Adsorptive and Bio Removal of Fluoride from Synthetic Waste Water by using Actinobacter Immobilized on the Surface of Sweet Lemon Peel

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Abstract: **This study carried out for the comparison between the adsorptive removal and Bio removal (simultaneous adsorption and biodegradation/bio-accumulation). Bio removal study was done on sweet lemon peel. Actinobacter is a water living micro-organism which survives in waste water. Micro-organism (Actinobacter) immobilized on the surface of sweet lemon peel. The size of micro-organism is greater than the pore size of adsorbent. The removal of fluoride occurred due to the accumulation of bacteria. Adsorption and bio-accumulation process execute simultaneously but mainly fluoride removed by the bioaccumulation. Active sites of the adsorbent are blocked due to immobilization of micro-organism on the surface of adsorbent. Different optimizing parameters are studied like adsorbent dose, pH, initial concentration and contact time for bio-removal process. Removal efficiency of fluoride increased from 59.59 % to 94.47 % in optimum conditions of contact time (87 h), pH 4.0 and dose 14 g/l for 20 mg/l initial concentration of fluoride. Simple adsorption process removal efficiency was 59.59 % at optimum conditions of contact time (60 min), pH 4.0 and dose 16 g/l. Adsorption isotherm parameters are well fitted for Freundlich whereas simple adsorption follow Langmuir isotherm model. Adsorption kinetic model well fitted for pseudo second order for both process but the rate constant is less than the adsorption process. Kinetic result revealed that bio removal is a slow process but increase the removal efficiency.**

Keywords: Fluoride; Actinobacter; Sweet lemon peel; Bio-removal;

1. INTRODUCTION

Fluoride is one of the essential mineral of drinking water, which is required for the dental and skeleton growth of the human body (1). It is useful as well as harmful, depending upon the consumption of fluoride concentration in drinking water. Consumption of drinking water with high concentration of fluoride causes to severe health problem like fluorosis, arthritis, retarded development of neuron, kidney problem, thyroid problem and many more (2). Countries like China,

India, Pakistan and Thailand are facing the problem of fluoride contamination in drinking water for a long time (3). Due to rapid growth of new industries, this problem has extend worldwide. Fluoride contaminated wastewater is released excessively by aluminum, zinc, fertilizer, semiconductor, glass, electroplating, steel, oil Refinery and pesticide industries (4). Various methods like precipitation, electrocoagulation, membrane separation, ion exchange and adsorption have been attempted for defluoridation (5). Among the methods mentioned, adsorption is widely accepted due to low cost, highly efficient, eco-friendly, easy handling and a wide variety of adsorbent availability. Many researchers have attempted a various type of adsorbents for defluoridation such as synthetic resin, red mud, fibrous adsorbent, bone char, fly ash, activated carbon and polymeric materials. The drawbacks of adsorbents mentioned above are low adsorbent capacity, less selectivity, cumbersome and time-consuming synthesis process. All these drawbacks create hindrance in practical application adsorbent in the removal of fluoride. 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). The ever increasing demand of water has caused considerable attention to be focused towards recovery and re-use of waste waters (6).

Purification of waste water based on simultaneous adsorption and biodegradation/ bioaccumulation basically two types mechanism involved. The first common effects are microbial cell and adsorbent (7). The availability of adsorbents increased the surfaces of liquid -solid phase. Microbial cells, pollutants, enzymes and oxygen are adsorbed. Physicochemical reaction is also possible due to surface catalysis on the surface of adsorbent. Microbial enzymes (Actinobacter) immobilized to surface of adsorbent, bring extra cellular 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. When simultaneous adsorption and bioaccumulation /biodegradation occurred, the removal efficiency of fluoride and waste water quality considerably enhanced (8). The second mechanism is mentioned by many authors (9), they reported an opposite results as earlier was described, which explained that the steady decreased in the elimination of pollutants, after several adsorption cycles.

This present study is carried out for the comparison between the adsorptive removal and Bio removal (simultaneous adsorption and biodegradation/bio-accumulation). Generally all the organic compounds are biodegradable in our environment. But in the case of fluoride, it is an ionic form of atom; it would be accumulate by the bacteria. Fluoride mainly removed by simultaneous adsorption and bio-accumulation. For optimization and model development, all the experiments were performed on a batch scale using synthetic wastewater. Bio removal study was done on sweet lemon peel. Actinobacter is a water living micro-organism which survives in waste water. Micro-organism (Actinobacter) immobilized on the surface of sweet lemon peel.

2. EXPERIMENTAL

2.1. Materials and Methods

Calcium Chloride, Agar, Tryptone, Yeast Extract, Millipore water, Sweet lemon peels adsorbents, Bacteria (Actinobacter) were used in this research work. All the chemicals used in this study were obtained from Himedia Laboratories Pvt. Ltd. Mumbai India. Stock solution containing 20 mg/l fluoride was prepared by diluting 1 ml of 2000 mg/l fluoride in 100 ml millipore water (Q-H2O, Millipore Corp. with resistivity of 18.2 MX-cm). Stock solution of 2000 mg/l is prepared by dissolving 0.442 mg of extra pure sodium fluoride in 100 ml of millipore water. Microbial culture obtained from MTCC centre Chandidgarh India.

2.2. Growth of Bacteria

Growth is orderly increase in quantity of the cellular constituents. It depends upon the ability of the cell to form new protoplasm from nutrients available in the environment. Growth of bacteria corresponds to increase in cell mass and ribosome's, synthesis of new cell wall, duplication of chromosomes and plasma membrane, septum formation and division of cell. Bacterial population growth studies require inoculation of viable cell into a sterile broth medium and inoculation of the culture under optimum pH, temperature and shaking speed. Under these condition s, the cell will reproduce rapidly and dynamic of the microbial growth can be charted by means of a population growth curve which is plotted between increase in number of cell and time.

2.3. Batch 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). All the batch experiments were conducted for the optimization of parameters like contact time, initial concentration, pH and dose of adsorbents. Microbial culture grows in 21 hour and dead phase started after 71 h from the study of growth curve of microbial culture. A preliminary test showed that the equilibrium adsorption and bio-degradation contact time was obtained after 86 hour. At the end of this period, the solutions were centrifuged and residual concentrations of fluoride at the equilibrium were determined.

3. RESULTS AND DISCUSSIONS

3.1 Optimization of pH value

Fig. 1 show the % removal of fluoride at different *pH* conditions. It affects the simultaneous adsorptive biodegradation of the pollutants. During SAB, optimum removal of pollutants occurred mostly in pH range of 6 to 7. SAB study is a slow process. In our case maximum fluoride removal (93.14%) occurred at pH of 4. From the study it has been observed that there was no significant difference in fluoride removal during pH range of 4 to 8. At pH 8, fluoride removal was 92.3%. So we had performed the next optimization parameters like time, initial concentration and dose of adsorbents at the neutral pH range.

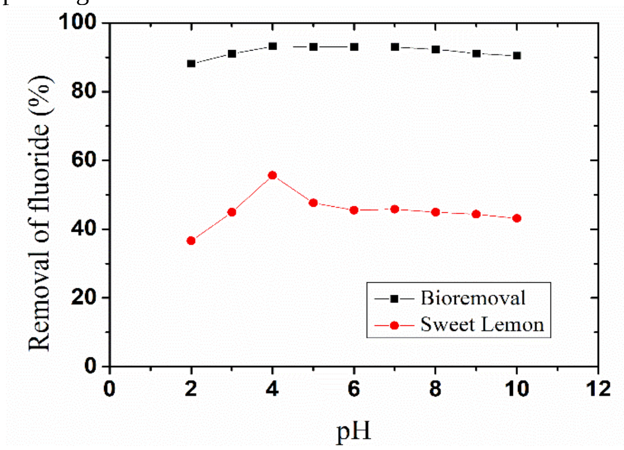

Fig.1: Effect of pH on the removal of fluoride.

3.2 Variation of fluoride removal with Adsorbent dose

Adsorbent dose effect was studied on fluoride between the ranges of 4-20 mg/l at 20 mg/l of fluoride. Fig. 2 show the effect of adsorbent dose on removal of fluoride. Micro-organism takes the time 21 h to grow, adsorbent had added to immobilize the microorganism at adsorbent surface for 12 h and then pollutant was be added. The experiments have carried out at 30˚C at 120 rpm for 70 h after the addition of pollutant. From Fig. 2, the % removal of fluoride increases linearly with dose of the adsorbent up to the 14 mg/l, after that % removal efficiency is almost same for all rest dose of the adsorbent. Fluoride removal efficiency was almost same after certain value of adsorbent dose so optimum adsorbent dose was.14.0mg/l.

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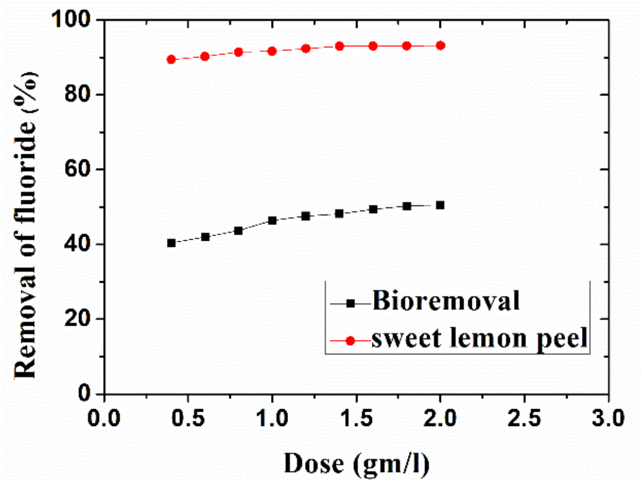

Fig. 2: Effect of adsorbent dose on the bio removal of fluoride

3.3 Effect of contact time on removal efficiency

The contact time is also the main optimization parameter for removal efficiency of fluoride. Fig. 3 shows the relation between the % removal of fluoride and contact time (h) for bio removal of fluoride. From Fig. 3 it can be seen that removal efficiency be increased with contact time, but after certain time removal efficiency remains nearly same. Optimum time for biological process is high (87 h) as compare to the value in case of adsorption for sweet lemon peel adsorbent. Table 1 shows the comparative value of optimization parameter between adsorptive and bio adsorptive process. From the comparison between these two processes, removal of fluoride strongly affected by types of adsorbent used. Contact time for SAB process was very high as compare to adsorption.

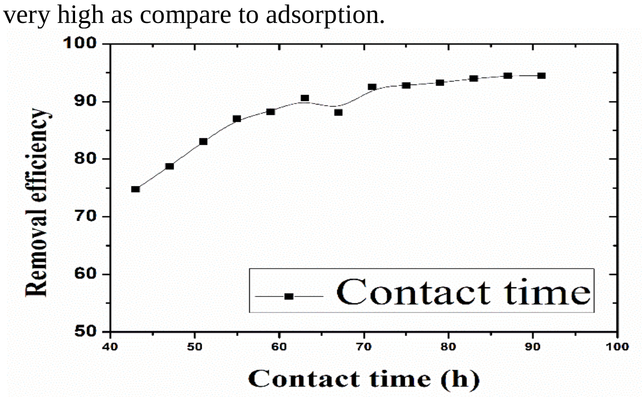

Fig. 3: Percentage removal of fluoride with contact time (h) by the bio removal process.

Table 1: Optimization parameters between adsorptive and bio adsorptive process.

Process	Adsorption	SAB
Initial Conc.(mg/l)	20	20
Contact Time	60 min	87 h
Optimum Dose(g/l)	16	14
Optimum pH	4	4
Adsorption Capacity qe(mg/g)	0.752	1.35
Removal (%)	59.55	94.47

3.4 Initial concentration

Percentage removal of fluoride is decreases as increasing the initial fluoride concentration in case of bio removal (bio accumulation) whereas adsorption and adsorption capacity is increases as increasing the concentration of fluoride until the equilibrium was reached for a definite time (87 h) as shown in Fig. 4.. It has been found from the comparison between adsorption and bio accumulation processes, adsorption capacity as well as percentage removal both are high. Percentage removal of fluoride at equilibrium was obtained 94.47 % at 20 ppm concentration after 87 h.

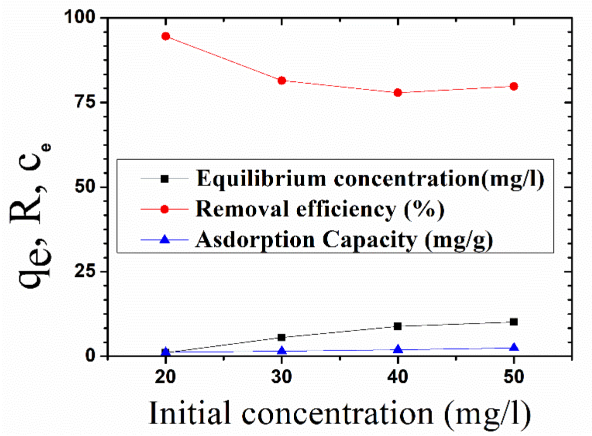

Fig. 4: variation of Residual concentration c_e (mg/l), adsorption capacity q_e (mg/g), and % removal *R* (%) with initial concentration (mg/l).

From the comparison between the adsorption and simultaneous adsorption and bioaccumulation, removal of fluoride increased at optimum pH, contact time, dose and same initial concentration. Adsorption capacity is also increased for simultaneous adsorption and bioaccumulation process. Contact time for SAB process is very high as compare to adsorption.

3.5 SAB Adsorption Kinetics

3.5.1 Pseudo-first order model:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \qquad (1)$$

Where q_t and q_e (mg/g) are adsorption after time t and at equilibrium correspondingly and k_1 (h^{-1}) is rate constant for the first order model.

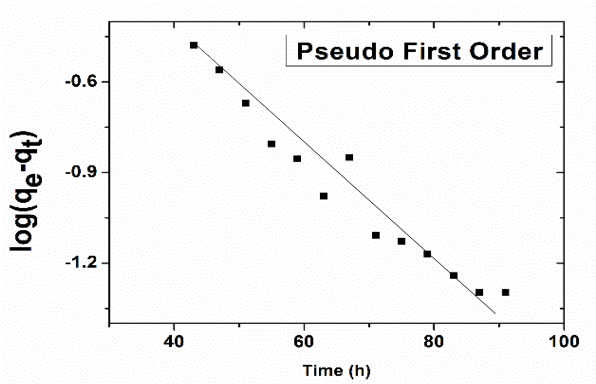

Fig-5: Pseudo First order kinetics plotted between log(q_e-q_t) versus time (h)

3.5.2 Pseudo-second-order model:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \qquad (2)$$

Where q_t, q_e (mg/g) are adsorption capacity after time t and at equilibrium correspondingly. K_2 (g mg^{-1} h^{-1}) is rate constant for second order models. From the comparison table adsorption capacity of bio removal process is greater than adsorptive.

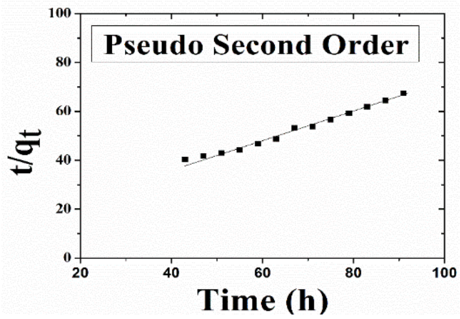

Fig-6: Pseudo second order kinetics plotted between log(q_e-q_t) versus time (h).

Table 2: Comparison between kinetic study of bio-removal and adsorption processes.

Adsorbent	Pseudo-first order			Pseudo-second order		
	K_1	q_{ecal} (mg/g)	R^2	K_2	q_{ecal}(mg/g)	R^2
SAB	0.042 (h^{-1})	8.133	0.955	0.0245 (h^{-1})	1.73	0.9879
SWL	0.086 (min-[1])	0.509	0.966	0.295 (min-[1])	0.795	0.998

Table 2 shows the kinetic study in bio-removal and adsorption process. In both processes that Pseudo-second-order kinetic model favors because it's greater reggration coefficient value. Calculated adsorption capacity q_{ecal} (1.73 mg/g) for bio removal adsorption is too close to experimental value (q_e =1.35) for second order kinetic. Similarly for Adsorptive process experimental value (0.752 mg/g) is near as to the calculated value (0.795 mg/g). So both processes follow the Pseudo-second-order kinetic model.

3.6 SAB adsorption isotherms

Since SAB and Adsorption are isothermal processes; adsorption isotherms are used to explain these processes. The fundamental importance of the equilibrium adsorption isotherms is to design of adsorption system [8]. Parameters of Bioaccumulation equilibrium and Adsorption are easily characterized by adsorption isotherms. These parameters are helpful in determining the adsorption capacity of adsorbent materials. In order to evaluate an adsorption isotherm, it is fundamental to develop an equation which precisely represents the results and which may be used for design purpose. Conventional adsorption models are used to describe the equilibrium established between adsorbed component on the adsorbent and unabsorbed component in solution (represented by adsorption isotherms). To analyze the equilibrium data for adsorption and bioaccumulation of fluoride by sweet lemon peel-immobilized *Actinobacter*, Langmuir, Freundlich,Temkin and linear adsorption models were used. Fig. 7 shows the equilibrium data for adsorption and bioaccumulation of fluoride by sweet lemon peel-immobilized *Actinobacter*, Langmuir, Freundlich,Temkin and linear adsorption models.

The Langmuir model is as given in equation

$$q_e = \frac{KaC_e}{1 + aCe} \quad (3)$$

Where K and a are isotherm constants. Langmuir constant (K) is fluoride adsorbed per unit weight of adsorbent, at equilibrium time. Langmuir constant (a), energy related to adsorption (i.e. affinity of the binding sites).

Langmuir equation is valid for monolayer sorption unto a surface with a finite number of identical sites. The basic assumption of Langmuir model is that sorption takes place at specific sites within the adsorbent. Separation factor is the essential characteristics of Langmuir isotherms can be described in equation below: $R_L = \frac{1}{1+aC_e}$ (4)

The separation factor (R) indicates the isotherm shape as follows: $R < 1$ unfavourable, $R > 1$ unfavourable, $R = 1$ linear, $0 < R < 1$ favourable and $R = 0$ irreversible.

The Freundlich isotherm model is given in equation:

$$q_e = K_f C^{1/n} \quad (5)$$

Where, $K_f$and n are Freundlich constants. $K_f$is roughly an indicator of the adsorption capacity and n is the adsorption intensity.

The Freundlich isotherm is used for heterogeneous surface energy systems [10].

Temkin Model Equation given as:

$$q_e = \frac{RT}{b_T} ln(A_T) + \frac{RT}{b_T} ln(C_e) \quad (6)$$

Where R is the gas Constant, T is temperature (K), q_e adsorption capacity (mg/g), c_e equilibrium concentration (mg/l) and A_T and b_T are the adsorption constants.

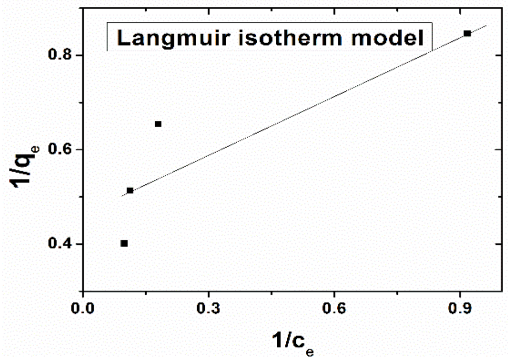

Fig. 7(a): Graph for langmuir isotherm model plotted between $1/q_e$ vs $1/c_e$ for bio removal

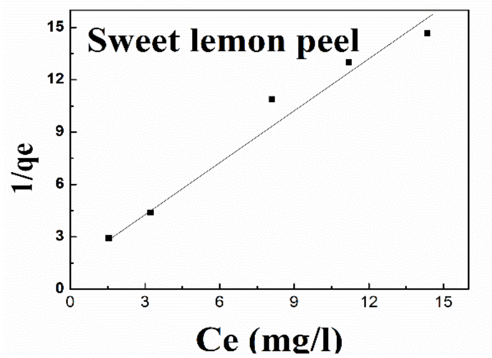

Fig. 7(b): Graph for langmuir isotherm model plotted between $1/q_e$ vs $1/c_e$ foradsorption.

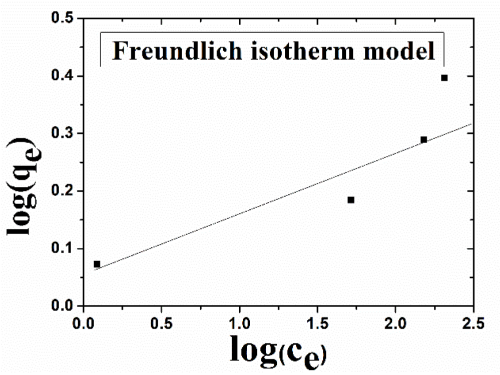

Fig. 7(c):Graph for Freundlich isotherm model plotted between $\log(q_e)$ vs $\log(c_e)$ for bio removal

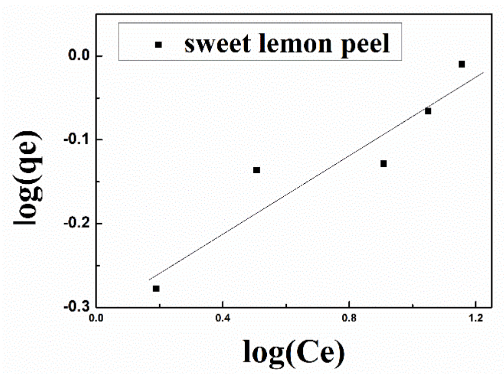

Fig. 7(d):Graph for Freundlich isotherm model plotted between $\log(q_e)$ vs $\log(c_e)$ for Adsorption

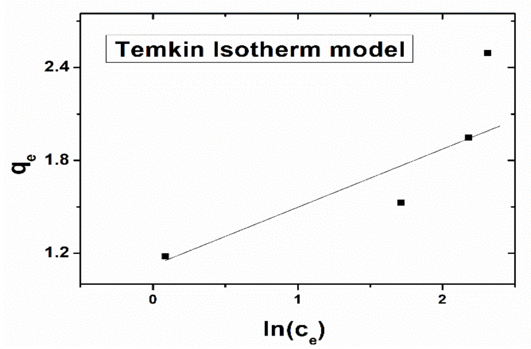

Fig. 7(e): Graph for Temkin isotherm model plotted between q_e vs $\ln(c_e)$ for bio removal.

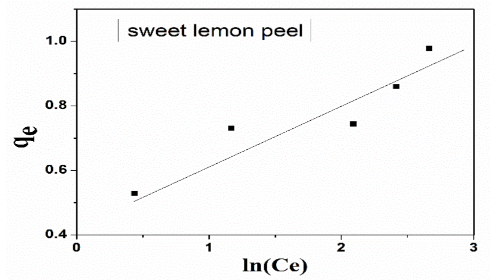

Fig. 7(f): Graph for Temkin isotherm model plotted between q_e vs. $\ln(c_e)$ for adsorption.

Table 3: Comparison between adsorptive and bio adsorptive isotherm model parameters.

Process	Adsorbent	Langmuir			Freundlich			Temkin		
		K(mg/g)	a(l/mg)	R^2	K_f(mg/g)	N	R^2	A_T	b_T	R^2
Adsorption	SLP	0.554	1.037	0.971	0.500	4.219	0.883	16.69	14987	0.872
SAB	SLP Actinobacter micro-organism	12.62	4.147	0.856	4.120	0.292	0.882	106.18	2519.1	0.789

From the study of isotherm models for both processes, it has been found that the values of isotherms parameters for all models have increased by using bioaccumulation processes as shown in Table 3.

4. CONCLUSIONS

From the comparative study results revealed that Removal efficiency of bio removal is very high (94.45 %) as compare to sweet lemon peel (59.59 %). From the adsorption kinetics results shows that bio removal process is very slow process. Its follow the pseudo second order kinetics. Rate constant for bio removal is less than the adsorptive process. Removal process occurred due the bio-accumulation fluoride by the bacteria because adsorbent active sites are covered by the micro-organism. Bio removal process is a very time consuming process as compare to the adsorptive process. Bio removal process follows the Freundlich isotherm model whereas adsorptive process is well suited for Langmuir isotherm model.

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