Asian Journal of Chemistry; Vol. 30, No. 2 (2018), 427-433

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2018.21082

Biosorption of Fluoride from Aqueous Solutions Using *Bacillus subtilis* Biomass

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Received: 7 October 2017; *Accepted*: 21 November 2017; *Published online*: 31 December 2017; AJC-18718

Biosorption of fluoride from aqueous solutions by using *Bacillus subtilis* was characterized. The effect of initial concentration of fluoride ion on the adsorption process was investigated. The experimental data for removal of fluoride showed the better fit with the Langmuir isotherm than with the Freundlich or Temkin isotherms. An initial fluoride concentration of 100 mg/L was found to be optimal for adsorption efficiency. Scanning electron microscopy and energy dispersive X-ray spectrometry (SEM-EDX) analysis proved that the fluoride was biosorbed onto the biomass. Fourier transform infrared (FTIR) spectra indicated the involvement of various functional groups in the adsorption process.

Keywords: Biosorption, Isotherms, Fluoride, *Bacillus*, SEM-EDX, FTIR.

INTRODUCTION

Water is an essential natural resource for sustaining environment and life. Groundwater is increasingly polluted for many reasons, including increased disposal of hazardous wastes, sewage, deep percolation from intensively cultivated fields, surface impoundments and liquid and solid waste from industries [1,2]. Throughout India, water contamination with hazardous materials such as arsenic, fluoride, nitrate, sulfate, pesticides and heavy metals is increasing [3,4].

Contamination of water with fluoride occurs by both natural processes and human activities. Several minerals contain fluoride, so leaching of fluoride by rainwater contaminates the water resources [5]. Further, fluoride compounds are used extensively as raw materials in fertilizers, aluminum industries and semiconductors and hence toxic wastes released into the water resources will increase contamination [6,7].

Fluoride can be either detrimental or beneficial to animals and humans depending on its concentration in drinking water and the total amount ingested [8]. According to the WHO, the permissible upper limit of fluoride in drinking water is 1.5 ppm for maintenance of healthy bones and teeth [9]. The WHO estimates that about 260 million people worldwide are consuming drinking water with fluoride above the permissible limit [10]. The presence of excessive fluoride can cause dental or skeletal fluorosis which is a chronic disease manifested by mottling of teeth in mild cases and softening of bones and neurological damage in severe cases [11,12]. Regions reporting more than 1.5 ppm of fluoride in water due to agricultural, natural and industrial activities include many Indian states such as Kerala, Andhra Pradesh, Tamilnadu, Uttar Pradesh, Jammu and Kashmir, Orissa, Gujarat, Punjab, Karnataka and Rajasthan [13].

Current methods for removal of fluoride from water are precipitation and adsorption [14]. Aluminum and calcium salts precipitate fluoride by forming CaF_2 and AlF_3 to reduce the concentration of fluoride from 10-20 to 2 ppm [15]. With the technique of adsorption, fluoride is adsorbed onto a fixed packed bed or resin or a membrane [16]. Many other techniques such as electro dialysis, ion exchange and Donnan dialysis, are available but they are not frequently applied because they are expensive, time-consuming and continuous regeneration and cleaning is required [15,17,18]. Hence, low-cost adsorbents need to be developed for use in the removal of fluoride from water resources.

Many natural and low-cost materials have been used as adsorbents to remove fluoride from industrial wastewater and drinking water such as clays [19], red mud [20,21], ground nut or cashew nut shell carbon [22], aligned carbon nanotubes [23], zirconium impregnated coconut shell carbon [24] and amorphous alumina supported on carbon nanotubes [25].

It is important to develop or find low-cost adsorbents with greater adsorption capacities to remove fluoride [13]. In this context, application of adsorbents obtained from microbial sources has become of interest in recent years. Different microorganisms other than bacteria have been used as effective fluoride adsorbents including *Spirogyra* [26], *Pleurotus ostreatus* [27], *Aspergillus penicilloides, Mucor racemosus* [28] and *Anabaena fertilissima* [29].

Gram-negative bacteria *Shewanella* sp. was employed to study fluorine adsorption. In this study, a Gram-positive bacterial biomass (*Bacillus subtilis*) has been used as an adsorbent for the removal of fluoride.

Bacillus subtilis is non-pathogenic and non-toxic bacteria having generally regarded as safe (GRAS) status. Many species of *Bacillus* have metal binding properties [30,31] with the potential to adsorb lead, cadmium, mercury and chromium [32,33]. Hence, the aim of the present study was to evaluate the adsorptive capacity of *B. subtilis* for fluoride removal from contaminated water resources.

EXPERIMENTAL

The stock culture of *Bacillus subtilis* was maintained on nutrient agar plates and subcultured every month. Biomass was prepared by inoculating the strain into nutrient broth [34] and incubating at 37 °C for 24 h by rotating at 150 rpm. The bacterial cells were harvested by means of centrifugation at 8000 rpm for 10 min and then washed twice with ultrapure water before being used in the fluoride adsorption experiments.

Stock solution of fluoride was prepared by dissolving 0.5 g of sodium fluoride in 50 mL of deionized water. The stock solution was then appropriately diluted to obtain the test solution of desired fluoride concentration.

Batch adsorption experiments were carried out in 250 mL Erlenmeyer flasks containing fluoride solution at concentrations ranging from 10 to 100 mg/L. Biomass concentration was maintained at 1 g/L throughout the studies. The pH of the solution was adjusted to pH 6.0 [19] using 1 N NaOH and 1 N HCl. The flasks were then agitated at 150 rpm in an orbital shaker at room temperature for 24 h. Appropriate blanks were maintained and analyzed simultaneously along with the experimental flasks. After the incubation, the sample solutions were centrifuged at 7000 rpm for 10 min and the supernatant and pellet were analyzed separately. The extent of biosorption was studied by varying fluoride concentration (10-100 mg/L).

The total concentration of the non-adsorbed fluoride ion in the supernatant was analyzed by a standard complexone colorimetric method. The equilibrium adsorption capacity of the *B. subtilis* biomass at the corresponding equilibrium conditions was calculated using the following mass balance equation [35].

$$q_e = \frac{(C_i - C_e)V}{m}$$

where q_e is the amount of the fluoride ion uptake by the biomass (mg/g) in the equilibrium; C_i is initial fluoride concentration in the solution (mg/L); C_e is the equilibrium fluoride concentration in solution (mg/L); V is volume of the medium (L); and m is the amount of the biomass used in the reaction mixture (g).

The ratio of adsorbed fluoride ion concentration at equilibrium to the initial concentration of fluoride ion, which is defined as the adsorption yield (R %), is calculated from the equation [36]:

$$R\ (\%) = \frac{C_i - C_e}{C_i} \times 100$$

where C_i is the initial fluoride ion concentration (mg/L) and C_e is the residual fluoride ion concentration in solution at equilibrium (mg/L).

Equilibrium relationships between adsorbent and adsorbate are described by various adsorption isotherms. In the present study, the most widely used models, Freundlich, Langmuir and Temkin sorption isotherms were applied to test the fit of data.

The linearized Langmuir isotherm model is represented by the equation [37]:

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e}$$

where q_e is the amount of fluoride ion adsorbed per gram of adsorbent (mg/g); C_e is the equilibrium concentration of the fluoride ions (mg/L); q_m is the maximum uptake capacity of the biomass (mg/g) and k_L is the Langmuir adsorption constant (L/mg). Based on the experimental data, the constants K_L and q_{max} are evaluated from the slope and the intercept of the linear plot of $1/q_e$ *versus* $1/C_e$

The affinity (R_L, hall isolation factor) of the adsorbent (biomass) to the adsorbate (fluoride ion) was calculated using the following equation [38]:

$$R_L = \frac{1}{1 + k_L C_i}$$

where C_i is the highest initial concentration of the adsorbate (mg/L).

The linearized Freundlich isotherm model is described by the following equation [39]:

$$q_e = K_F C_e^{1/n}$$

where K_F is a constant between biosorption capacities and n is an experimental parameter which can be evaluated from the linear plot of log q_e *versus* log C_e.

The Temkin isotherm model has been given by the following equation [40]:

$$q_e = \frac{RT}{b} \ln(AC_e)$$

The linearized form of the equation can be represented as:

$$q_e = B \ln A + B \ln C_e$$

where B = RT/b, b is the Temkin isotherm constant; A is Temkin isotherm equilibrium binding constant (L/g); R is universal gas constant (8.314 J/mol/K); T is the temperature at 803 K and B is constant related to the heat of sorption (J/mol). The constants A and B are obtained from the slope and intercept by plotting the quantity adsorbed (q_e) against ln C_e.

The morphology and elemental composition of *Bacillus subtilis* before and after biosorption were observed under scanning electron microscope equipped with energy dispersive X-ray spectrometry. A drop of biomass sample was dried on a clean silicon wafer and electron conductivity was created externally to the sample by sputtering with gold nanoparticles using a gold sputter coater ('Mini' sputter coater). Coated cells were applied with electron acceleration voltage of 5 KeV and viewed under high-resolution scanning electron microscope

(FEI Quanta FEG 200 HRSEM). The EDX analysis was performed with energy dispersive scattering system attached with scanning electron microscope at 20 KeV.

The IR spectra of *B. subtilis* biomass, before and after adsorption of fluoride ions, were recorded by FTIR spectroscopy (Thermo Nicolet Avatar 370 FTIR, Madison, US). FTIR characterization was performed to identify chemical functional groups present on the *B. subtilis* biomass that might be involved in fluoride ion adsorption. The samples were dried and mixed with KBr (1:200) and pressed to obtain transparent discs. The discs were then analyzed by using FTIR spectrophotometer. The IR spectra were recorded within the scanning range of 4000-400 cm^{-1} [10].

RESULTS AND DISCUSSION

In this study, the biomass of *B. subtilis* has been used for the removal of fluoride ions from the water resources. *B. subtilis* biomass is accepted as having GRAS status.

Removal of fluoride from water has been carried out with low-cost adsorbents from a range of plant sources and chemical compounds such as chalk powder, orange peel, activated carbon and concrete [36]. Alum sludge was used for the removal of fluoride ions from aqueous solutions [41]. *B. subtilis* removed various metal ions from contaminated water resources [42].

When the initial fluoride concentration varied from 10 to 100 mg/L with a constant biomass adsorbent dose of 1 g/L, the amount of adsorbed fluoride ions increased (Table-1). At low initial fluoride concentration, the number of available sites for adsorption is high [36]. The amount of fluoride ion adsorbed increased with increase in initial fluoride ion concentration. These findings also support other studies where increased initial fluoride concentration resulted in increased equilibrium adsorption capacity of the biomass [43]. Further, percentage removal of fluoride ions decreased from 64 to 37 % with the increase in initial fluoride concentration. Other studies also reported decrease in percentage removal of fluoride with increased initial fluoride ion concentration [10,19,44] (Table-2). The experimental conditions employed by other studies for the removal of fluoride are different from the present study. Also, the other studies have employed microbial biomass (algae, fungi, Gram-negative bacteria) but have different surface compositions.

One of the main parameters required for the design of an adsorption system is the adsorption capacity of the adsorbent. The distribution of fluoride ions between the solid and liquid phase is a measure of the position of equilibrium in the adsorption process [45]. Fitting the experimental results to the theoretical model enables the calculation of descriptive parameters. The relationship between the amount of fluoride remaining in the solution to the adsorbed fluoride onto the biomass is described by an isotherm [46].

In the present study, the adsorption potential of *B. subtilis* was evaluated by using three classical adsorption isotherm models: Langmuir, Freundlich and Temkin isotherm models at an initial fluoride concentration of 100 mg/L, pH 6.0, temperature 30 °C, shaking speed 150 rpm and contact time of 24 h respectively.

The Langmuir adsorption isotherm model, probably the most used and best known applied isotherm, is essential in assessing the saturated monolayer adsorption efficiency of the adsorbent [47]. The Freundlich adsorption isotherm models the adsorption on heterogeneous surfaces and for multilayer adsorption [13]. Temkin isotherm is an early model and its derivation is characterized by a uniform distribution of binding energies. It is excellent for predicting the conversely complex adsorption systems including the liquid phase adsorption [48].

The constants of Langmuir, Freundlich and Temkin isotherms (q_{max}, K_L, K_F, n, A, B) were evaluated from the corresponding linear plots (Figs. 1-3). The maximum adsorption capacity (q_{max}) for fluoride ions obtained by the Langmuir model was 2.283 mg/g of biomass. At the maximum initial fluoride concentration (C_i = 100 mg/L), the value of R_L was measured as 0.0011. The values of A = 1.323 L/g and B = 3.9388 J/mol indicate that the heat of sorption is a physical adsorption process. Based

TABLE-1
AMOUNT OF FLUORIDE ADSORBED (q_e; UPTAKE CAPACITY) AND PERCENTAGE VALUES FOR FLUORIDE OBTAINED FROM THE COLORIMETRIC METHOD AT DIFFERENT INITIAL CONCENTRATIONS OF FLUORIDE ION (30 °C, 150 rpm) WITH 1 g/L of BIOMASS

S. No.	Initial concentration of NaF (mg/L)	Initial concentration C_i (mg/L)	Final concentration C_e (mg/L)	Amount of F^- biosorbed q_e (mg/g)	Percentage removal of F^-
1	10	4.5	1.6	2.9	64.4
2	20	9.0	2.9	6.1	57.7
3	50	22.5	13.2	9.3	41.3
4	100	45.0	29.3	15.7	37.3

TABLE-2
COMPARATIVE STUDY OF FLUORIDE REMOVAL BY VARIOUS MICROORGANISMS

S. No.	Microorganism	Decrease (%)	Initial fluoride concentration (mg/L)	Experimental conditions	Ref.
1	*Pleurotus ostreatus*	52-20.8	5-25	30 °C, 100 rpm, 0.1 g of biomass, contact time of 480 min at pH 7	[27]
2	*Pleurotu seryngii*	92-67	5-25	30 °C, 100 rpm, 0.1 g of biomass, contact time of 240 min at pH 2	[10]
3	*Spirogyra*	64-20	5-25	30 °C, 100 rpm, 0.1 g of biomass, contact time of 480 min	[44]
4	*Trichoderma harzianum*	36-15	2-8	30 °C, 100 rpm, 0.4 g of biomass, contact time of 60 min at pH 7	[43]
5	*Spirogyra* sp-IO2	62-17.5	5-25	30 °C, 100 rpm, 0.1 g of biomass, contact time of 180 min at pH 7	[26]
6	*Bacillus subtilis*	64.4-37.3	10-100	30 °C, 100 rpm, 0.1 g of biomass, contact time of 24 h at pH 6	Present study

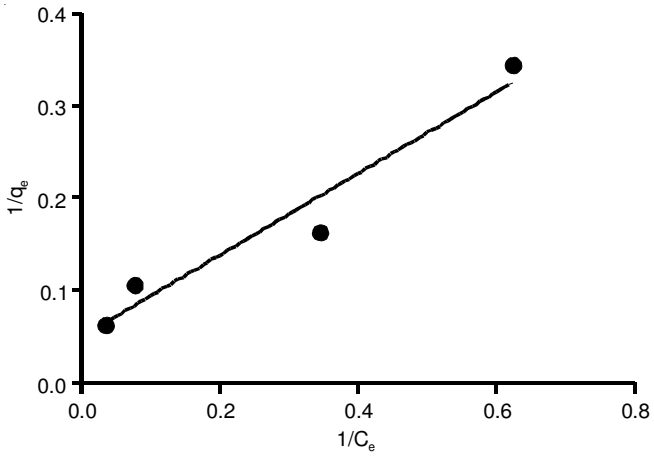


Fig. 1. Linearized Langmuir adsorption isotherm for biosorption of fluoride ions by *B. subtilis* at a biomass concentration of (1 g/L)

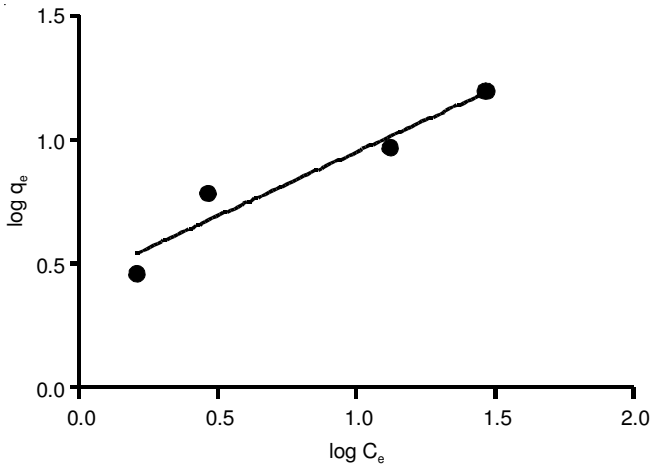


Fig. 2 Linearized Freundlich adsorption isotherm for biosorption of fluoride ions by *B. subtilis* at a biomass concentration of (1 g/L)

on the regression coefficient (R^2), the Langmuir model (R^2 = 0.9473) was found to be the better fit than the Freundlich (R^2 = 0.9284) and Temkin (R^2 = 0.9298) isotherm models. Similarly, various studies reported either Freundlich isotherm model [35,39] or Langmuir isotherm model [37,49] as the better fit to explain the biosorption behaviour of various adsorbents involved in the removal of fluoride ions.

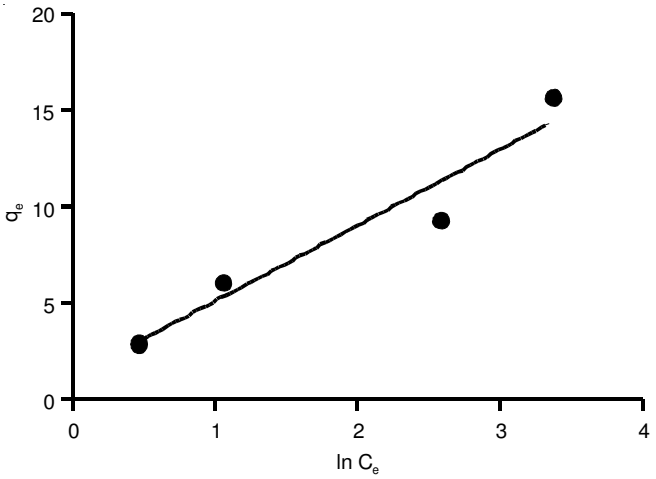
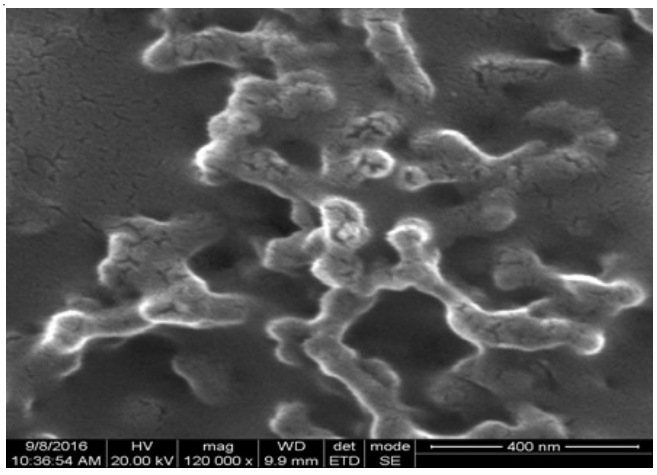
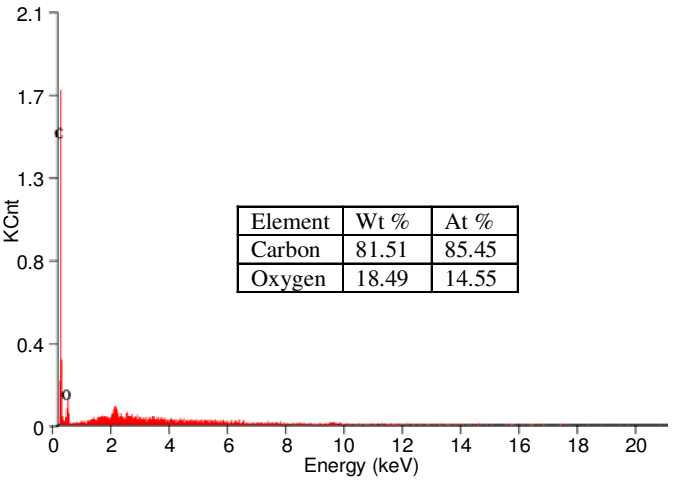


Fig. 3. Linearized Temkin adsorption isotherm for biosorption of fluoride ion by *B. subtilis* at a biomass concentration of (1g/L)

SEM micrographs and elemental composition studies (Figs. 4a-4d) of *B. subtilis* before and after fluoride adsorption are reported here. Compared to the control (unloaded biomass), the fluoride treated biomass appeared to have swollen and spherical cells. The bridges between cells seemed shorter, thicker and fewer in the fluoride treated biomass. The elemental composition of the biomass shows the presence of fluoride peak in the fluoride treated biomass along with the carbon and oxygen peaks that are present in the control biomass. The weight percent of the fluoride increased with the increase in initial fluoride concentration indicating that the fluoride is biosorbed onto the biomass of *B. subtilis*. Morphological changes were reported in the white rot fungus *Pleurotus eryngii* where the biomass appeared adhesive as a result of fluoride biosorption [10]. An uneven surface texture along with irregular surface was observed in control biomass of *Spirogyra* species [26]. However, there are no previous reports of such observations as a result of fluoride biosorption using bacterial biomass as a biosorbent.

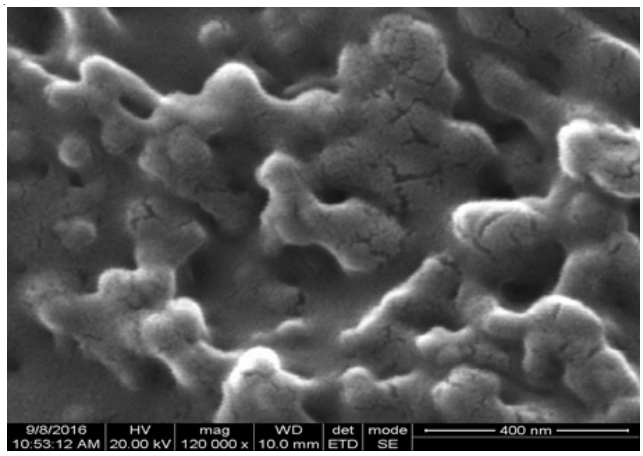
The functional groups that are present on the surface of bacterial cells play a vital role in adsorption. Comparison of FTIR spectrum of control and fluoride treated biomass helps in identifying the functional groups involved in adsorption by the characteristic peaks associated with them. The potential of adsorption is strongly influenced by the surface properties

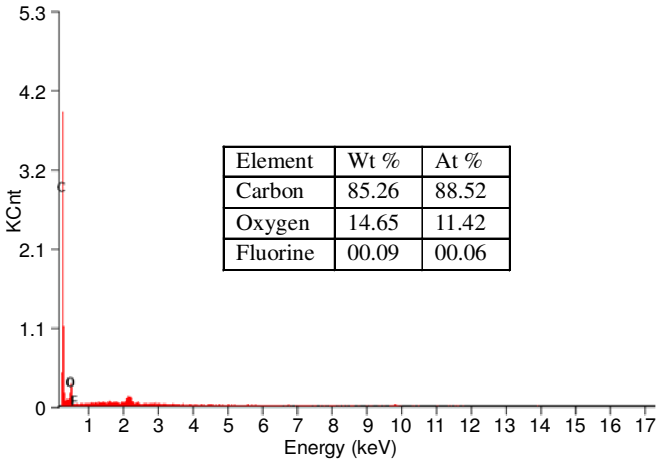




Element	Wt %	At %
Carbon	81.51	85.45
Oxygen	18.49	14.55

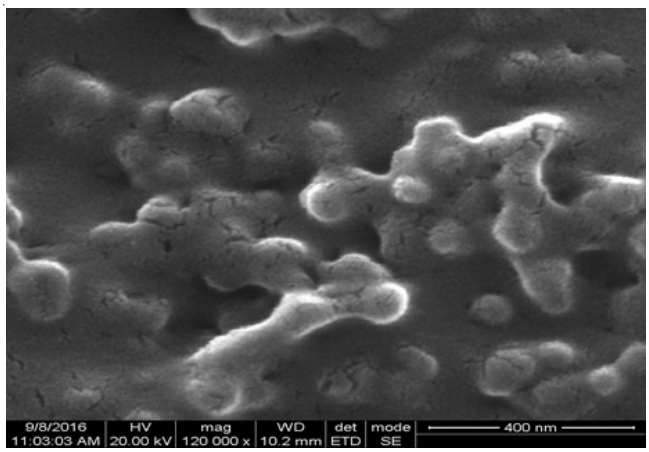
Fig. 4a. SEM image, EDX spectra and elemental composition of unloaded biomass at pH 6

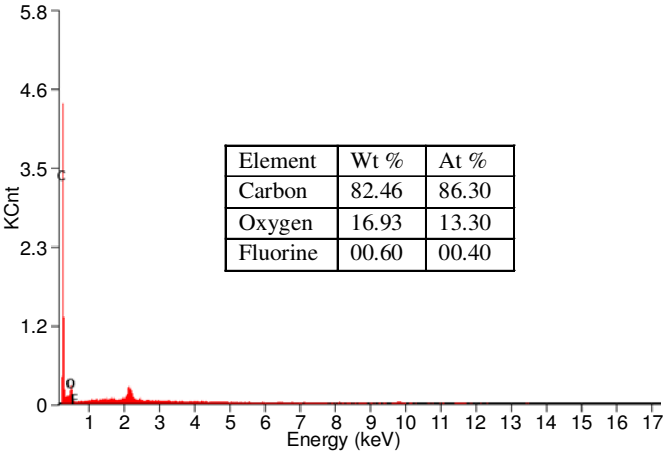




Element	Wt %	At %
Carbon	85.26	88.52
Oxygen	14.65	11.42
Fluorine	00.09	00.06

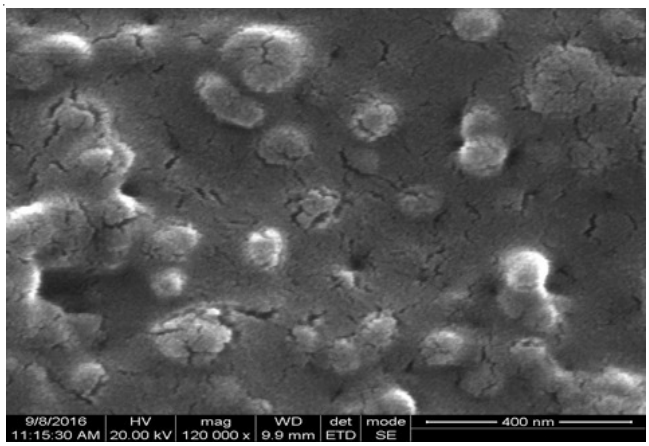
Fig. 4b. SEM image, EDX spectra and elemental composition of biomass loaded with 20 mg/L of NaF at pH 6

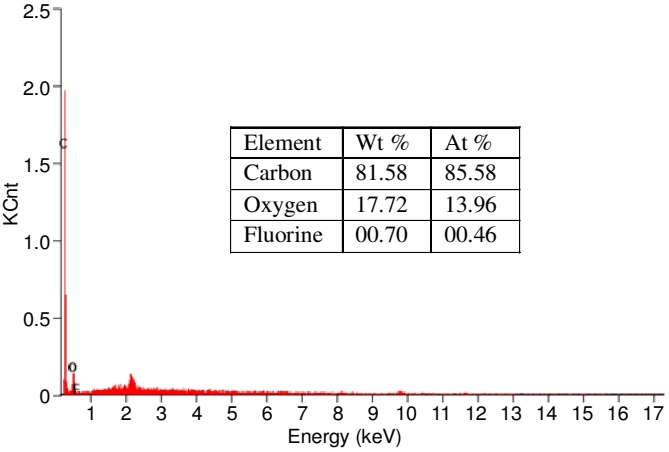




Element	Wt %	At %
Carbon	82.46	86.30
Oxygen	16.93	13.30
Fluorine	00.60	00.40

Fig. 4c. SEM image, EDX spectra and elemental composition of biomass loaded with 50 mg/L of NaF at pH 6





Element	Wt %	At %
Carbon	81.58	85.58
Oxygen	17.72	13.96
Fluorine	00.70	00.46

Fig. 4d. SEM image, EDX spectra and elemental composition of biomass loaded with 100 mg/L of NaF at pH 6

of the adsorbent such as type and number of functional groups. FTIR spectroscopy is a valuable technique due to its high sensitivity in detecting the changes in the functional groups.

The FTIR analysis of the bacterial (*B. subtilis*) biomass, before and after fluoride biosorption was carried out within the wavelength range of 4000-450 cm^{-1} (Figs. 5 and 6). The spectra were interpreted based on the information acquired from literature [10.26,50].

Compared with the control spectra, there are several changes in the spectral pattern of the treated biomass. The control biomass displayed a number of absorption peaks, reflecting the complex nature of the biomass. A peak at 3388.14 cm^{-1} region is due to the stretching of the N–H bond of amino groups and indicative of bonded hydroxyl group. A change in peak position (3401.57 cm^{-1}) in the spectrum of the fluoride loaded samples indicates the binding of fluoride with amino and/or hydroxyl groups.

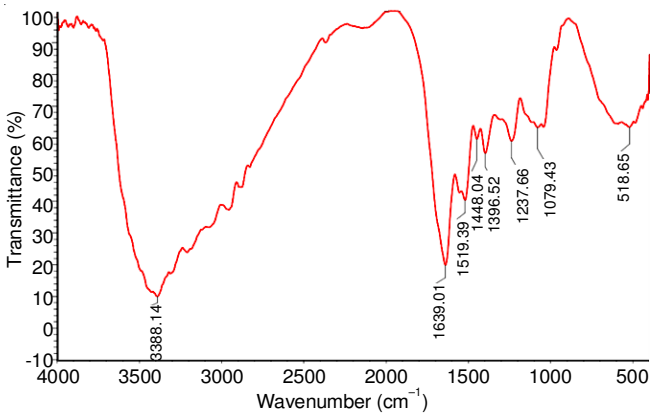


Fig. 5. FT-IR spectra of *B. subtilis* biomass at pH 6

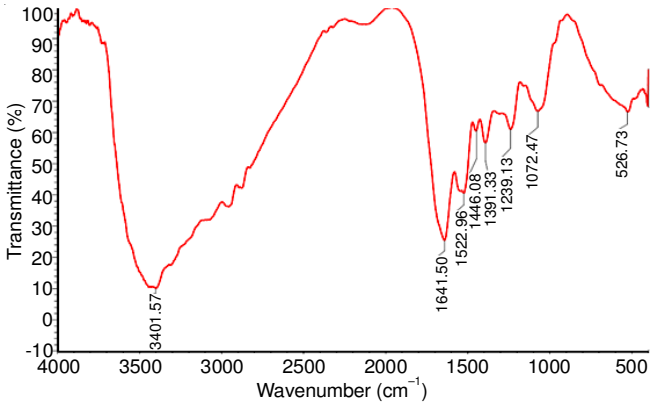


Fig. 6. FT-IR spectra of *B. subtilis* biomass biosorbed with fluoride ions at pH 6

The bonds C=O of amide I and NH or C=O combination of the amide II band were present at 1639 and 1519 cm^{-1}, respectively, in the control spectrum, indicating the presence of carboxyl groups. Interestingly, the peak at 1519 cm^{-1} showed considerable change when fluoride is present suggesting an interaction of fluoride ions with the carboxyl groups. The peaks at 1396 and 1237 cm^{-1} are attributable to the bending of O-H and stretching of C-O of carboxylate ion group (COO^-), respectively. The shift in these peaks to 1391 and 1239 cm^{-1}, respectively in the spectrum of fluoride treated biomass is indicative of their involvement in fluoride ion adsorption. The peak at 1079 cm^{-1} is due to the hydroxyl groups from the saccharides. A significant change in the peak at 1072 cm^{-1} in this region of treated biomass shows that hydroxyl groups of the saccharides are involved in fluoride adsorption. In the spectra, the peak at 518 cm^{-1} is indicative of C-O bonds of the saccharides. Similar changes in the FTIR spectrum due to binding of fluoride ions to the biomass of *Spirogyra* were reported [26]. The variations in the peak intensities at 3380, 1654, 1539, 1456, 1238 and 1078 cm^{-1} are in line with those reported by other researchers [10,13,35,37].

Conclusion

Hence, the study suggests that the biomass of *B. subtilis* can be used as an effective biosorbent to remove fluoride ions from water. Langmuir adsorption isotherm showed the better fit of the experimental data than the Freundlich or Temkin isotherms. SEM images and EDX spectra of the biomass proved that the fluoride ions are biosorbed. Based on FTIR spectrum analysis of biomass, we identified functional groups present on the surface that are involved in fluoride ion removal from water resources.

ACKNOWLEDGEMENTS

The authors thank SMS LABS, Chennai, India for their support in providing data for fluoride colorimetric method. The authors also acknowledge to Sophisticated Test and Instrumentation Center (SAIF), Kochi, India and IIT Madras for FTIR and SEM-EDX analysis, respectively. The authors are also grateful to Dr. Lindsay Brown, University of Queensland, Australia for suggesting the corrections in the manuscript for english.

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