

# Valorization of waste micro-algal biomass – collected from coke oven effluent treatment plant and evaluation of sorption potential for fluoride removal

Gargi Biswas, Philips Prince Pokkatt, Aratrika Ghosh, Biswajit Kamila, Kalyan Adhikari and Susmita Dutta

## ABSTRACT

Fluoride contamination in groundwater is now becoming a global concern. In the present study, removal of fluoride using dry biomass (DBM) of microalgal consortium of *Chlorococcum infusioenum* and *Leptolyngbya foveolaurum*, collected from coke-oven effluent treatment plant, Durgapur, India, has been investigated. The large volume of algal bloom in the industrial effluent has created a serious disposal issues and caused severe environmental concerns. Biosorption technique has been carried out to valorize the waste algae biomass into potential adsorbent. Response Surface Methodology (RSM) is used to model and optimize fluoride removal. Maximum fluoride removal (72%) is obtained at pH 4, 5 mg/L initial fluoride concentration, 0.5 g/L adsorbent dose (AD), and 25 °C temperature during one-factor-at-a-time (OFAT) analysis. The optimum condition of removal as specified by RSM is – initial concentration of fluoride: 30 mg/L, pH: 4.5, AD: 3.5 g/L and temperature: 30 °C. FESEM-EDX, FTIR and BET-isotherm studies are done to characterize raw and fluoride treated biomass. Lagergren-first order kinetic model and Freundlich isotherm model, are found to analyze best kinetic and equilibrium data, respectively. Adsorption capacity of DBM has been found to be 34.36 mg/g. The kinetics of fluoride removal has been well described by COMSOL Multiphysics.

**Key words** | biosorption, COMSOL Multiphysics, defluoridation, microalgae consortium, RSM, waste valorization

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## NOMENCLATURE

$A$	IC (mg/L)	$K_F$	Freundlich isotherm constant [(mg/g) (L/mg) <sup>1/n</sup> ]
$B$	pH	$K_L$	Langmuir isotherm constant (L/mg)
$b'$	Tempkin isotherm constant	$K_T$	Tempkin isotherm constant ( )
$B'$	Tempkin constant related heat of sorption (J/mol)	$K_{DB}$	Dubinin-Radushkevitch constant (g <sup>2</sup> /kJ <sup>2</sup> )
$C$	AD (g/L)	$k_1$	Adsorption rate constant as used in Lagergren first order adsorption rate equation (min <sup>-1</sup> )
$C_{exp,i}$	Experimental values of fluoride concentration (mg/L)	$k_2$	Adsorption rate constant as used in Pseudo second order adsorption rate equation (g mg <sup>-1</sup> min <sup>-1</sup> )
$C_{sim,i}$	Simulated values of fluoride concentration (mg/L)	$k_3$	Intra particle diffusion rate coefficient (g mg <sup>-1</sup> min <sup>-0.5</sup> )
$C_o$	Initial fluoride concentration (mg/L)	$N$	Total number of experiments
$C_e$	Residual liquid phase concentration of fluoride at equilibrium time (mg/L)	$n$	Number of factors
$c$	Concentration at any time (mg/L)	$n_c$	Centre point
$C''$	Moris-Weber constant.	$q_e$	Solid phase concentration of fluoride at equilibrium (mg/g)
$D$	Temperature (°C)		
$d$	Diffusivity of fluoride element within the solution (m <sup>2</sup> /s)		

$q_t$	Solid phase concentration of fluoride at time 't' (mg/g)
$q_{\max}$	Maximum adsorption capacity of the adsorbent (mg/g)
R1	Removal of fluoride (%)
R	Universal gas constant (8.31 J/mol/K)
T	Temperature (K)
$t$	Contact time (min)
$\bar{U}$	Stirring velocity (m/s)
$x_i, x_j$	Factors (Independent variables)
Y	Response of system
$\beta_0$	Constant coefficient
$\beta_i$	Linear coefficient
$\beta_{ii}$	Quadratic coefficient
$\beta_{ij}$	Interaction coefficient
$\epsilon'$	Dubinin-Radushkivich isotherm constant
$\epsilon$	Residual error
$\rho$	Density of contaminant solution (g/cc)

## INTRODUCTION

The presence of fluoride ions in potable water has unique effects on human health (Venkata Mohan *et al.* 2007). For a concentration ranging from 0.5 to 1.5 mg/L, fluoride is essential for the development and formation of dental enamel (Hiremath & Binnal 2013). However, prolonged exposure with higher fluoride concentration (>1.5 mg/L) causes enamel-decay and osteosclerosis (Biswas *et al.* 2016). It has been observed that lower calcium and higher bicarbonate alkalinity favor high fluoride concentration (hydro-geochemical origin) in groundwater (Biswas *et al.* 2017). In India, approximately sixty million people in nineteen states have been poisoned through consumption of well water contaminated with excessive fluoride in the range of 0.5–20 mg/L (Veeraputhiran & Alagumuthu 2011). Birbhum and Bankura districts of West Bengal, an eastern province of India, have been recorded to be fluoride contaminated districts with concentration in the range of 1.5–13 mg/L (WBPHEd 2006).

Several methods have been developed for the defluoridation of water such as membrane technology, ion exchange, chemical precipitation and adsorption (Biswas *et al.* 2017). Among different processes, adsorption is found as an effective approach and the application of biosorption for fluoride removal using bio-materials was studied by several researchers (Bhatnagar *et al.* 2002; Kumar *et al.* 2015). Biosorption, a physicochemical process, utilizes dry dead biomass to remove pollutants and deals with sorption of

the chemicals on the biological matrix (Bhatnagar *et al.* 2002). This approach has significant edge over the conventional processes like, no production of chemical sludge, and effectiveness in the treatment of wastewater (Kumar *et al.* 2015). Furthermore, since the non-living biomass does not require any nutrient/minerals for growth or metabolic system, the operation costs become minimized. Application of dead algal biomass is a potent bioremediation technology due to their availability, cheapness and effectiveness for wastewater treatment (Bhatnagar *et al.* 2002; Kumar *et al.* 2015). Algal blooms are the overgrowth of different types of algae in clean/waste water and have a negative impact on several industries. Treated wastewater usually contains high concentration of nutrients (e.g. phosphate, nitrate, etc) that may cause algal bloom on the surface of storage ponds' water. The negative impact is not limited up to the toxic effect of algae, but also includes their abundance which may provoke the operational problems and increase of BOD, pH and TSS (EPA 2017). Hence, the reuse or discharge of such water needs removal of algae. Such removed algal biomass, thus can be valorized as potential biosorbent. It is a newly devised substitute to the prevailing methods to remove pollutant from wastewater. The important functional groups of dead algal biomass are carboxyl, phosphate, hydroxyl, sulphate, etc. Ions can bind with biomass by processes like adsorption, ion exchange and chemisorptions on surface pores (Hiremath & Binnal 2013). Usually microalgal or cyanobacterial biomasses have been studied in a large scale for removal of various heavy metals (Sen *et al.* 2017). However, biosorption of anionic pollutants (eg: phosphate, nitrate, fluoride, etc.) is much lower than cationic contaminants such as heavy metals. Uptake of cationic pollutants is high when solution pH is higher than pH 7, however, better removal of anionic components can be obtained at low pH (<pH<sub>zpc</sub>) (He and Chen 2014). Application of dead micro algal biomass for defluoridation of wastewater in batch contactors has been reported in few literatures (Bhatnagar *et al.* 2002; Venkata Mohan *et al.* 2007; Hiremath & Binnal 2013). However, application of algal biomass for treatment of fluoride contaminated groundwater or industrial wastewater is very terse. Therefore, biosorption using inexpensive algal biomass for treatment of real wastewater is the thrust of the present work.

The present study investigates the removal of fluoride using dry biomass (DBM) of micro-algal consortium of *Chlorococcum infusionum* and *Leptolyngbya foveolaurum*, as a potential biosorbent. The consortium was collected from storage tank of coke-oven wastewater effluent treatment plant after biological treatment. A comprehensive

study starting from collection, preparation, characterization, kinetic and equilibrium studies of defluoridation from synthetic solution have been carried out. A large number of experiments are required to optimize multivariable systems to examine the best possible level, which is a time consuming process (Kushwaha & Dutta 2017). Such effort can be reduced by altering a number of variables at a time and the main objective of Response Surface Methodology (RSM) is to establish an experiential model using statistical equation to attain a suitable result at a minimum effort (Myers et al. 2005). Therefore, RSM has been used for optimization of defluoridation parameters. So far as known, no report on application of COMSOL Multiphysics to predict the kinetics of biosorption of pollutant using algal biomass has been published. In the present article, COMSOL Multiphysics has been employed to predict kinetics of biosorption of fluoride using DBM. Finally, defluoridation of groundwater, and Coal Bed Methane (CBM) produced water has been done using prepared biosorbent and reported in the article.

## MATERIALS AND METHODS

### Collection, preparation and characterization of biosorbent

The algal bloom was collected from water surface of storage tank of coke-oven effluent treatment plant, being used to hold the wastewater after biological treatment, Durgapur, India (Latitude: 23°50'92"N, Longitude: 87°32'10"E). After collection, fresh micro-algal lump was washed with water carefully to remove dirt and chemicals. The washed biomass was then spread on a tray and dried under sunlight for one week. The biomass was then kept in the hot air oven at 60 °C for 24 h. The dried biomass was then ground to obtain 90 µ sized powdered biomass as final biosorbent. The eppendorf tube containing aqueous suspension of live micro-algal sample was sent to BSI (Botanical Survey of India, Ministry of Environment & Forests, Kolkata, India) for identification and the algal biomass was identified as the consortium of *Chlorococcum infusionum* (green alga) and *Leptolyngbya foveolaurum* (cyanobacterium).

Bulk density, specific gravity, pH<sub>zpc</sub>, BET surface area and pore volume of native biosorbent were determined (Biswas et al. 2016). Specific sized particle (90 µ) was used in each case. BET (Brunauer Emmett Teller) of native DBM was determined by BET analyzer (Quantachrome, Poremaster 60, USA). pH<sub>zpc</sub> of native biosorbent was determined by following standard protocol (Biswas et al. 2016).

The test consortium was incubated in fluoride loaded solution with 10 mg/L initial concentration (IC) of fluoride for 12 h. The cyanobacterial biomass was then centrifuged to get separated from solution, and dried. FESEM (Field Emission Scanning Electron Microscopic image), EDX (Energy Dispersive X-ray analysis) and FTIR (Fourier Transform Infrared spectroscopy) studies were performed to characterize the native and fluoride loaded DBM. Field Emission Scanning Electron Microscope (ZEISS SIGMA VP, Japan) was used to take FESEM images of native and fluoride loaded DBM to obtain their topographical characteristics at specific magnification. EDX study (ZEISS SIGMA VP, Japan) was performed to obtain elemental composition of the samples. FTIR analysis of native and fluoride loaded DBM were done by FTIR spectrometer (Spectrum 100, Perkin-Elmer, USA) to determine the functional bends and stretches at specific frequencies. Wave number was kept in between 400–4,000 cm<sup>-1</sup>.

### Biosorption of fluoride

Sodium fluoride (Merck) (2.21 g) was added in 1 L of de-ionized water (DW) to make 1,000 mg/L of fluoride stock. It was diluted with requisite amount of distilled water to get desired fluoride concentration. All the experiments were done thrice. Several parameters such as adsorbent dose (AD) and pH were varied in the range of 0.04–0.5 g/L and 2–12, respectively. In the present study, pH of solution was adjusted by adding 4(N) hydrochloric acid or 1(N) sodium hydroxide. Definite amount of DBM (0.05 g in 100 mL) was contacted in 10 mg/L of fluoride solution varying initial pH (2–12). The samples were collected after 150 min of operation. The solution containing spent DBM was separated by centrifugation at 5,500 rpm for 5 min and clear solution from top section was experimented for remaining F<sup>-</sup> by Ion-meter (4 Star, B 36531, Thermo-scientific) using TISAB (total ionic strain adjustment buffer) III-Thermo Scientific. Similarly, effect of AD (0.04–0.5 g/L) was examined. The optimum pH as analyzed from previous set of experiments was maintained and solution with 10 mg/L fluoride concentration was used. The experimentation was conducted at ambient temperature of 25 °C with shaking speed of 150 rpm.

### Kinetic and equilibrium studies

A thorough kinetic study was done to observe the performance of DBM in removal of fluoride from simulated solution. Experiments were run for 150 min at 150 rpm and 25 °C. IC of fluoride was varied within 5–50 mg/L for both kinetics

and equilibrium studies and other parameters viz AD and pH were kept constant at optimum condition.

### Conductivity study of DBM

To assess the ionic characteristics of DBM samples (native and fluoride treated form), conductivity analysis was done with both native biomass and fluoride loaded biomass. Fluoride loaded forms were prepared by contacting 0.05 g of DBM with fluoride solution of 10 mg/L concentration for 120 min. The biomass was separated from solution by centrifugation and dried in air oven. Equal amount (0.05 g) of native, and fluoride loaded DBM samples were added in definite amount of DW individually and the variation of conductivity was taken upto 120 min using multi-parameter tester (PCSTestr 35, EUTECH instrument, Thermo Scientific). The conductivity of distilled water was measured as control for same time spam.

### Optimization of fluoride biosorption using RSM

In the present study, the statistical design for optimization of fluoride sorption was done using the RSM and the most popular Central Composite Design (CCD) was chosen to analyze the experimental data (Myers *et al.* 2005). RSM enumerates the relationship between responses and the fundamental independent input parameters (Myers *et al.* 2005).

$$Y = f(x_1, x_2, \dots, x_n) \quad (1)$$

Total experiments required to carry out, depends on the number of input factors. In case of four input parameters, total number of experiments can be obtained as follows:

$$N = 2^n + 2n + n_c = 2^4 + 2 \times 4 + 6 = 30 \quad (2)$$

The results of all sets were determined and an experiential 2<sup>nd</sup> order polynomial equation has been obtained to correlate the results with three independent factors for removal of fluoride by DBM.

$$Y = \beta_0 + \sum_{i=1}^n \beta_i x_i + \sum_{i=1}^n \beta_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \beta_{ij} x_i x_j + \varepsilon \quad (3)$$

Four parameters viz., IC, pH, AD and temperature were considered as input variables. They were varied as per the design prepared by Design Expert 8.0.6 software to obtain final optimum conditions. The basic system was prepared

by using analysis of variance (ANOVA), consists of input and output responses and optimized by estimating the statistical conditions. The min (−1) and max (+1) point of IC of fluoride, pH, AD and temperature were 10 and 90 mg/L, 2 and 12, 0.5 and 4.5 g/L, and 25 and 45 °C, respectively.

### Regeneration study and toxicity characteristics leaching procedure (TCLP) test

Regeneration of any adsorbent can be justified by adsorption-desorption experiment (Venkata Mohan *et al.* 2007; Kushwaha & Dutta 2017). Three sets of adsorption-desorption experiments were carried out in DW, 0.1 (N) hydrochloric acid, and 0.1 (N) sodium hydroxide solution individually, up to three round. After adsorption, the resultant fluoridated DBM was semi-dried at 60 °C for 5 min and reintroduced for desorption study. A single round consisted of 100 min run-time of adsorption and 50 min run-time of desorption, when IC, AD, and temperature were kept at optimum values, as obtained from RSM.

Fluoride loaded DBM having solid phase fluoride concentration was subjected to TCLP test (EPA 1992). TCLP test was used to assess the risk of fluoride leaching to the environment (EPA 1992). An extraction solvent was prepared following the standard protocol of EPA (1992). The solvent was mixed with solid in the solvent- solid ratio of 10 L/Kg (EPA 2017) and then agitated at 150 rpm for 18 h at 30 °C. Thereafter, the mixture was filtered and tested for remaining F<sup>−</sup> in the clear solution. The test was carried out at pH 3, 5, 7 and 11.

### Removal of excess fluoride from groundwater and CBM produced water

Field survey by West Bengal Public Health Engineering Department (WBPHEd), has shown that groundwater in some villages at Bankura dist. of West Bengal, India is effected with excess fluoride (WBPHEd 2006). Hence, groundwater samples were collected from several wells and tubewells of that affected area. Therefore, collected samples were characterized using standard protocol (Clesceri *et al.* 2012).

CBM recovery is associated with production of huge volume of underground water (Mendhe *et al.* 2017). The coal seams are depressurized by pumping out water for regular gas production (Liu *et al.* 2013). To maintain produced water quality, it is essential to manage through some combinations of treatments (Mendhe *et al.* 2017). CBM produced water is mostly characterized with high TDS (total dissolved

solids) and salinity (Mendhe *et al.* 2017). It consists of mainly sodium (Na), bicarbonate ( $\text{HCO}_3$ ), chloride (Cl), iron (Fe), calcium (Ca), fluoride (F) and other trace elements. Before discharging the CBM produced water, several treatments are done based on the quality of the water. This work is focused on removal of excess fluoride using DBM from CBM produced water, collected from Raniganj Coalfield, area of West Bengal, India. Similar to groundwater, CBM produces water was characterized (Clesceri *et al.* 2012).

After characterization, groundwater, and CBM produced water were treated with 0.05 g of DBM in 100 mL for 120 min. Removal studies were performed at pH 4, the optimum values as analyzed by RSM, and at their native pH (7.8 and 8.8). After 120 min, the spent DBM was separated by centrifugation and supernatant was analyzed for residual fluoride concentration.

## THEORETICAL ANALYSIS

### CFD modeling

COMSOL (4.3.a) Multiphysics was chosen to develop and solve a model for the above discussed batch mode adsorption process using equations of Lagrange's-first order model of adsorption (Augier *et al.* 2008). In order to solve the above equations, a suitable model of the reactor system was established with fine mesh size, mesh configuration and boundary conditions as maintained during experimentation. The model is mesh independent. Based on the real geometry of the reactor system, the model was developed. To simplify the model few assumptions were made, such as:

1. The adsorbent used in the experimentation was considered of equal size with uniform porosity.
2. An adsorbent bed is considered settled at the bottom and the system was stationary throughout the process.
3. The volume of the adsorbent bed was considered free of fluoride.
4. Mass transfer resistance in the system was very small and considered as negligible.
5. Biosorption resistance was encountered.
6. The whole system was isothermal as well as isobaric.

## Results and discussions

### Characterization of DBM

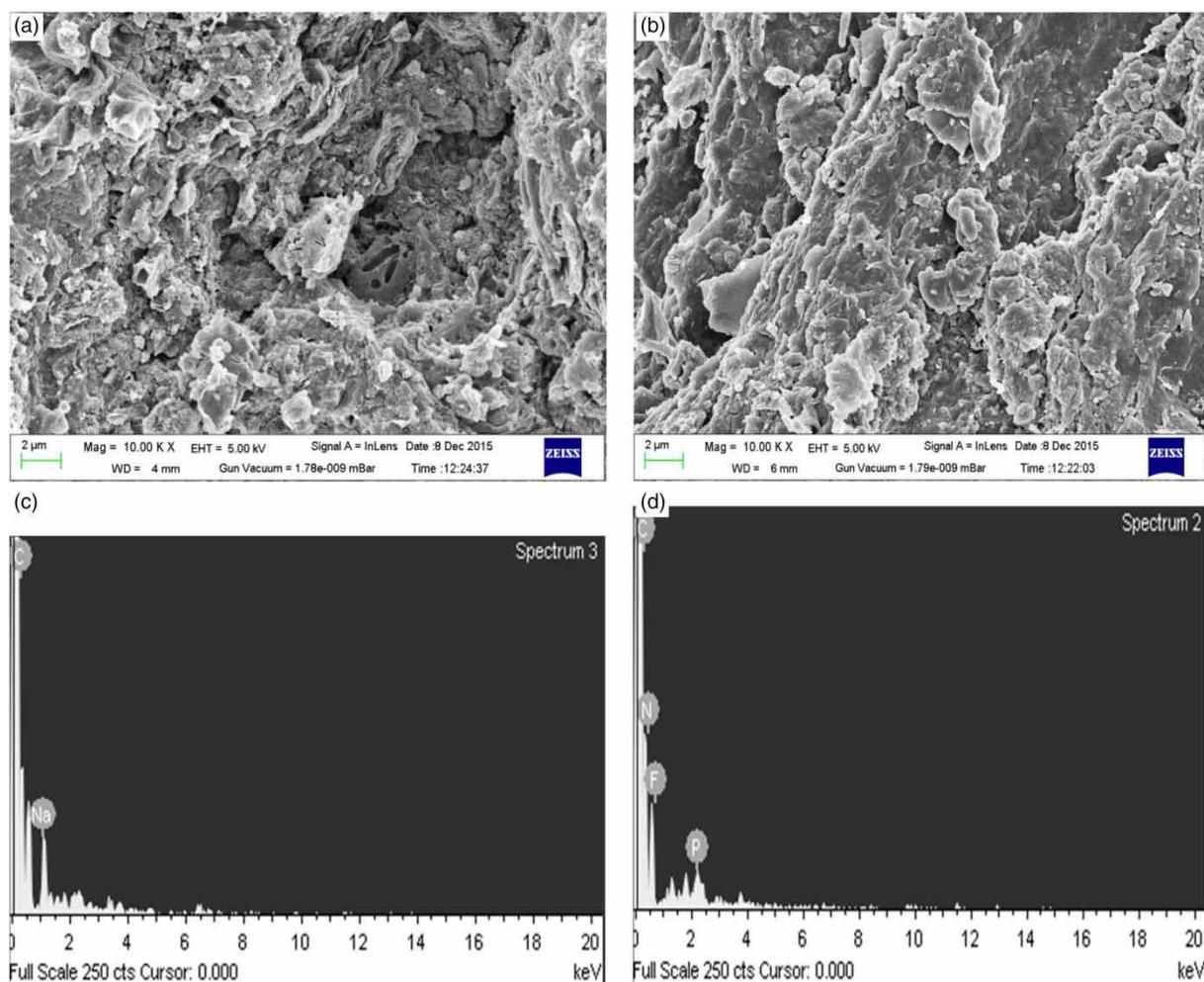
Physico-chemical characterization of DBM has been done in terms of the specific gravity, bulk density, surface area,

pore volume and  $\text{pH}_{\text{zpc}}$ . The results are shown in Table 1. The specific gravity, bulk density of DBM are 1.0463, and 0.76 g/cc, respectively.  $\text{pH}_{\text{zpc}}$  of DBM has been found as 6.8. It indicates that the surface of DBM shows positive charge in the solution having pH lower than 6.8, and thus, binds with negatively charged ions ( $\text{F}^-$ ) in the solution. The result is in agreement with Hiremath & Binnal (2013), for the algal biomass of *Spirulina platensis*. BET surface area and pore volume of DBM have been found as 2.365  $\text{m}^2/\text{g}$  and 0.013  $\text{cc}/\text{g}$ , respectively.

FESEM images were taken for both native and fluoride treated DBM, as shown in Figure 1(a) and 1(b), respectively. It can clearly be seen from the images that the surface of both adsorbents are not homogenous. However, before adsorption of fluoride on DBM, the rough surface textures along with many small pores are observed; whereas after adsorption, comparatively smooth surface is observed. The elemental compositions of raw and fluoride loaded consortium biomass as obtained from EDX study, are shown in Figure 1(c) and 1(d). DBM contains 91% carbon (C), 6% nitrogen (N) and 3% phosphorus (P). After treatment with fluoride, DBM contains 2% fluoride (F), 90% carbon (C), 1% phosphorus (P) and 7% nitrogen (N), which clearly indicates the fluoride sorption on DBM surface. Nitrogen adsorption and desorption isotherm studies of native DBM (Figure 1(e)) reveals the mesoporous nature of DBM, which reconfirms the surface morphology as obtained from FESEM images. The biosorption behaviour is depended on the functional groups of DBM surface, the primary sites of fluoride sorption. FTIR data of raw (Figure 1(f)) and fluoride treated (Figure 1(g)) DBM have been done to scrutinize the changes in spectra due to introduction of fluoride in the later case. The responsible bonds such as  $\equiv\text{C}-\text{N}<$  (Stretch),  $-\text{C}-\text{O}$  (bend),  $-\text{O}-\text{H}$  (stretch),  $\text{C}=\text{C}$  (strong bend) and phenolic groups are observed at the wave number of 1,054, 1,269, 1,406, 3,433, 1,560, 1,648 and 2,922  $\text{cm}^{-1}$ , respectively. However, FTIR spectrogram of fluoride treated DBM shows some different spectra. The presence of  $-\text{CHF}_3$

Table 1 | Physical characterization of DBM

Property	Value
Bulk Density	0.76 g/cc
Specific gravity	1.0463
$\text{pH}_{\text{zpc}}$	6.8
Surface area	2.365 $\text{m}^2/\text{g}$
Pore volume	0.013 $\text{cc}/\text{g}$



**Figure 1** | (a) Morphological details (FESEM image) of native DBM, (b) Morphological details (FESEM image) of fluoride loaded DBM, (c) Elemental analysis (EDX study) of native DBM, (d) Elemental analysis (EDX study) of fluoride loaded DBM, (e) Nitrogen adsorption-desorption isotherm curve of native DBM, (f) FTIR study of native DBM, (g) FTIR study of fluoride loaded DBM. (continued.)

group (Tri-fluoro methyl) at the wave number of  $1,205\text{ cm}^{-1}$  confirms the adsorption of fluoride on DBM. The other characteristic bonds such as  $\equiv\text{C-N}<$  ( $1,050\text{ cm}^{-1}$ ),  $-\text{O-H}$  ( $1,408$  and  $3,431\text{ cm}^{-1}$ ),  $\text{C}=\text{C}$  ( $1,652\text{ cm}^{-1}$ ) and phenolic group ( $2,924\text{ cm}^{-1}$ ), are shifted as observed in fluoride loaded form (Figure 1(g)). Hence, the fluoride adsorption onto DBM has initially been proved.

### Biosorption of fluoride

one-factor-at-a-time (OFAT) analysis has been done to determine optimum condition of biosorption of fluoride using DBM. From Figure 2(a), it is seen that, as pH increases from 2 to 4, fluoride removal increases from 43% to 47.1%. However, when pH increases from 4 to 12, fluoride removal decreases from 47.1 to 2.66% (Figure 2(a)). Surface of algae

contains a number of molecular groups, such as: amino, phosphate, carboxyl, thiol, etc (Bhatnagar *et al.*, 2002). Protonation of the cell wall depends on the pH of the solution, i.e., the positive charged surface [ $\text{H}^+$  (cationic) type] of DBM at  $\text{pH} < \text{pH}_{\text{zpc}}$  conditions (Hiremath & Binnal, 2013). Biswas *et al.* (2016) reported the maximum fluoride sorption capacity at pH lower than  $\text{pH}_{\text{zpc}}$ . Since highest removal is obtained at pH 4, it has been chosen as the optimum pH for removal of fluoride. Figure 2(b) reveals that the maximum removal is achieved at 0.5 g/L of AD for the present biosorbent. At lower ADs (0.04–0.2 g/L), fluoride removal is less because of low availability of active sites, as reported in several literatures (Venkata Mohan *et al.* 2007). Though the removal increases with the increase in AD, 0.5 g/L is selected as best AD from the economic point of the view (Venkata Mohan *et al.* 2007).

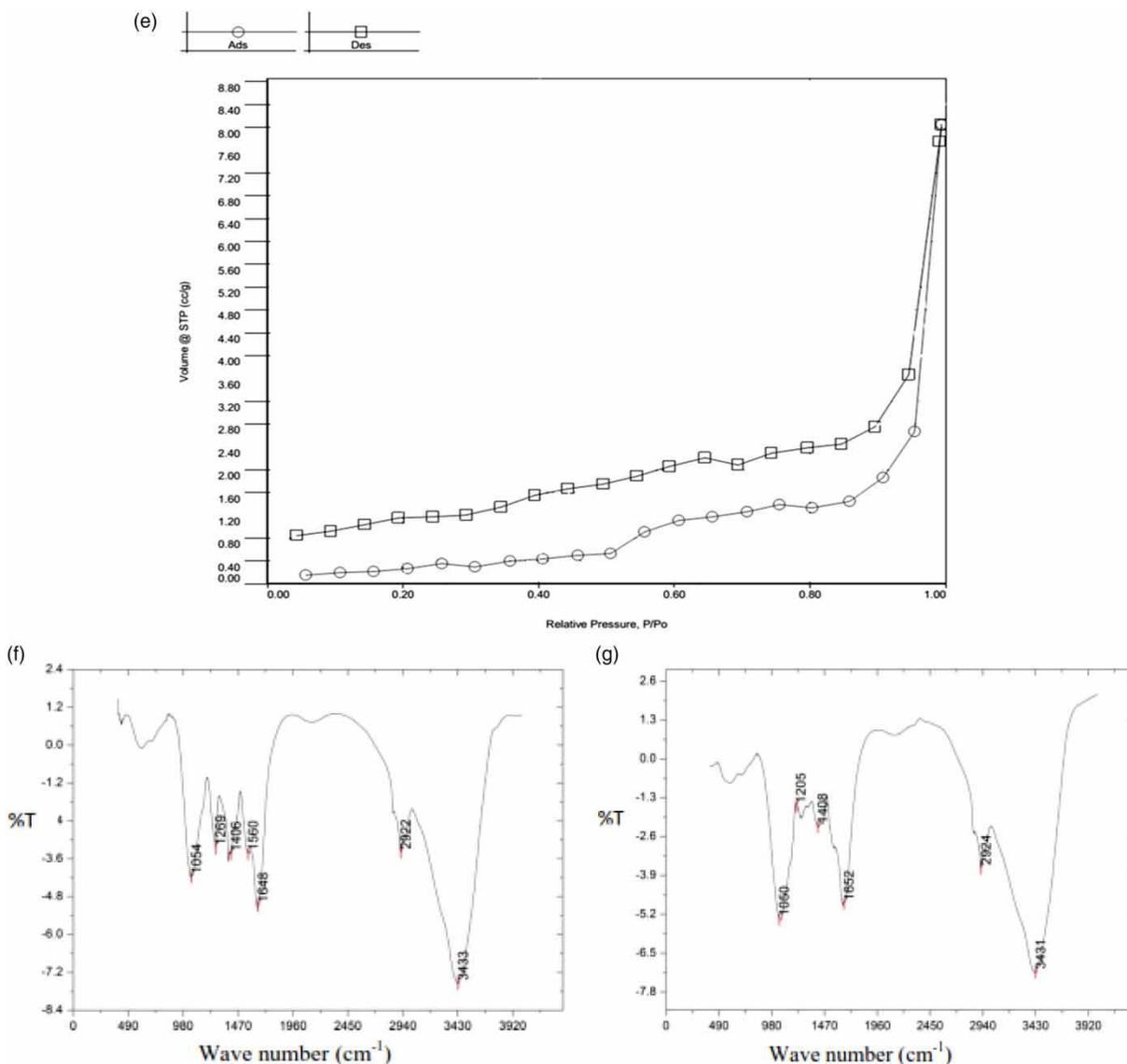
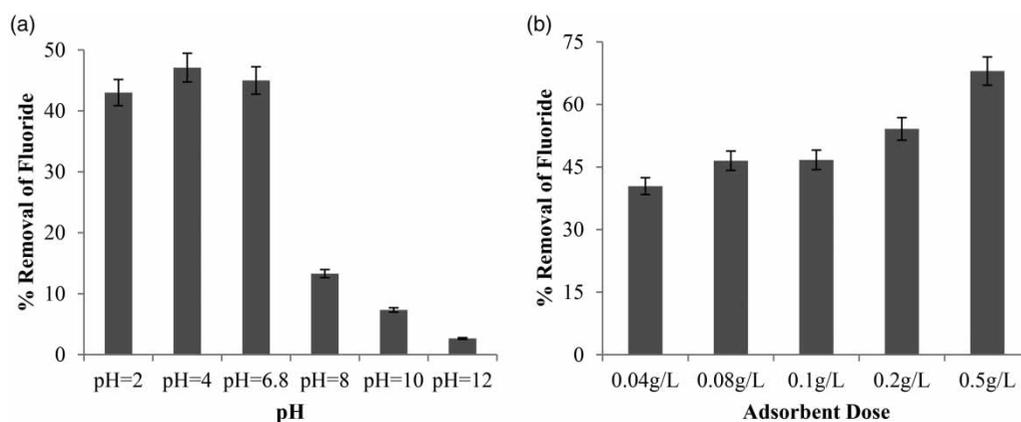


Figure 1 | Continued.

### Kinetic and equilibrium studies on biosorption of fluoride

To appraise the fluoride biosorption function using DBM and to estimate the kinetic parameters, a detailed kinetic study has been done at optimum condition as obtained from OFAT analysis, such as: 0.5 g/L AD and pH 4. Volume of the solution, shaking speed and temperature are maintained 100 ml, 150 rpm and 25 °C, respectively. The variation of fluoride removal (%) with time considering different IC of fluoride as parameter is shown in Figure 3. It is seen that, the removal achieves equilibrium condition gradually after 90 min. Maximum 72%, 67.4%, 42.5% and

36.1% have been removed from 5, 10, 25 and 50 mg/L of IC, respectively. The lower removal at higher IC may be due to the competitive nature of the overloaded  $F^-$  ions and the limitation of the active-sites on DBM (Bhatnagar *et al.* 2002). Furthermore, the higher removal at lower IC signifies the process as kinetically controlled rather than mass transfer limited one. Kinetic data have been fitted to three kinetic models viz., Lagergren first-order, Ho pseudo-second order and Moris-Weber model. It has been seen that the kinetic data fit best to Lagergren first-order model with  $R^2$  value of 0.89 to 0.9. The experimental  $q_e$  matches quite well with simulated data for Lagergren first-order model. The values of kinetic parameters are shown in



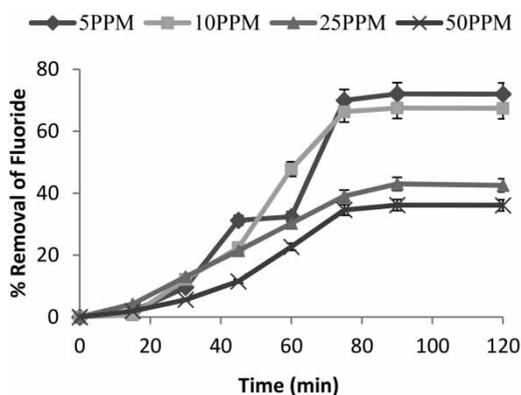
**Figure 2** | (a) Effect of solution pH on fluoride removal using DBM (IC = 10 mg/L, AD = 0.04 g/L, Temp = 25 °C). (b) Effect of adsorbent doses on fluoride removal using DBM (IC = 10 mg/L, pH = 4, Temp = 25 °C).

**Table 2.** Lagergren (1898) presented a first-order rate equation to describe the kinetic process of liquid solid phase adsorption of oxalic acid and malonic acid onto charcoal. It can be presented as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (4)$$

The significance of fitting of kinetic data to Lagergren first order model may be attributed to the dependence of binding of fluoride to the surface of DBM with first order relationship.

Equilibrium study has been done at different IC of fluoride, ranging from 5 to 50 mg/L at an AD of 0.5 g/L, pH 4, shaking speed 150 rpm, contact time of 120 min and 25 °C temperature. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models have been used to fit the equilibrium data and it is seen that  $R^2$  value (0.9894) of Langmuir isotherm model holds good to predict equilibrium



**Figure 3** | Kinetics study at different initial concentrations of fluoride (pH = 4, AD = 0.5 g/L, Temp = 25 °C, Shaking speed = 150 rpm).

condition. This indicates the monolayer coverage of  $F^-$  on DBM surface. Maximum adsorption capacity is obtained as 34.36 mg/g (Table 3). From kinetic and equilibrium studies, it can be concluded that DBM can be used as a good biosorbent for defluoridation purpose. A comparative study has been made based on the defluoridation works of other scientists (Table 4).

#### Application of COMSOL multiphysics to predict kinetics of fluoride removal using DBM

A transient convection–diffusion equation was employed in COMSOL Multiphysics to study the experimental phenomena for removal of Fluoride. The transient convection–diffusion equation is given in Equations (4) and (5):

$$\frac{\partial}{\partial t}(\rho C) + \nabla \cdot (\rho \bar{U} C) = \nabla \cdot (d \nabla \cdot C) + S \quad (5)$$

$$S = -q_e*(1 - \exp(-k_1*t)) \quad (6)$$

In Equation (4), first and second terms of left hand side are accumulation and convective mass transport terms, respectively. In right hand side, the first term is diffusive term and second is source term. To validate and justify the mechanism of fluoride removal and the kinetic parameters obtained during experimentation of fluoride adsorption using dead biomass of micro algal consortium, such model is proposed. The experimental system is shown in the schematic diagram (Figure 4(a)). Assuming same kinetic parameters as obtained during experimentation, boundary conditions, Lagrange's first order model of adsorption, and fine mesh size, the model predicts the removal of fluoride

**Table 2** | Values of kinetics parameters

Parameter	Lagergren-first order model $\log(q_e - q_t) = \log q_e - k_1 t$				Pseudo second order model $\frac{t}{q_e} = \frac{1}{k_2} \times \frac{1}{q_e} + \frac{t}{q_e}$			Moris-Weber model $q_t = k_3 t^{1/2} + C'$	
	IC (mg/L)	$q_e(\text{exp})$	$k_1$	$q_e$	$R^2$	$k_2$	$q_e$	$R^2$	$k_3$
5	7.34	0.0113	7.795	0.8913	$2.2 \times 10^{-2}$	-3.234	0.5017	1.0416	0.8726
10	12.48	0.0261	16.575	0.8648	$3.9 \times 10^{-3}$	2.445	0.3781	1.7746	0.9212
25	24.9	0.0235	29.008	0.9003	$1.7 \times 10^{-6}$	370.37	0.0432	3.028	0.968
50	37.6	0.0346	40.546	0.8648	$1.0 \times 10^{-4}$	44.44	0.4656	5.3401	0.8798

**Table 3** | Values of equilibrium parameters

Adsorption Isotherm Model	Expression	Constants
Langmuir model	$\frac{1}{q_e} = \frac{1}{q_{\max} K_L C_e} + \frac{1}{q_{\max}}$	$R^2 = 0.9894$ $q_{\max} = 34.36$ $K = 0.186$
Freundlich model	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	$R^2 = 0.9796$ $1/n = 1.9425$ $K_F = 0.0289$
Temkin model	$q_e = \frac{RT}{b'} \ln(K_T) + \frac{RT}{b'} \ln(C_e) \quad B' = \frac{RT}{b'}$	$R^2 = 0.9571$ $B' = 9.4165$ $K_T = 1.23$
Dubinin-Radushkevich model	$\ln(q_e) = \ln(q_{\max}) - K_{DB} \epsilon^2$	$R^2 = 0.7634$ $K_{DB} = 0.7623$ $q_{\max} = 25.41$

**Table 4** | Adsorption capacities of different biomass derived adsorbent for removal of fluoride

Adsorbent (biomass)	Adsorption capacity (mg/g)	Reference
<i>Spirogyra</i> sp. IO2	1.272	Venkata Mohan et al. (2007)
<i>Spirulina plantheis</i>	34.0	Hiremath & Poornima, 2013)
<i>Anabaena fertilissima</i> (Ca-treated)	7.0	Bhatnagar et al. (2002)
<i>Cholorococcum humicola</i> (Ca-treated)	4.5	Bhatnagar et al. (2002)
DBM	34.34	Present Study

with time for different initial fluoride concentration. The experimental data when placed over the model predicted data as shown in Figure 4(b), are found to be in good fit. It is seen that the model predicted data shows similar nature of removal in terms of residual fluoride as found during experimentation. As the concentration of the solution increases, biosorption rate decreases i.e. there is no such mass transfer resistance rather than biosorption resistance. So it may be concluded that the system is biosorption controlled system. Thus, from the above observation it can be said that the model developed is capable of predicting

residual fluoride concentration vis-à-vis fluoride removal. To further justify the validity of the model root mean square error (RMSE) and average error is calculated for all the cases using Equations (6) and (7), as shown in Table 5.

$$RMSE = \frac{\sqrt{\sum_{i=1}^N (C_{\text{exp},i} - C_{\text{sim},i})^2}}{N} \quad (7)$$

$$Error(\%) = \left[ \frac{C_{\text{exp}} - C_{\text{sim}}}{C_{\text{exp}}} \right] \times 100 \quad (8)$$

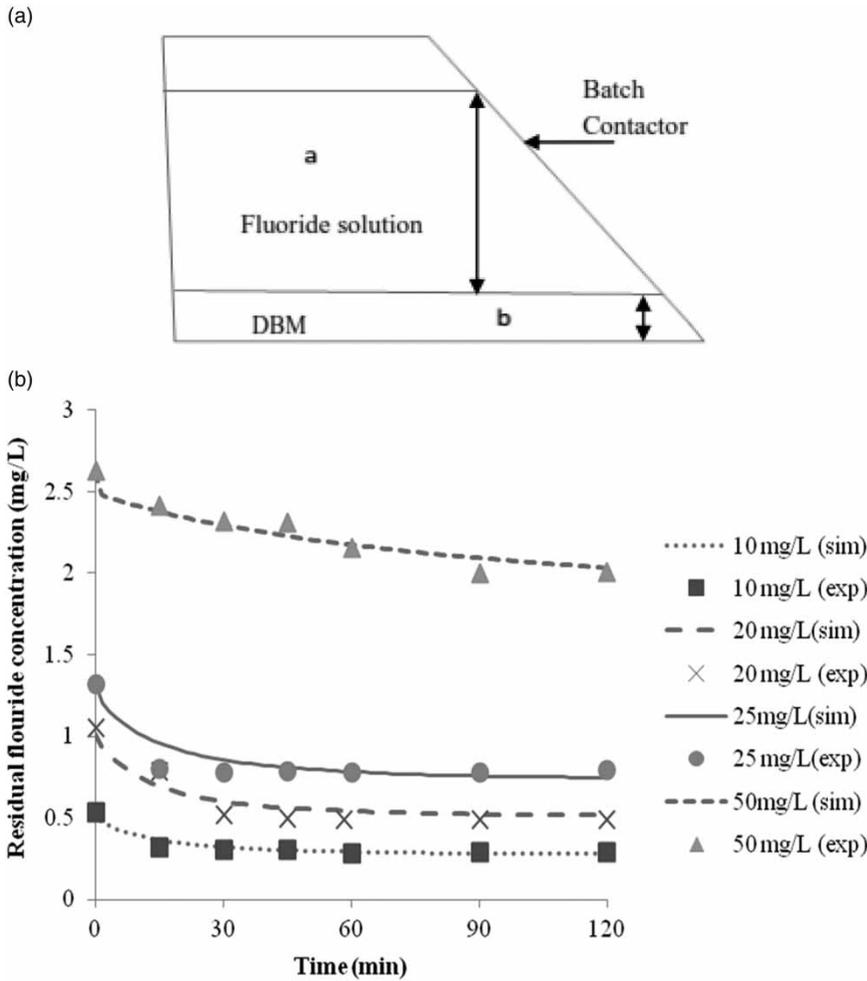


Figure 4 | (a) Schematic diagram of 1/4<sup>th</sup> of the 250 mL conical flask (a: Fluoride solution; b: adsorbent DBM). (b) COMSOL Multiphysics predicted data (line) and the experimental results (point) of residual fluoride concentration for different initial fluoride concentration with time.

**Conductivity study of DBM**

Conductivity analysis has been carried out to assess the ionic property of DBM. Figure 5 shows the change in conductivity of solution with time under four different conditions, (1) distilled water (DW), (2) Simulated solution of fluoride (DW + F), (3) DBM in distilled water (DW + DBM), and (4) Fluoride

loaded DBM in distilled water (DW + DBMF). From the figure, it is seen that conductivity of DBM in distilled water

Table 5 | RMSE and error (%) calculations for different initial concentration

IC (mg/L)	RMSE	Error (%)	
		Avg. Error	Max. Error
10	0.0186	4.13	13.69
20	0.05	5.9	19.76
25	0.0048	8.9	15.98
50	0.051	1.87	4.66

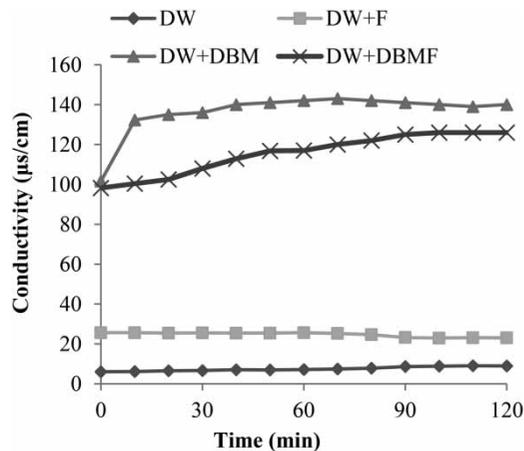


Figure 5 | Conductivity analysis of DBM with time.

is maximum (143  $\mu\text{S}/\text{cm}$ ) and the conductivity is lowest for distilled water only. The conductivity of fluoride loaded DBM in distilled water is 126  $\mu\text{S}/\text{cm}$ , which is lower than DBM in distilled water (DW + DBM). The highest conductivity with native DBM confirm the presence of different ions in the solution which may have come from algal biomass. The presence of ionic functional groups is already seen in FTIR study (Figure 1(f)). The lower conductivity of fluoride loaded DBM may be due to the binding of fluoride with the ionic functional groups as present on the surface of DBM and thus, release of functional groups in solution is restricted. Lower conductivity of Fluoride loaded DBM

in distilled water confirms that the adsorption is chemisorptive in nature (Oura *et al.* 2003).

### Optimization using RSM

Four key parameters viz., pH, AD, IC and temperature have been varied as input condition according to CCD (Table 6). Defluoridation by DBM has been considered as final response, which have been analysed using ANOVA (Table 7). The F-value (22.49) obtained from ANOVA implies the significance of the model. As suggested by ANOVA, quadratic model has been fitted to the responses. The Equation (8) has been achieved in terms of coded factors has been given below:

$$R1 = 38 - 1.34^*A - 4.8^*B + 1.37^*C - 5.32^*D + 1.4^*AB - 0.09^*AC + 1.08^*AD - 0.68^*BC + 3.49^*BD - 1.25CD - 0.23^*A^2 - 1.63^*B^2 - 0.97^*C^2 + 0.94D^2 \quad (9)$$

$R^2$ ,  $R^2_{Adj}$  and  $R^2_{pred}$  have been obtained as 0.954, 0.912 and 0.738, respectively. The higher  $R^2$  data indicates the good fitting of the model to the investigational data.

**Table 6** | Experimental design and response of fluoride biosorption study

SI no	IC (mg/L)	pH	Dose (g/L)	Temperature ( $^{\circ}\text{C}$ )	Removal (%)
19	50	2	2.5	35	38
18	90	7	2.5	35	36
13	30	4.5	3.5	40	35
3	30	9.5	1.5	30	31.2
1	30	4.5	1.5	30	51.2
28	50	7	2.5	35	38
23	50	7	2.5	25	54.5
16	70	9.5	3.5	40	28
22	50	7	4.5	35	38.5
5	30	4.5	3.5	30	59.2
21	50	7	0.5	35	30.6
9	30	4.5	1.5	40	33
27	50	7	2.5	35	38
17	10	7	2.5	35	39
24	50	7	2.5	45	30
4	70	9.5	1.5	30	29
10	70	4.5	1.5	40	32.5
8	70	9.5	3.5	30	33.8
2	70	4.5	1.5	30	42.5
12	70	9.5	1.5	40	29
6	70	4.5	3.5	30	47
11	30	9.5	1.5	40	30
14	70	4.5	3.5	40	32
20	50	12	2.5	35	25.8
26	50	7	2.5	35	38
29	50	7	2.5	35	38
25	50	7	2.5	35	38
7	30	9.5	3.5	30	32.5
15	30	9.5	3.5	40	28
30	50	7	2.5	35	38

**Table 7** | ANOVA and statistical response of fluoride biosorption study

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	1737.99	14	124.14	22.49	<0.0001 significant
A-IC	43.47	1	43.47	7.87	0.0133
B-pH	553.92	1	553.92	100.34	<0.0001
C-AD	45.1	1	45.1	8.17	0.012
D-T	681.6	1	681.6	123.47	<0.0001
AB	31.64	1	31.64	5.73	0.0302
AC	0.14	1	0.14	0.025	0.8753
AD	18.71	1	18.71	3.39	0.0855
BC	7.43	1	7.43	1.35	0.2643
BD	195.3	1	195.3	35.38	<0.0001
CD	25.25	1	25.25	4.57	0.0493
A <sup>2</sup>	1.56	1	1.56	0.28	0.6027
B <sup>2</sup>	73.64	1	73.64	13.34	0.0024
C <sup>2</sup>	26.13	1	26.13	4.73	0.046
D <sup>2</sup>	24.7	1	24.7	4.47	0.0515
Residual	82.8	15	5.52		
Lack of Fit	82.8	10	8.28		
Pure Error	0	5	0		
Cor Total	1820.79	29			

Significant model terms are  $B$ ,  $D$ , and  $BD$ . Moreover, interactive effect of pH and temperature is significant. Figure 6 shows the interactive effect of pH and Temperature on removal of fluoride using DBM. When pH increases from 4.5 to 9.5 at a temperature of 30 °C, the removal decreases from 33.3% to 30.7%, and at a temperature of 40 °C, the removal decreases from 50.7% to 34.5%. The lower removal at higher pH condition has already been observed during OFAT analysis (Figure 2(a)). pH higher than  $pH_{zpc}$  leads to negative charge on the surface of biosorbent and thus, results in lower removal of fluoride. During selection of optimum condition the following criteria have been set: IC of fluoride: in range, Optimum values of IC of fluoride, pH of the solution, AD and temperature are obtained as 30 mg/L, 4.5, 3.5 g/L and 30 °C, respectively. The predicted removal of fluoride as analyzed by RSM is 56.9%, which is in accordance with the experimental one (58%).

#### Regeneration study, toxicity characteristics leaching procedure (TCLP) test and CHNS study of DBMF

In Figure 7(a), three successive sorption/desorption rounds have been performed with three different desorption

condition. A consistent reduction in adsorption capacity has been noticed for each new cycle after total adsorption-desorption series (Figure 7(a)). The adsorption capacities have been reduced from 5.71 mg/g (IC: 30 mg/L; AD: 3.5 g/L) after first cycle of adsorption to 4.57 mg/g (distilled water), 4.28 mg/g (0.1 N HCl) and 2.85 mg/g (0.1 N NaOH) after third cycle of adsorption. Furthermore, relatively more effective reusability has been noticed when the loaded biomass has been desorbed with 0.1 N HCl (Figure 7(a)). On the other hand, usage of acid incurs cost to the process. Therefore, from economical point of view, distilled water can be used as desorption medium for the present DBM system.

After TCLP test at pH 3, the maximum 0.62 mg/L of fluoride is found (Figure 7(b)) in the supernatant which has been leached out from fluoride laden DBM and such concentration is much below from the leachable permissible fluoride level (150 mg/L) as suggested by Waste Classification Guidelines (2008). Therefore, the present study indicates that the fluoride laden DBM passes the TCLP tests successfully, and it can be disposed safely or used as bio-fertilizer (Waste Classification Guidelines 2008).

CHNS study of fluoride treated DBM is done for further assessment of used biomass (Figure 7(C)). From Figure 7(C),

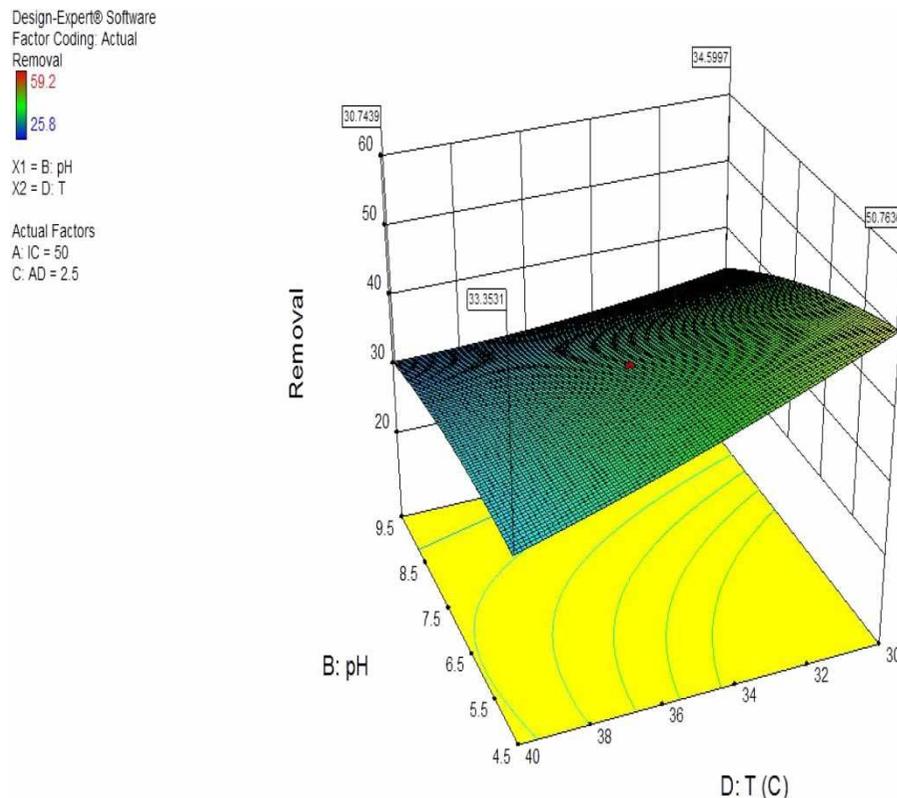
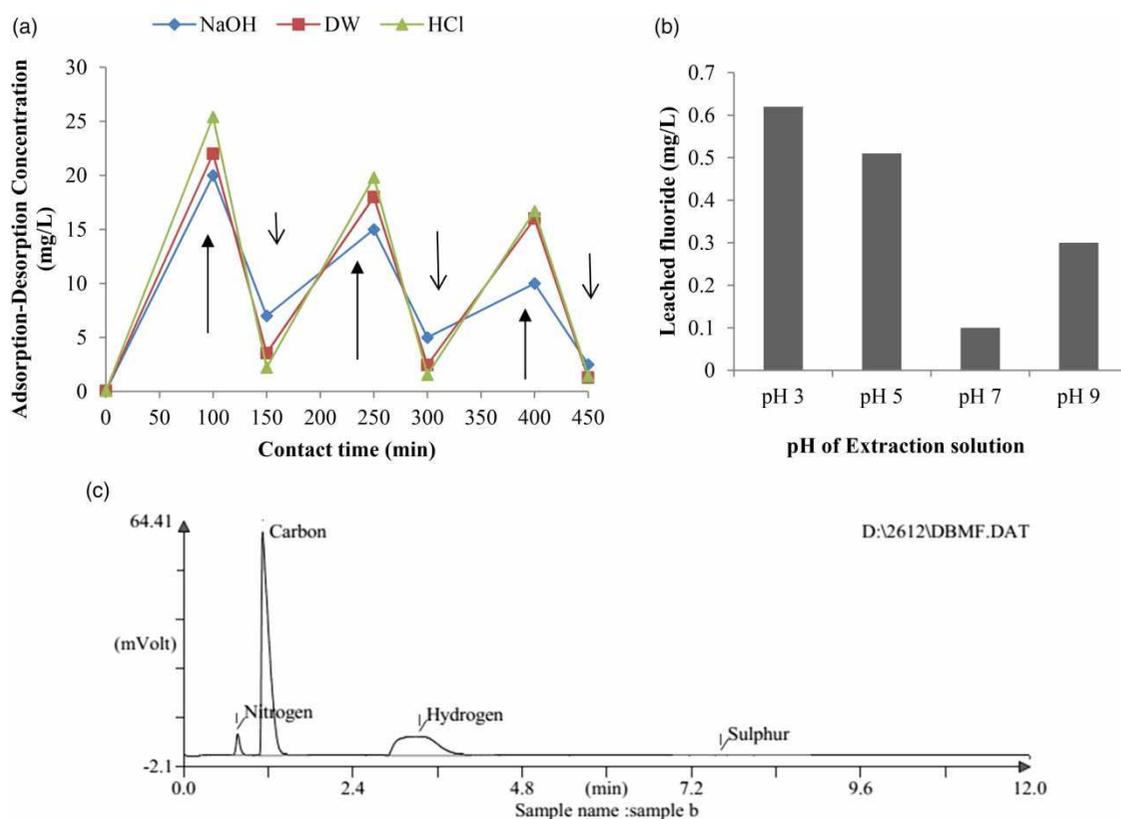


Figure 6 | Effect of pH and Temperature on the removal of fluoride.



**Figure 7** | (a) Pattern of Adsorption-Desorption of Fluoride ( represents desorption; represents adsorption). (b) TCLP test of fluoride loaded DBM. (c) CHNS study of fluoride laden DBM.

Carbon, Nitrogen, Hydrogen and Sulphur contents of the fluoride loaded DBM are obtained as 36.185, 3.965, 5.365 and 0.658%, respectively. The study shows that the used biomass can be used as feedstock for different types of bio-fuel production utilizing large carbon-source, which may come under the future scope of the study.

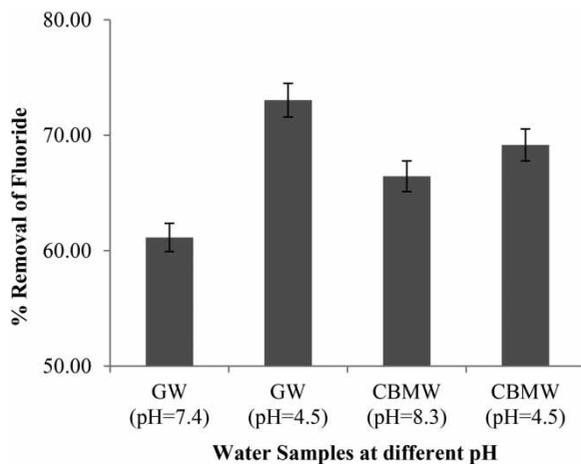
### Comparison between removal of excess fluoride from groundwater and CBM produced water

The mineralogical properties of groundwater sample have been determined. pH, TDS, total hardness, total alkalinity, chloride, iron and fluoride are obtained as 7.4, 470 mg/L, 255 mg/L, 367 mg/L, 100 mg/L, 12.2 mg/L and 4.71 mg/L, respectively. The groundwater sample (100 mL) has then been treated with DBM in batch mode with 3.5 g/L AD at two pH conditions, viz., at groundwater own pH (7.4), and optimum pH (4.5) as analyzed by RSM. From Figure 8, it is seen that after 120 min of contact time, 61.14% and 73.03% removal are obtained at pH 7.4 and pH 4.5, respectively. Final concentration of fluoride in

treated groundwater sample at pH 4.5 is 1.27 mg/L i.e. below the allowable limit as set by Bureau of Indian Standard (BIS 2012).

The physico-chemical properties of raw CBM produced water are determined as: pH 8.8, TDS: 570 mg/L, Salinity: 398 mg/L, Carbonate: 209 mg/L, Chloride: 287 mg/L, Fluoride: 9.24 mg/L, Nitrate: 18.6 mg/L, Sulphate: 15.8 mg/L, Sodium: 201 mg/L, Potassium: 15.9 mg/L, Calcium: 85.8 mg/L, Magnesium: 7.5 mg/L and Iron: 1.65 mg/L. After treatment with DBM, 66.45% and 69.16% removal of fluoride have been obtained after 120 min of contact time from CBM produced water, at pH 8.8, and pH 4.5, respectively (Figure 8). Final concentration of fluoride at pH 4.5 was 2.85 mg/L, which is near the value of industrial effluent acceptable limit (2 mg/L) as set by EPA (EPA 2017).

Therefore, it can be assured that higher level of fluoride can be removed from both groundwater and CBM produced water using DBM under optimum condition. Since in both the cases, the treated water meets the permissible limit, the biosorption of fluoride using the present algal consortium biomass may be considered as a potent technology for removal of fluoride.



**Figure 8** | Removal of fluoride from groundwater (GW) and CBM produced water (CBMW) at different pH.

## CONCLUSION

Dead biomass (DBM) of micro-algal consortium (*Chlorococcum infusionum* and *Leptolyngbya foveolaurum*) has been used for biosorption of fluoride from both synthetic and real wastewater. Both kinetic and equilibrium studies have been performed to assess the efficacy of present DBM in removal of fluoride. Percentage removal decreases from 72 to 36.1%, when initial fluoride concentration increases from 5 to 50 mg/L, at AD: 0.5 g/L, pH: 4, shaking speed: 150 rpm, volume of solution: 100 ml, contact time: 120 min and temperature 25 °C. The higher removal at lower initial fluoride concentration indicates that the process as kinetically controlled rather than mass transfer limited one. Equilibrium data have been found to fit well to Langmuir isotherm model. Adsorption capacity of DBM has been found as 34.36 mg/g. RSM has been employed to determine optimum conditions for fluoride removal., Predicted removal of fluoride (56.9%) at optimum conditions (IC = 30 mg/L, AD = 3.5 g/L, pH = 4.5, Temp = 30 °C) as analyzed by RSM matches quite well with experimental one (58%). From the observation of COMSOL Multiphysics, it can be said that the model developed is capable of predicting residual fluoride present vis-à-vis fluoride removal., Conductivity analysis of native and fluoride loaded biomass indicate the binding of fluoride onto biomass and restriction of release of ionic group from biomass in later case. As the fluoride-bearing solid biomass passes the TCLP tests successfully, it can be classified as a non-toxic waste, and disposed safely. Finally the groundwater and CBM produced water have been treated at optimum pH (4.5) and at their native pH. In both the cases, removal is more at optimum pH

and final concentration of fluoride meets permissible limit. Therefore, the present DBM, having good fluoride adsorption capacity could be used for treatment of industrial wastewater as well as fluoride contaminated groundwater.

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