ASIAN JOURNAL OF PHARMACEUTICAL AND CLINICAL RESEARCH

INNOVARE ACADEMIC SCIENCES
Knowledge to Innovation

Vol 9, Suppl. 3, 2016

Online - 2455-3891
Print - 0974-2441

Research Article

TREATMENT OF FLUORIDE BEARING CONTAMINATED WATER USING SIMULTANEOUS ADSORPTION AND BIODEGRADATION IN A LABORATORY SCALE UP: FLOW BIO-COLUMN REACTOR BY *JAVA PLUM SEED*

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Received: 16 July 2016, Revised and Accepted: 17 September 2016

ABSTRACT

Objective: Here, we aimed for the treatment of fluoride bearing contaminated water using simultaneous adsorption and biodegradation in a bio-column reactor by using java plum seed.

Methods: We immobilized *Acinetobacter baumannii* bacteria on the java plum seed in the bio-column reactor. The water used contained a sample of fluoride with concentration of 20 mg/L. The bed depth service time design model and empty bed residence time were used to analyze the performance the bio-column. We examined and observed closely the effect of different operating parameters such as flow rate of bed depth and initial concentration on this simplified bio-column reactor design model. Desorption experiment was conducted to evaluate the possibilities of regeneration and to reutilize of media.

Results: We observed that the bio-column reactor is capable to reduce the concentration of the pollutants in the effluent water below their permissible limit. Reduction in DO along the bed height of the reactor was also observed, which supports the aerobic nature of the bacteria.

Conclusion: The experimental results were encouraging and indicate that java plum (*Syzygium cumini*) seed is a feasible option to use as a biosorbent to remove fluoride in the bio-column reactor.

Keywords: Bio-reactor, Simultaneous adsorption and biodegradation, Flow rate, *Acinetobacter baumannii* MTCC 11451, Physicochemical adsorption, Bed depth service time, Empty bed residence time.

 DOI: http://dx.doi.org/10.22159/ajpcr.2016.v9s3.14136

INTRODUCTION

Fluorine with atomic number 9 is the 13th most abundant element of the earth's crust. It constitutes about 0.03% of earth's crust mass. It occurs mainly in the form of chemical compounds such as sodium fluoride or hydrogen fluoride, which are present in minerals fluorspar, fluorapatite, topaz, and cryolite. Fluoride is frequently encountered in minerals and in geochemical deposits and is generally released into subsoil water sources by slow natural degradation of fluorine contained in rocks. Fluoride is beneficial to health if the concentration (CF) of the fluoride ion (F-) in drinking water is <1.5 mg/L (WHO 1994). A higher concentration causes serious health hazards. Even though extensive studies have been conducted, there seems to be no effective cure for diseases caused by fluoride. Therefore, it is advised to drink water having a fluoride concentration less than certain value. Hence, drinking water with C_F > 1.5 mg/L (1 mg/L in India) needs treatment (WHO 1994). The concentration of fluoride in industrial wastewater varies from 15 mg/l to 20 mg/l after coagulation process. Fluoride waste water industries are glass, electroplating, aluminum, steel, chemical industries, and oil refinery. The ever increasing demand for water has caused considerable attention to be focused toward recovery and reuse of industrial wastewater [2]. In the treated water, amount of element (Fluoride) minimized to come within permissible limits by BSI as shown in Table 1 [1].

Biological and adsorption processes are a common phenomenon in our natural ecosystem. In the environment, organic pollutants are generally degraded by simultaneous adsorption and biodegradation/bioaccumulation (SAB). Purification of waste water is based on SAB/bioaccumulation involved basically two types of mechanism. The first one common effect of microbial cell and adsorbent [3]. The availability of adsorbents increased the surfaces of liquid–solid phase. Microbial cells, pollutants, enzymes, and oxygen are adsorbed. The physicochemical reaction is also possible due to surface catalysis on the surface of adsorbent [4]. Microbial enzymes *Acinetobacter baumannii* immobilized to surface of adsorbent bring extracellular biodegradation/bioaccumulation on adsorbed pollutants (Fluoride). Bio-regeneration depends on adsorbent adsorption capacity. It is highly increased and the adsorbent adsorption system is continuing for a long time compared to simple adsorption process. As a result, when simultaneous adsorption and bioaccumulation/biodegradation occur, the removal efficiency of fluoride and waste water quality is considerably better [5]. The second mechanism is mentioned by many authors [6-8]; they reported opposite results as earlier was described, which explained that the steady decreased in the elimination of pollutants, after several adsorption cycles.

METHODS

Chemicals

All the chemicals used in this study were of analytical reagent grade and obtained from Himedia Laboratories Pvt. Ltd., Mumbai, India. All the solutions were prepared in milli-Q water (Q-H_2O, Millipore corp. with resistivity of 18.2 MΩ- cm). Fluoride solution of 2000 mg/L was prepared by dissolving 4.42 g of sodium fluoride (NaF) in 1 l of millipore water.

Strains and medium

A. baumannii MTCC 11451is used to complete this study. This bacterium was supplied by Microbial type culture collection, Chandigarh, India. The strains were revived according to the instructions given by MTCC (MTCC guidelines). Cultures were stored on agar plates till further use and were subcultured after every 15-30 days. All inoculations were performed in aseptic conditions in laminar air flow unit (Rescholar Equipment, India). The composition of growth media specific to above-mentioned strains in given strains is given in Table 3.

Table 1: Permissible Limit of various elements in drinking water by BSI

Parameter	Requirement desireable limit
Colour	5
Turbudity	10
pH	6.5-8.5
Total hardness	300
Calcium as Ca	75
Magnesium as Mg	30
Copper as Cu	0.05
Iron	0.3
Manganese	0.1
Chlorides	250
Sulphates	150
Nitrates	45
Flouride	0.6-1.2
Phenols	0.001
Mercury	0.001
Cadmium	0.01
Selenium	0.01
Arsenic	0.05
Cyanide	0.05
Lead	0.1
Zinc	5.0
Anionic detergents	0.2
Chromium as Cr^{+6}	0.05
Poly nuclear aromatic hydrocarbons	-
Mineral oil	0.01
Residual free chlorine	0.2
Pesticides	Absent
Radio active	-

Table 2: Salient feature of bio-column reactor

Description	Value
Diameter of reactor (cm)	8.0
Total height of reactor (cm)	100
Volume of reactor (liters)	5.03
Number of sampling point (cm)	5.0
Height of sampling point (cm)	100
Diameter of sampling point (cm)	1.25
Total weight of absorbent (g)	2420
Density of bed (g/mL)	0.7166
Actual volume of reactor (L)	1.623

Table 3: Composition of media for microorganisms

Micro-organisms	Media compositions (g/l)
A. baumannii (MTCC 11451)	Sodium chloride, NaCl (10) Tryptone (10) Yeast extract (5)

A. baumannii: Acinetobacter baumannii

Acclimatization

The acclimatization of all four strains in fluoride environment was performed as follows:

The culture was subcultured from agar plate in 100 ml of steam sterilized prescribed media (Table 3) in 250 ml round bottom flask. The media was supplemented with 20 mg/l of fluoride. The conical flask was agitated/incubated in an incubator shaker (Metrex MO-250, India) at room temperature (30°C) with an agitation speed of 120 rpm for 24 hrs. After 24 hrs, the synthetic medium in flask turned turbid indicating significant bacterial growth in the flasks.

Batch biodegradation experiments

Batch experiments were carried out in 250 ml round bottom flask with working volume of sample 100 ml at 30°C and 120 rpm in an incubator cum-orbital shaker (Metrex, MO-250, India). The flask was covered with both cotton plug and aluminum crimp cap. All the flasks containing growth medium were steam sterilized in autoclave at 121±1°C for 45 minutes at 15 psi pressure. All the batch experiments were conducted for the optimization of parameters such as contact time, initial concentration, pH, and dose of adsorbents. Microbial culture grows in 21 hrs and dead phase started after 71 hrs from the study of growth curve of microbial culture. A preliminary test showed that the equilibrium adsorption and biodegradation contact time was obtained after 86 hrs. At the end of this period, the solutions were centrifuged, and residual concentrations of fluoride at the equilibrium were determined.

Analytical method

For biodegradation studies, appropriate volumes of samples were withdrawn and centrifuged using Remi Lab centrifuge at 9000 rpm for 10 minutes. The supernatant was analyzed for fluoride by SPANDS method at 570 nm. The SPADNS (trisodium 2-parasulfophenylazo- 1,8-dihydroxy -3,6-napthalene disulfonate or 4,5 -dihydroxy-3- paraphenylazo-2,7 -naphthalenedisulfonic acid trisodium salt) method of determination of fluoride in drinking water is a simple and a rapid technique with high accuracy. It can be applied directly to most water samples without prior pre-treatment and is not very sensitive to the other ions which are usually found in potable water (Jacobson and Weinstein 1977). The reagent used in this method, i.e., SPADNS - ZrOCl2 is a red colored complex, which changes color when it reacts with fluoride. The change in concentration of SPADNS - ZrOCl2 causes a change in the transmitted light, which is detected by the colorimeter. The reaction between fluoride and SPADNS reagent is rapid, and hence, the samples can be tested within 10 minutes after adding them to the reagent. SPADNS reacts with zirconyl chloride to give a wine - red colored complex which further reacts with fluoride to give a new complex (Fig. 4.1). The bacterial growth was measured as optical density (absorbance) by UV-Vis spectrophotometer (HACH DR. 5000) at 600 nm after 86 hrs and was expressed in terms of biomass concentration.(mg dry weight/L). [9] Fig. 1 shows various reactions involved in the SPANDS method for estimation of fluoride.

Experimental setup

This experiment is carried in a bioreactor column of SS pipe with an objective to remove fluoride from industrial wastewater. The schematics diagram of the experimental setup is shown in Fig. 2. SS pipe column of various length (Z_1=20, Z_2=40, Z_3=60, Z_4=80 and Z_5=100 cm) and 8 cm internal diameter were used while the height of reactor is 100 cm and net volume 5.03 lit. It was equipped with a total of four equidistant ports (excluding inlet and outlet) of 1.25 cm diameter for collecting liquid sample along the height of reactor. The top and bottom portion were connected with the main column by two flange joints, supported on SS screen (mesh no: 16 BSS, width aperture: 1.00 mm). The reactor is filled with weighted amount of Java plum seeds (Bio adsorbent) having a particle size of 2-4 mm as a fixed-bed absorber. The bed was supported and closed by cotton pad and rubber, respectively, to prevent the flow of adsorbent together with the effluent. Then, the bed was rinsed with distilled water and left overnight to ensure a closely packed arrangement of particle without voids, channels, or cracks. Synthetic fluoride solution of known concentration (20 mg/l) was fed through a bed of Java plum seeds in up-flow mode to avoid channeling due to gravity and to ensure a uniform distribution of the effluent thought out the column. The experiments were carried out at room temperature. A peristaltic pump was used to control the flow rates (12, 23 and 40 ml/minutes) and maintained constant during each experiment. Periodic flow rate check carried out by collecting sample at the effluent for a given time and measured using measuring cylinder. A sample of effluent was collected at 1 h interval and analyzed by spectrophotometric (SPADNS) method for fluoride ion concentration using UV spectrophotometer (Hach, DR 5000). The volume of treated water was measured at 1 h interval, and the average flow rate was calculated based on these values because the flow rate becomes unstable as the bed depth is high due to a higher flow resistance. The desired breakthrough concentration (C_b) was determined at 7.5% of the initial concentrations (20 mg/l).

The empty bed residence time model (EBRT)

The EBRT is a design producer for the design of an absorber. Major design parameters are:

1. EBRT or empty bed contact time (EBCT)
2. Adsorbent exhaustion rate

These parameters can be correlated for a fixed bed column to determine the operating and capital costs of adsorption system [10,11]. Negrea *et al*. [12] and Guo *et al.* [13] have been reported that EBCT is a critical parameter in the adsorption processes specially if the adsorption mainly depends on the contact time between the adsorbent and adsorbate.

The EBRT is defined as the time required for the liquid to fill the empty column and it determines the residence time during which the solution treated is become constant with the adsorbent:

$$\text{EBRT(minute)} = \frac{\text{Bed volume}}{\text{Volumetric flow rate of the liquid}} \quad (1)$$

The adsorbent exhaustion rate is the mass of the adsorbent used per volume of liquid treated at the breakthrough:

$$\text{Adsorbent exhaustion rate (g/L)} = \frac{\text{Mass of adosrbent used}}{\text{Volume of liquid treated at breakthrough}} \quad (2)$$

The adsorbent exhaustion rates are plotted against the EBRT values, and a single operating line can be constructed to correlate these two variables. Thus, to select the optimum combination of adsorbent exhaustion rate and the liquid retention time, the operating line should first be established.

The equations 1 and 2 reveal that with the lower adsorbent exhaustion rate, volume treated at the breakthrough point become larger and hence longer EBRT and smaller amount of adsorbent are needed per unit volume of feed treated which implies a lower operating cost; however, larger column will have to used. On the other hand, the higher the adsorbent exhaustion rate, the smaller the EBRT, the higher the operating cost and smaller column are needed which will reduce the construction cost.

RESULTS AND DISCUSSION

Fixed-bed design models

The bed depth service time model (BDST), the model (EBRT) and the Thomas model are selected for this study which is used to predict, optimize, and describe the fixed-bed column operation, respectively.

BDST model

Fig. 3 shows the BDST plots (T_b versus D), which is constructed from the Table 4 for the influent fluoride concentration of 20 mg/l and flow rates of 12, 23 and 40 ml/minutes at 7.5% breakthrough time for 20, 40, 60 and 100 cm bed heights. The coefficients N_o and K for the three flow rates are calculated based of equation.

$$T_b = \frac{N_0 D}{C_0 V} - \frac{1}{KC_0 \ln\left(\frac{C_0}{C_b} - 1\right)}$$

Where,

T_b: Service at breakthrough point (h)

No: Bed capacity (mg cm^3)

D: Packed-bed column depth (cm)

v: Linear flow rate through the bed (cm h^{-1})

C_0: Influent fluoride concentration (mg/L)

C_b: Breakthrough fluoride concentration (mg/L)

K: Adsorption rate constant (L mg^{-1} h^{-1}).

The equation of a straight line on BDST curve can be expressed as y = ax+b;

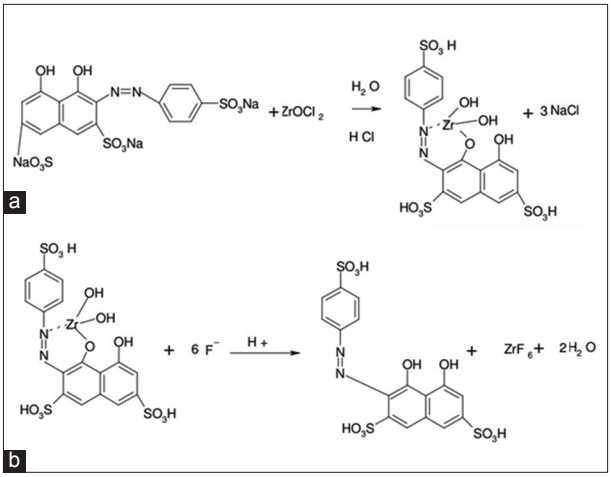


Fig. 1: (a) Formation of the SPADNS - ZrOCl2 complex. (b) Reaction of the complex with fluoride ions

Fig. 2: Experimental setup with biocolumn reactor

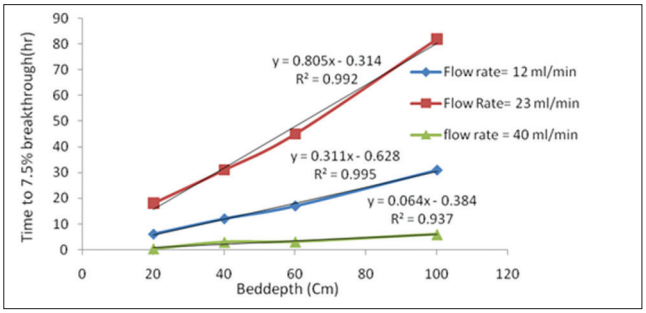


Fig. 3: Bed depth service time model plot at 7.5% breakthrough in a fixed-bed column at different flow rates

Where,

y: Service time

x: Bed depth

a: Slope

b: Ordinate intercept.

The numerical value of the slope (a) = N_0/C_0V and the intercept (b) = $-\frac{1}{KC_0 \ln\left(\frac{C_0}{C_b} - 1\right)}$, the adsorptive capacity of the system, N_0 and the rate constant, K, can be evaluated from the slope and intercept of a straight line plotted as the service time against the bed depth from experimental data, respectively. The minimum bed depth (D_{min}), which

represents the theoretical depth of adsorbent able to prevent the adsorbent concentration from exceeding C_b, is obtained when $T_b = 0$, according to the following equation:

$$D_{min} = \frac{v \ln\left(\frac{C_0}{C_b} - 1\right)}{KN_0}$$

The slope of the line presented by y=ax+b can be used to predict the performance of the bed if there is change in the initial solute concentration C_{01} to a new C_{02}. Hutchins [14] proposed that the new slope a_2 and new intercept b_2 can be estimated by equation.

$$a_2 = \frac{a_1 C_{01}}{C_{02}}$$

$$b_2 = \frac{b_1 C_{01}}{C_{02}} \frac{\ln\left(\frac{C_{02}}{C_b} - 1\right)}{\ln\left(\frac{C_{01}}{C_b} - 1\right)}$$

McKay *et al*. [15] stated that if design data are required for a change in volumetric flow rate of solute to the some adsorption system, the new slope with the intercept remaining unchanged can be written as:

$$a_2 = \frac{a_1 Q_1}{Q_2} = \frac{a_1 v_1}{v_2}$$

Effect of flow rate

The performance of a bio-column reactor is highly determined by its flow rate. Contact time is directly proportional to flow rate thus increasing in flow rate will increase in contact time which will eventually result in less concentration of pollutants in the output. However, we must consider the fact with increase in flow rate treatment capacity of the reactor decreases. In literature, a wide range of flow rate values has been used. In general, for laboratory purposes flow rate with a low value is used to treat industrial water by indigenous bacteria. In the said process, tap water (without inoculated media) is passed for 2-3 days to get a biolayer of bacteria. However, the longer flow rate is normally used for the treatment of industrial effluents, where bacteria inoculated media is used to develop the bio-layer on the adsorbent bed. In this study, we choose three flow rate (12, 23 and 40 ml/minutes) and study the effect of flow rate on the fluoride concentration in the treated water. Fig. 4 depicts data collected from the top of the reactor. This follows the trend observed [16]. From Fig. 4, it is evident that for all the flow rate values the fluoride concentration in the treated water increases initially and after ~4-5 hrs, it starts to decrease. After 30 hrs, the fluoride concentration in the treated water reduces to ~1.5 ppm, which is below the minimum concentration layer of fluoride in industrial wastewater. The maximum concentration of fluoride in the treated water is found after ~3 hr of operation, which reduces gradually with operation time. This indicates that the bacteria take some time to adjust in the continuous operation of the reactor. A similar observation has been reported recently during the fluoride removal in a bio-column reactor using SRB [17]. With the increase in flow rate value, the contact time of the water sample with the bio-layer increases. Due to this reason fluoride concentration in the treated water using a flow rate value of 18 hrs is less than those obtained by flow rate values of 12 hrs and 6 hrs. For lower flow rate values, the water sample gets lower contact time with adsorbent and at the initial stage of operation and it leaves the reactor before the bacteria of the bio-film cope up with the continuous operation. Hence, at the initial stage of operation the fluoride removal is less. With the increase in time, bacterial mass accommodates them in the continuous mode of operation, as a result of the observed effect of flow rate on the fluoride removal becomes negligible after ~30 hrs. Hence, flow rate of 23 ml/minutes is sufficient for the biotreatment process.

Effect of bed height

When we vary bed height keeping flow rate constant, we observe a change in contact time of the sample. Figs. 5-7 show the effect of changing bed height on the fluoride concentration in treated water at flow rate of 12, 23, and 40 ml/minutes. Figures were in good agreement with the trend as mentioned in literature [16]. From Figs. 5-7, it is clear that

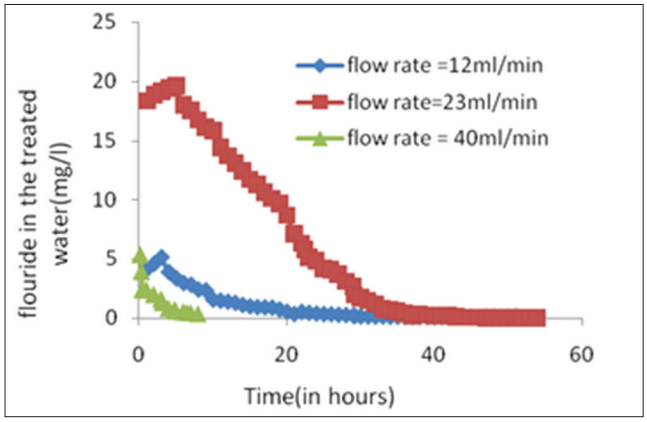


Fig. 4: Effect of flow rate on the fluoride removal in the biocolumn reactor (height=100 cm, initial fluoride concentration= 20 mg/L)

Table 4: Data of variable bed depth at a fixed flow rate in a fixed-bed biocolumn reactor for the removal of 20 mg/l of fluoride by java plum seeds (Bio adsorbent)

Q flow rate (ml/minute cm²)	Bed height (cm)	Bed volume (cm³)	Weight of adsorbent m (g)	EBRT (minute)	V_b (L)	T_b (hrs)	Adsorbent exhaustion rate (g/L)
12 ml/minutes 0.1886 (ml/minutes cm²)	20	1272.34	483.4	106.03	4.403	6	109.78878
	40	2544.68	969.1	212.01	9.023	12	107.403303
	60	3817.02	1451.9	318.0	12.104	17	119.952082
	100	6361.7	2419.9	530.14	21.342	31	113.386749
23 ml/minute 0.3615 (ml/minutes cm²)	20	1272.34	483.4	55.319	22.783	18	21.2175745
	40	2544.68	969.1	110.639	43.472	31	22.2925101
	60	3817.02	1451.9	165.957	63.696	45	22.79421
	100	6361.7	2419.9	276.595	74.131	82	32.6435634
40 ml/minute 0.6287 (ml/minute cm²)	20	1272.34	483.4	31.808	1.074	0.45	450.09311
	40	2544.68	969.1	63.617	7.574	3	127.950885
	60	3817.02	1451.9	152.68	12.084	3.16	120.150612
	100	6361.7	2419.9	159.04	19.276	6	125.539531

EBRT: Empty bed residence time

fluoride concentration decreases to ~1.5 ppm which is MCP of fluoride in wastewater after 7, 12, 6 and 10 hrs after starting reactor from point P_1, P_2 P_3 and P_5, respectively, when flow rate was 12 ml/minutes. All of the data were recorded in Tables 4 and 5. Initially, bacteria took some time to settle them in the continuous flow of operation of the reactor. From Figs. 4-6, we can observe that when we decreases bed height, decrease in contact time is noted which results into lower fluoride removal from waste water. After some time when bacteria are adjusted in the reactor, the effect of bed height tends to diminish.

Effect of EBCT

Fig. 8 shows the plot in which adsorption exhaustion rate is represented on Y-axis and X-axis is denoted by EBRT. This graph is plotted at various adsorbent bed heights (20, 40, 60, 100 cm). From Figure, it can be clearly depicted that for flow rate 40 ml/minutes the value of adsorbent exhaustion rate decrease gradually with increase in EBRT. In Table 4, we have recorded various data which validated that with an increase in bed depth we can observe an increase in V_b, T_b and EBRT of the bio-column reactor. It is evident that with an increase in EBRT at a constant flow rate, we will get a higher value of bed volume, which gives access to treat more solution but results in lower adsorbent exhaust rate.

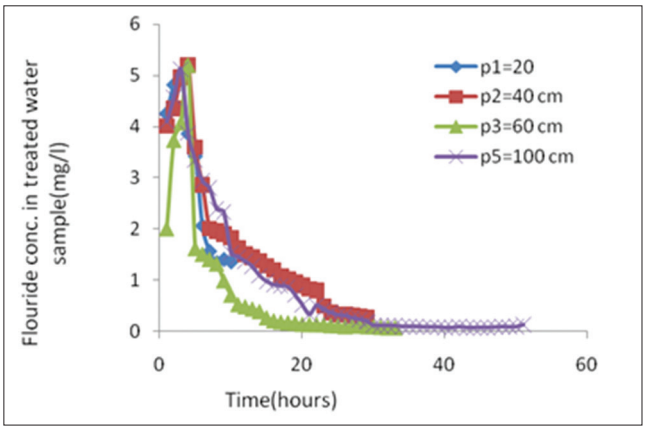


Fig. 5: Effect of bed height on fluoride removal in the bio-column reactor (Flow rate: 12 ml/minutes, initial fluoride concentration= 20 mg/L)

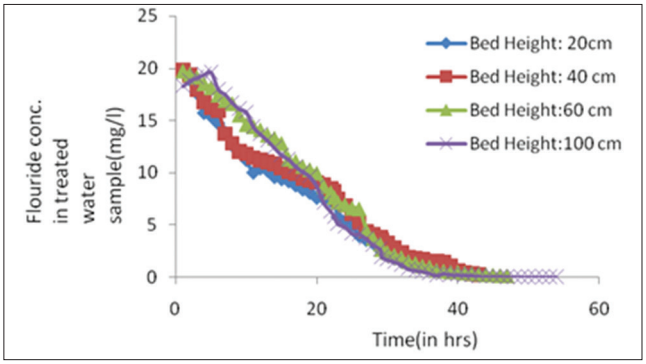


Fig. 6: Effect of bed height on fluoride removal in the bio-column reactor (Flow rate: 23 ml/minutes, initial fluoride concentration= 20 mg/L)

Variation of pH and dissolved oxygen (DO) of treated waste water with time

Another important point which is noted during the experiment is the slight change in the pH with the time as shown in Fig. 9 the graph plotted in Fig. 8 is for the waste water collected from top of bioreactor (height=100 cm) when flow rate of pollutant is 23 ml/minutes. From Fig. 8, it is evident

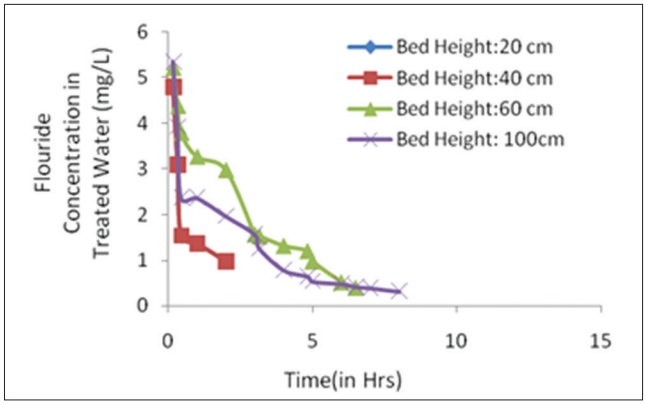


Fig. 7: Effect of bed height on fluoride removal in the bio-column reactor (flow rate: 40 ml/minute, initial fluoride concentration= 20 mg/L)

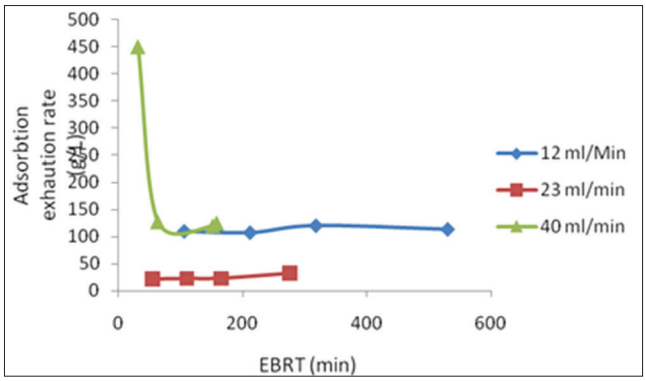


Fig. 8: Adsorbent exhaustion rate versus empty bed residence time model

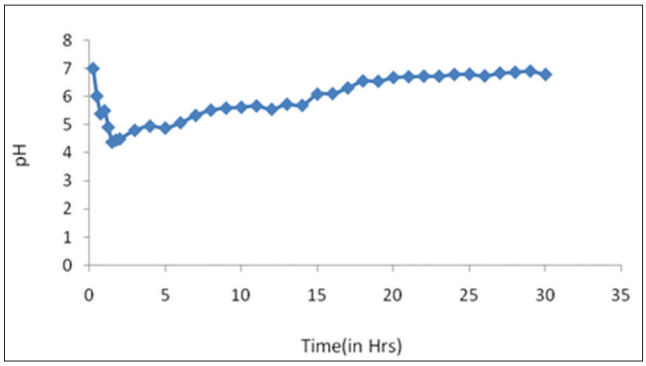


Fig. 9: Change of pH with time of operation in bio-column reactor

Table 5: Constant of BDST curve

Q flow rate (ml/minute cm^2)	V (cm/hr)	Slope (hr/cm)	Intercept (hr)	Depth D (cm)	N_0 (mg/L)	K (L mg^{-1} hr^{-1})	X (mg/g)	R^2
0.1886	11.316	0.311	−0.628	2.011	70.66	0.2	0.170635	0.995
0.3615	21.69	0.805	−0.314	0.744	182.9	0.4	0.865102	0.992
0.6287	37.722	0.064	−0.384	166.52	1.74	0.327	0.110087	0.937

BDST: Bed depth service time model

that initially the pH decreases slightly and starts to increase after 2 hrs of operation of the reactor, which signifies that the bacteria is adapted in the new environment. After around 25 hrs of operation, the pH reaches 7.5. A similar change in pH was reported recently on the arsenic removal using SRB in bio-column reactor [16,17]. The procedure and reason for such slight increase in pH is not well understood. However, some time back it has been reported that the reactions of molecular oxygen at the surface of the carbon results complex C_xO or C_xO_2. This adsorbed oxygen complex, in neutral solution, is sufficiently active to cause an oxidation of water as per the following reaction [18,19].

$$C_xO + H_2O = C_x + 2OH^-$$

The hydroxyl ion may combine with H_2O resulting in a net increase in the pH of the solution [19].

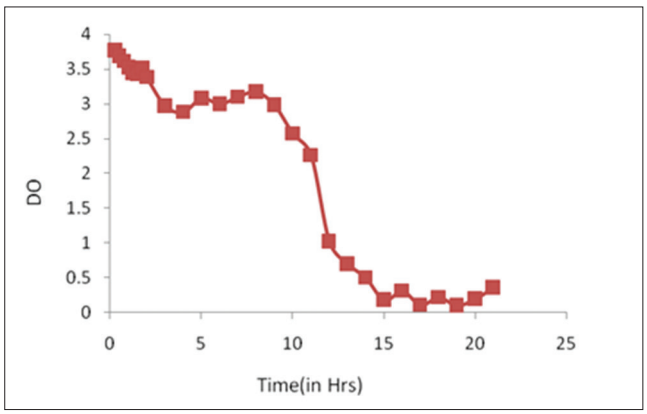


Fig. 10: Variation of dissolved oxygen with time

It is also observed that DO in treated wastewater is around ~3.9 mg/L in starting but after 15-16 hrs of operation it fell down to 0.19 mg/L as shown in Fig. 10. After that till the end of operation DO remains more or less constant. The probable reason for sudden decrease in DO could be settlement of bacteria. Once the bacteria is settled DO also reaches a constant value.

Characterization of java plum (bio-adsorbent)

Scanning electron micrograph (SEM)

The surface morphology of the Java plum was examined by SEM. Figs. 11a and b show the SEM of Java plum adsorbent used for adsorption studies. It was revealed from these figures that this adsorbent had irregular and porous surface. The difference in the adsorbent capacity of adsorbent was mainly due to difference in their surface porosity.

Energy dispersive X-ray spectroscopy (EDAX)

EDAX of Java plum before and after adsorption Fluoride ions are shown in Figs. 12 and 13 before and after adsorption of fluoride ions are shown

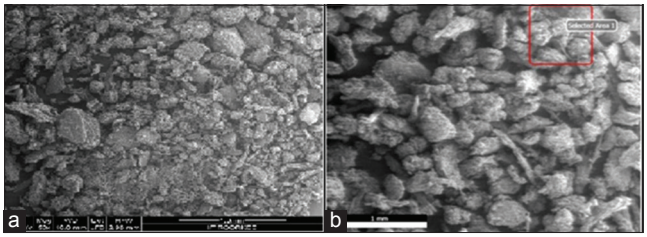
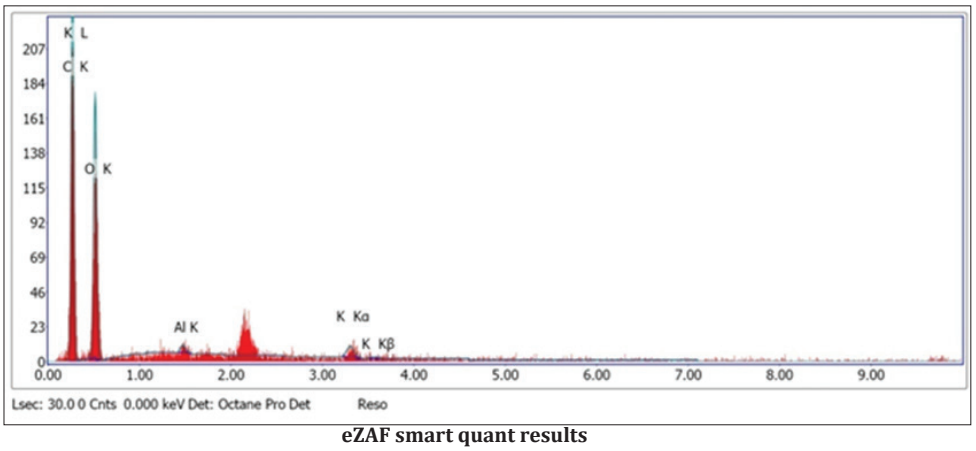


Fig. 11: Scanning electron micrograph micrograph of java plum seeds (a) before bio-adsorbtion/accumulation process (b) after bio-adsorption/accumulation process each shown at a magnification of ×50



eZAF smart quant results

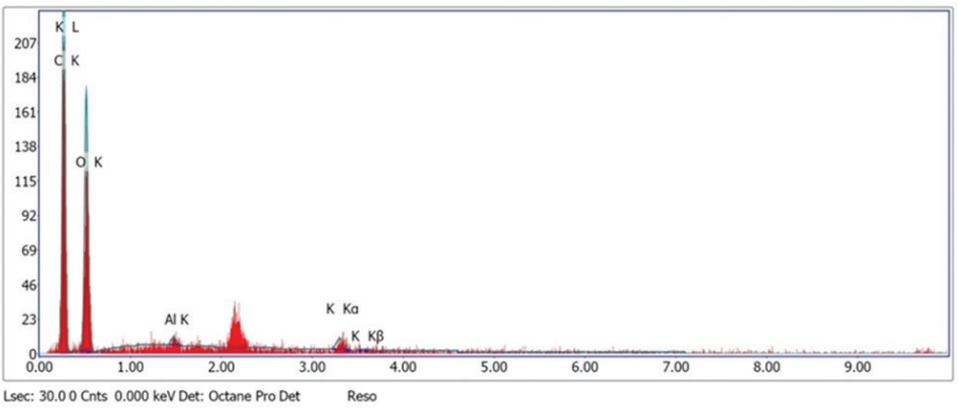
Element	Weight %	Atomic %	Net Int.	Error %
C K	48.97	56.83	65.9	7.16
O K	48.33	42.11	51.49	11.41
Al K	0.61	0.31	2.4	65.56
K K	2.09	0.74	4.99	31.42

Fig. 12: Energy dispersive X-ray spectroscopy image of java plum seeds before bio-adsorbtion/Accumulation process

Table 6: FTIR analysis for java plum adsorbent in tabular form

Wave number (cm^{-1})	3400-3500	2500-3300	1550-1650	1370-1390	970-1250
compound Groups	Amines N-H (1° amines), 2 bands	Carboxylic acids and derivatives O-H (very broad)	Amines NH_2 Scissoring (1° amines)	Alkanes CH_2 and CH_3 deformation	Alcohols and phenols C-O

FTIR: Fourier transform infrared



eZAF smart quant results

Element	Weight %	Atomic %	Net Int.	Error %
C K	49.72	57.83	61.39	8.3
O K	45.64	39.85	52.33	11.43
F K	0.37	0.27	0.37	93.79
Na K	1.53	0.93	3.62	46.14
Al K	0.55	0.29	2.36	65.93
Cl K	1.5	0.59	4.98	36
Ca K	0.68	0.24	1.45	66.52

Fig. 13: Energy dispersive X-ray spectroscopy image of java plum seeds after bio-adsorbtion/accumulation process

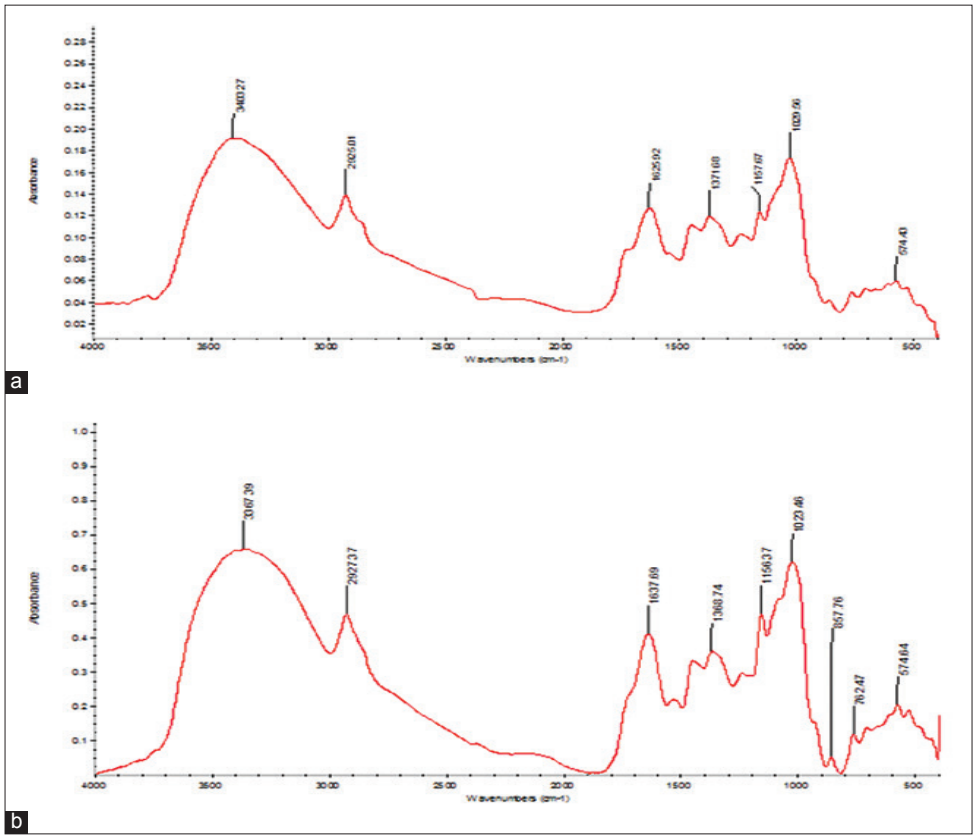


Fig. 14: (a) Fourier transform infrared analysis of java plum before adsorption of fluoride. (b)Fourier transform infrared analysis of java plum after adsorption of fluoride

Fig. 18a it is clear that various element such as carbon, oxygen and very small amount of calcium were present in virgin adsorbent but fluoride was not present there. When the EDAX of the adsorbent was carried out after the adsorption of fluorides ion, fluoride was present on the surface of adsorbent about 0.59 wt % which confirmed the adsorption of fluoride by this adsorbent.

Fourier transform infrared (FTIR)

Functional groups present in bio-adsorbents before and after adsorption of bio-adsorbents were determined using Fourier transform infrared spectroscopy (Thermo Nicolet, Magna 7600). The samples were prepared by pellet (pressed disk) method by mixing the same amount of KBr in each sample. The selected spectral range was from

4000 to 400 cm^{-1} Functional groups present on the surface of the peels are determined by the FTIR spectroscopy method. Figure shows FTIR spectra on various adsorbents, on the surface of adsorbent many functional groups are present.

The range of different wave number assign the functional groups present in the adsorbent. The amine bond stretching lie in the wave range of 3400-3500 cm^{-1}, similarly for the very broad O-H (2500-3300 cm^{-1}), NH_2 Scissoring stretching (1550-1650 cm^{-1}), alkanes (1370-1390 cm^{-1}), alcohols and phenols ion stretching (970-1250 cm^{-1}).

CONCLUSION

From the above discussions the following conclusions are drawn:

- The bio-column reactor is capable to reduce the concentration of the pollutants in the effluent water below their permissible limit.
- Bio-column reactor must be backwashed for effective continuous operation.
- At the initial stage, the flow rate and bed height have a significant influence on the removal of fluoride from the contaminated water. However, after some time of operation (approximately 24-25 hrs) such influence is negligible under the experimental conditions.
- Fluoride is removed after ~24 hrs of operation.
- DO reduce along the bed height of the reactor, which supports the aerobic nature of the bacteria.
- pH of the solution slightly decreases initially for the 1st hs and increases within small range (6.5-7.5).
- The BDST model was successfully applied to analyze the column performance and to evaluate the model parameter. The BDST equations of linear relationship between the bed depth and the service time were obtained with R^2=0.995, 0.992 and 0.937 for 12, 23 and 40 ml/minutes flow rate, respectively.
- The EBRT model which optimizes the EBRT and the sorbent utilization rate was successfully applied with optimum contact time greater than about 159.04, 276.59 and 530.14 minutes for 40, 23 and 12 ml/minutes flow rates, respectively, with the corresponding usage rate of 125.54, 32.64 and 113.39 g/L. The optimum dose for batch system was 3 g/100 mL.

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