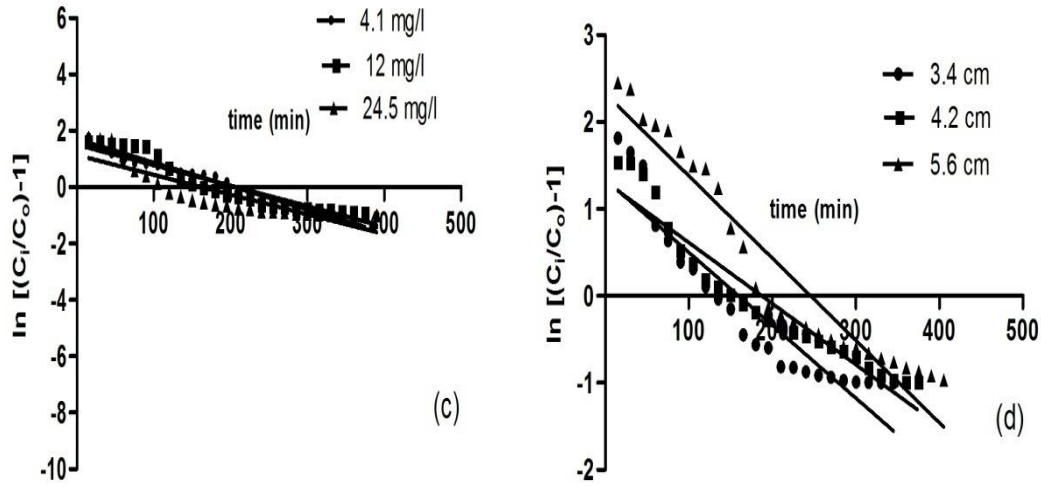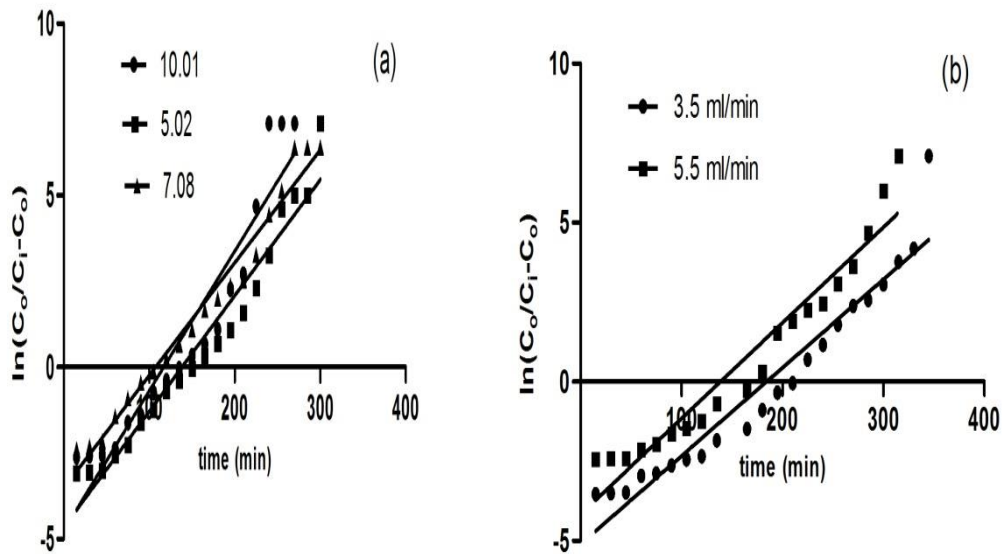

Figure1. FTIR spectrum of Limonite at 298K.

Figure 2. (a) SEM image of raw limonite and (b) SEM image of treated limonite

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Figure 3. X-ray diffraction of (a) untreated limonite (b) F- treated limonite

Figure 4 . Thomas model plot of ln (C_i/C_o -1) vs t (time) for defluoridation on to limonite at different (a) pH (b) flow rate (c) inlet conc. mg/l and (d) bed-height
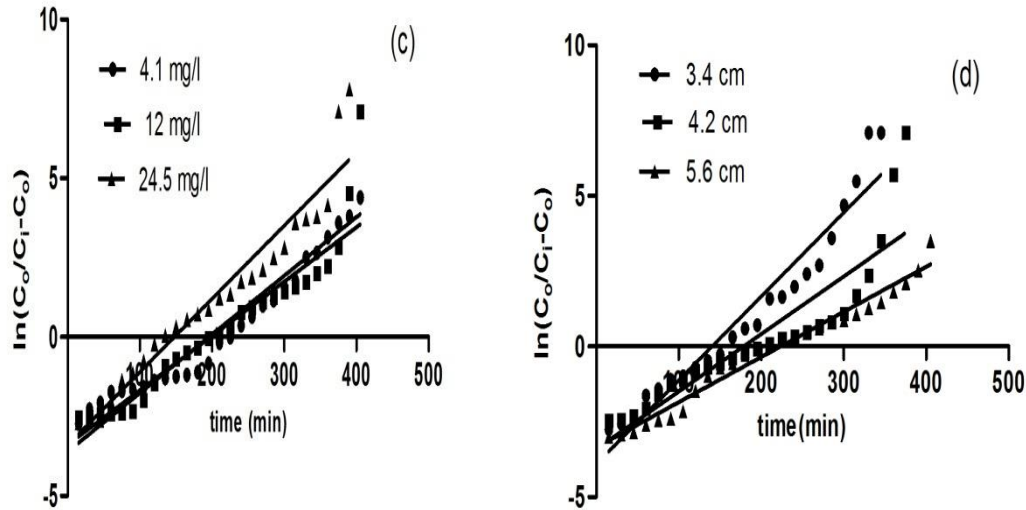
Figure 5. Thomas model plot of ln (C_o/C_i-C_o) vs t (time) for defluoridation on to limonite at different (a) pH (b) flow rate (c) inlet conc. mg/l and (d) bed-height
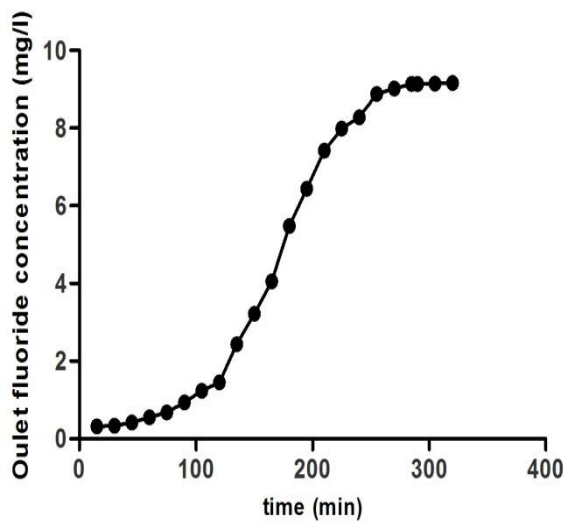

Figure 6. Breakthrough curve of fluoride removal through fixed-bed column of limonite (pH=5.05, F_r= 3.5 ml/min, B_H=5.6, C_i=10.5 mg/l and T=298K)