

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 a micro-algal consortium of *Chlorococcum infusionum* and *Leptolyngbya foveolaurum*, collected from a coke-oven effluent treatment plant, Durgapur, India, has been investigated. The large volume of algal bloom in the industrial effluent has created serious disposal issues and caused severe environmental concerns. A biosorption technique has been carried out to valorize the waste algae biomass into a 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 have been well described by COMSOL Multiphysics.

Key words | biosorption, COMSOL Multiphysics, defluoridation, micro-algae consortium, RSM, waste valorization

Gargi Biswas
Philips Prince Pokkatt
Aratrika Ghosh
Susmita Dutta (corresponding author)
Department of Chemical Engineering,
National Institute of Technology Durgapur,
Durgapur 713209,
India
E-mail: susmita_che@yahoo.com

Biswajit Kamila
Department of Chemical Engineering,
University of Calcutta,
Kolkata 700009,
India

Kalyan Adhikari
Department of Earth and Environmental Studies,
National Institute of Technology Durgapur,
Durgapur 713209,
India

NOMENCLATURE

A	IC (mg/L)	K_F	Freundlich isotherm constant [(mg/g) (L/mg) ^{1/n}]
B	pH	K_L	Langmuir isotherm constant (L/mg)
b'	Temkin isotherm constant	K_T	Temkin isotherm constant ()
B'	Temkin constant related heat of sorption (J/mol)	K_{DB}	Dubinin-Radushkevich constant (g ² /kJ ²)
C	AD (g/L)	k_1	Adsorption rate constant as used in Lagergren first order adsorption rate equation (min ⁻¹)
$C_{exp,i}$	Experimental values of fluoride concentration (mg/L)	k_2	Adsorption rate constant as used in pseudo second order adsorption rate equation (g mg ⁻¹ min ⁻¹)
$C_{sim,i}$	Simulated values of fluoride concentration (mg/L)	k_3	Intra particle diffusion rate coefficient (g mg ⁻¹ min ^{-0.5})
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''	Morris-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 ² /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
β_0	Constant coefficient
β_i	Linear coefficient
β_{ii}	Quadratic coefficient
β_{ij}	Interaction coefficient
ϵ'	Dubinin-Radushkevich isotherm constant
ϵ	Residual error
ρ	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 to 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 60 million people in 19 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 concentrations 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 to be 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 a significant edge over the conventional processes, such as 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 they have a negative impact on several industries. Treated wastewater usually contains high concentration of nutrients (e.g. phosphate, nitrate, etc) that may cause algal blooms on the surface of storage ponds' water. The negative impact is not limited to the toxic effect of algae, but also includes their abundance, which may provoke the operational problems and increase of biochemical oxygen demand (BOD), pH and total suspended solids (TSS) (EPA 2017). Hence, the reuse or discharge of such water needs removal of algae. Such removed algal biomass thus can be valorized as a potential biosorbent. It is a newly devised substitute for the prevailing methods to remove pollutants from wastewater. The important functional groups of dead algal biomass are carboxyl, phosphate, hydroxyl, sulphate, etc. Ions can bind with biomass by processes including adsorption, ion exchange and chemisorption on surface pores (Hiremath & Binnal 2013). Usually micro-algal or cyanobacterial biomasses have been studied at a large scale for removal of various heavy metals (Sen *et al.* 2017). However, biosorption of anionic pollutants (e.g.: 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_{ZPC}) (Hiremath & Binnal 2013). 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 a micro-algal consortium of *Chlorococcum infusionum* and *Leptolyngbya foveolaurum*, as a potential biosorbent. The consortium was collected from the storage tank of a 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 has 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 is known, no report on application of COMSOL Multiphysics to predict the kinetics of biosorption of a pollutant using algal biomass has been published. In the present article, COMSOL Multiphysics has been employed to predict the kinetics of biosorption of fluoride using DBM. Finally, defluoridation of groundwater, and Coal Bed Methane (CBM) produced water has been done using the prepared biosorbent and reported in the article.

MATERIALS AND METHODS

Collection, preparation and characterization of biosorbent

The algal bloom was collected from the water surface of the storage tank of a coke-oven effluent treatment plant, being used to hold wastewater after biological treatment, in Durgapur, India (Latitude: 23°50'92"N, Longitude: 87°32'10"E). After collection, the 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 a 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 an 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 a consortium of *Chlorococcum infusionum* (green alga) and *Leptolyngbya foveolaurum* (cyanobacterium).

Bulk density, specific gravity, pH_{zpc}, BET surface area and pore volume of the native biosorbent were determined (Biswas *et al.* 2016). A 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). The pH_{zpc} of the native biosorbent was determined by following standard protocol (Biswas *et al.* 2016). The test

consortium was incubated in a fluoride loaded solution with 10 mg/L initial concentration (IC) of fluoride for 12 h. The cyanobacterial biomass was then centrifuged to separate it from solution, and dried. Field emission scanning electron microscopic (FESEM) image, Energy dispersive x-ray (EDX) analysis and Fourier transform infrared (FTIR) spectroscopy studies were performed to characterize the native and fluoride loaded DBM. A FESEM 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. The EDX study (ZEISS SIGMA VP, Japan) was performed to obtain the elemental composition of the samples. FTIR analyses of native and fluoride loaded DBM were done by FTIR spectrometer (Spectrum 100, Perkin-Elmer, USA) to determine the functional bands and stretches at specific frequencies. The wave number was kept between 400–4,000 cm⁻¹.

Biosorption of fluoride

Sodium fluoride (Merck) (2.21 g) was added in 1 L of deionized water (DW) to make 1,000 mg/L of fluoride stock. It was diluted with the requisite amount of distilled water to get the desired fluoride concentration. All the experiments were done three times. 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, the pH of the solution was adjusted by adding 4(N) hydrochloric acid or 1(N) sodium hydroxide. A definite amount of DBM (0.05 g in 100 mL) was contacted in 10 mg/L of fluoride solution, varying the 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 a clear solution from the top section was experimented for remaining F⁻ by Ion-meter (4 Star, B 36531, Thermo-scientific) using TISAB (total ionic strength adjustment buffer) III-Thermo Scientific. Similarly, the effect of AD (0.04–0.5 g/L) was examined. The optimum pH as analyzed from the previous set of experiments was maintained and a solution with 10 mg/L fluoride concentration was used. The experimentation was conducted at an 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 forms), 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 an air oven. An equal amount (0.05 g) of native and fluoride loaded DBM samples was added in a definite amount of DW individually, and the variation of conductivity was taken to 120 min using a multi-parameter tester (PCSTestr 35, EUTECH instrument, Thermo Scientific). The conductivity of distilled water was measured as control for same time span.

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 number of experiments that are required to be carried out depends on the number of input factors. In the case of four input parameters, the 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 second 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, i.e., 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 the final optimum conditions. The basic system was prepared by using analysis of variance (ANOVA), consisting 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 rounds. 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 a TCLP test (EPA 1992). The 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[−] 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 of Bankura district of West Bengal, India, are affected by excess fluoride (WBPHEd 2006). Hence, groundwater samples were collected from several wells and tubewells of that affected area. Therefore, collected samples were characterized using the standard protocol (Clesceri *et al.* 2012).

CBM recovery is associated with production of a 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 it through some combinations of treatments (Mendhe *et al.* 2017). CBM produced water is mostly characterized by high TDS (total dissolved solids) and salinity (Mendhe *et al.* 2017). It consists mainly of sodium (Na), bicarbonate (HCO₃), 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, in the area of West Bengal, India. Similar to groundwater, the CBM produced 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 value 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 the 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, a 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 DISCUSSION

Characterization of DBM

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

pore volume and pH_{pzc} . The results are shown in Table 1. The specific gravity and bulk density of DBM are 1.0463 and 0.76 g/cc, respectively. The pH_{zpc} of DBM has been found to be 6.8. It indicates that the surface of DBM shows positive charge in a solution having a pH lower than 6.8, and thus binds with negatively charged ions (F^-) in the solution. The result is in agreement with Hiremath & Binnal (2013), for the algal biomass of *Spirulina platensis*. The BET surface area and pore volume of DBM have been found to be 2.365 m^2/g and 0.013 cc/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, a comparatively smooth surface is observed. The elemental compositions of raw and fluoride loaded consortium biomass as obtained from the 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 the DBM surface. Nitrogen adsorption and desorption isotherm studies of native DBM (Figure 1(e)) reveal the mesoporous nature of DBM, which reconfirms the surface morphology as obtained from FESEM images. The biosorption behaviour is dependent on the functional groups of the 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 numbers of 1,054, 1,269, 1,406, 3,433, 1,560, 1,648 and 2,922 cm^{-1} , respectively. However, an FTIR spectrogram of fluoride treated DBM shows some different spectra. The presence of $-\text{CHF}_3$ group (Tri-fluoro methyl) at the wave number of

Table 1 | Physical characterization of DBM

Property	Value
Bulk density	0.76 g/cc
Specific gravity	1.0463
pH_{zpc}	6.8
Surface area	2.365 m^2/g
Pore volume	0.013 cc/g

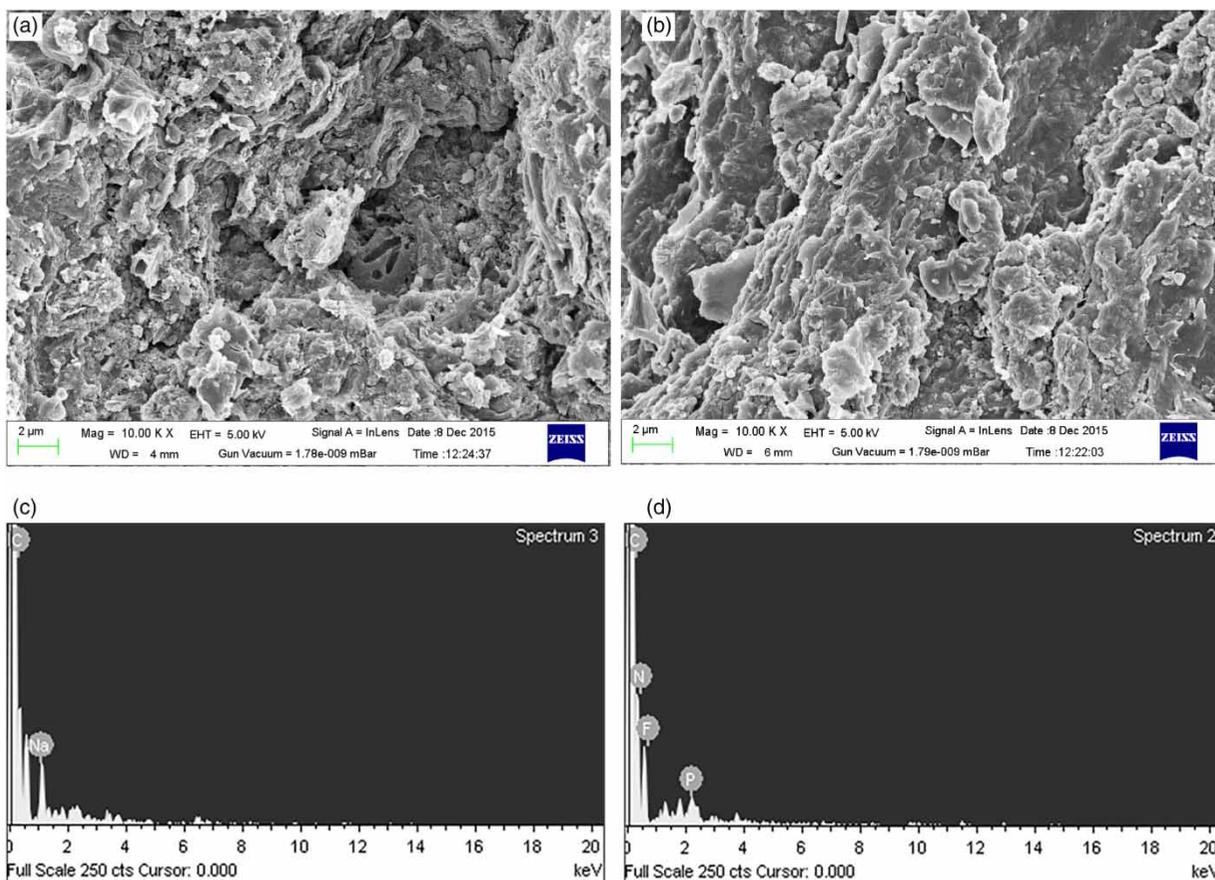


Figure 1 | (a) Morphological details (FESEM image) of native DBM, (b) morphological details (FESEM image) of fluoride loaded DBM, (c) elemental analysis (EDX study) of native DBM, (d) elemental analysis (EDX study) of fluoride loaded DBM, (e) nitrogen adsorption-desorption isotherm curve of native DBM,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

$1,205\text{ cm}^{-1}$ 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 the 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 the optimum condition of biosorption of fluoride using DBM. From Figure 2(a), it is seen that, as the pH increases from 2 to 4, fluoride removal increases from 43 to 47.1%. However, when the pH increases from 4 to 12, fluoride removal decreases from 47.1 to 2.66% (Figure 2(a)). The surface of the 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

[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 pH_{zpc} . Since the 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 lower because of the low availability of active sites, as reported in several literatures (Venkata Mohan *et al.* 2007). Although the removal increases with the increase in AD, 0.5 g/L is selected as the best AD from the economic point of the view (Venkata Mohan *et al.* 2007).

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

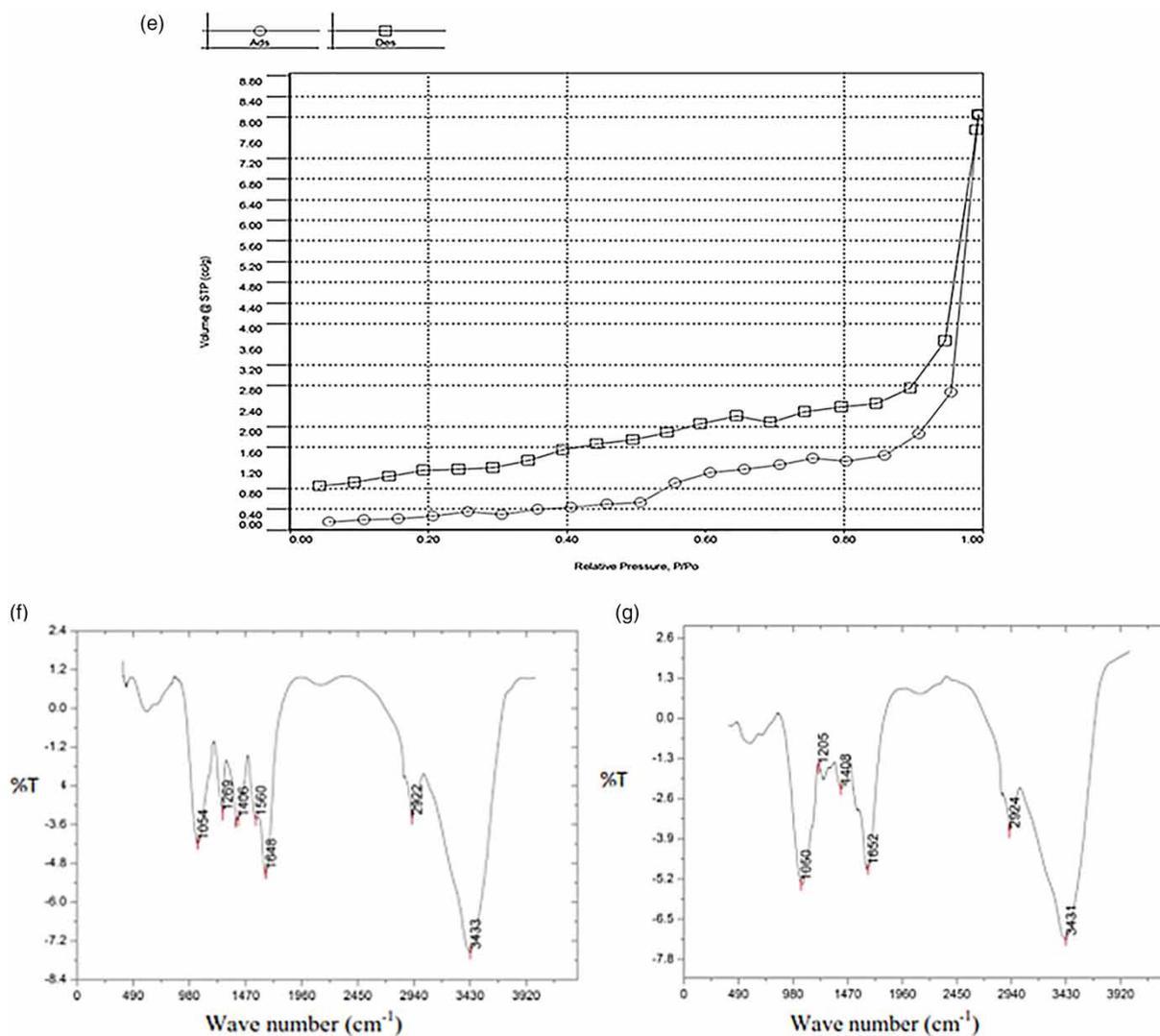


Figure 1 | Continued.

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 at 100 ml, 150 rpm and 25 °C, respectively. The variation of fluoride removal (%) with time considering different IC of fluoride as a 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 Morris-Weber model. It has been seen that the kinetic data fit best to the Lagergren first-order model with an R² value of 0.89 to 0.9. The experimental q_e matches quite well with simulated data for the Lagergren first-order model. The values of kinetic parameters are shown in 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:

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

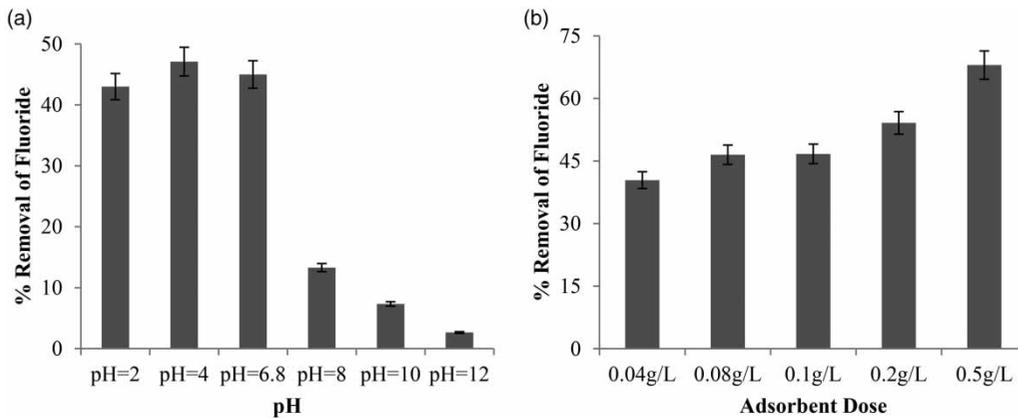


Figure 2 | (a) Effect of solution pH on fluoride removal using DBM (IC = 10 mg/L, AD = 0.04 g/L, Temp = 25 °C). (b) Effect of adsorbent doses on fluoride removal using DBM (IC = 10 mg/L, pH = 4, Temp = 25 °C).

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

Equilibrium studies have 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 the R^2 value (0.9894) of the Langmuir isotherm model holds good to predict equilibrium condition. This indicates the monolayer coverage of F^- on the 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 the purpose of defluoridation. A comparative study has been made based on the defluoridation works of other scientists (Table 4).

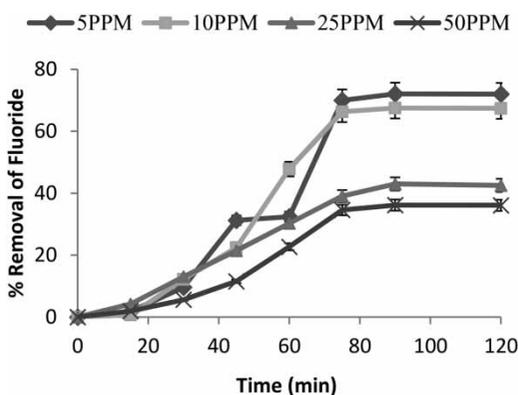


Figure 3 | Kinetics studies at different initial concentrations of fluoride (pH = 4, AD = 0.5 g/L, temp = 25 °C, shaking speed = 150 rpm).

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), the first and second terms of the left hand side are accumulation and convective mass transport terms, respectively. In the right hand side, the first term is a diffusive term and the second is a 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 the micro-algal consortium, such a model is proposed. The experimental system is shown in the schematic diagram (Figure 4(a)). Assuming the 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 with time for different initial fluoride concentrations. The experimental data, when placed over the model-predicted data as shown in Figure 4(b), are found to be a good fit. It is seen that the model-predicted data show a similar nature of removal in terms of residual fluoride as found during experimentation. As the concentration of the solution increases, the biosorption rate decreases, i.e., there is no such mass transfer resistance

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 $\frac{t}{q_e} = \frac{1}{k_2} \times \frac{1}{q_e^2} + \frac{t}{q_e}$			Morris-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	2.2×10^{-2}	-3.234	0.5017	1.0416	0.8726
10	12.48	0.0261	16.575	0.8648	3.9×10^{-3}	2.445	0.3781	1.7746	0.9212
25	24.9	0.0235	29.008	0.9003	1.7×10^{-6}	370.37	0.0432	3.028	0.968
50	37.6	0.0346	40.546	0.8648	1.0×10^{-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	$\ln(q_e) = \ln(q_{\max}) - K_{DB} \varepsilon^2$	$R^2 = 0.7634$ $K_{DB} = 0.7623$ $q_{\max} = 25.41$

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 <i>et al.</i> (2007)
<i>Spirulina plantheis</i>	34.0	Hiremath & Binnal (2013)
<i>Anabaena fertilissima</i> (Ca-treated)	7.0	Bhatnagar <i>et al.</i> (2002)
<i>Cholorococcum humicola</i> (Ca-treated)	4.5	Bhatnagar <i>et al.</i> (2002)
DBM	34.34	Present study

rather than biosorption resistance. So it may be concluded that the system is a 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.

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

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

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 the 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).

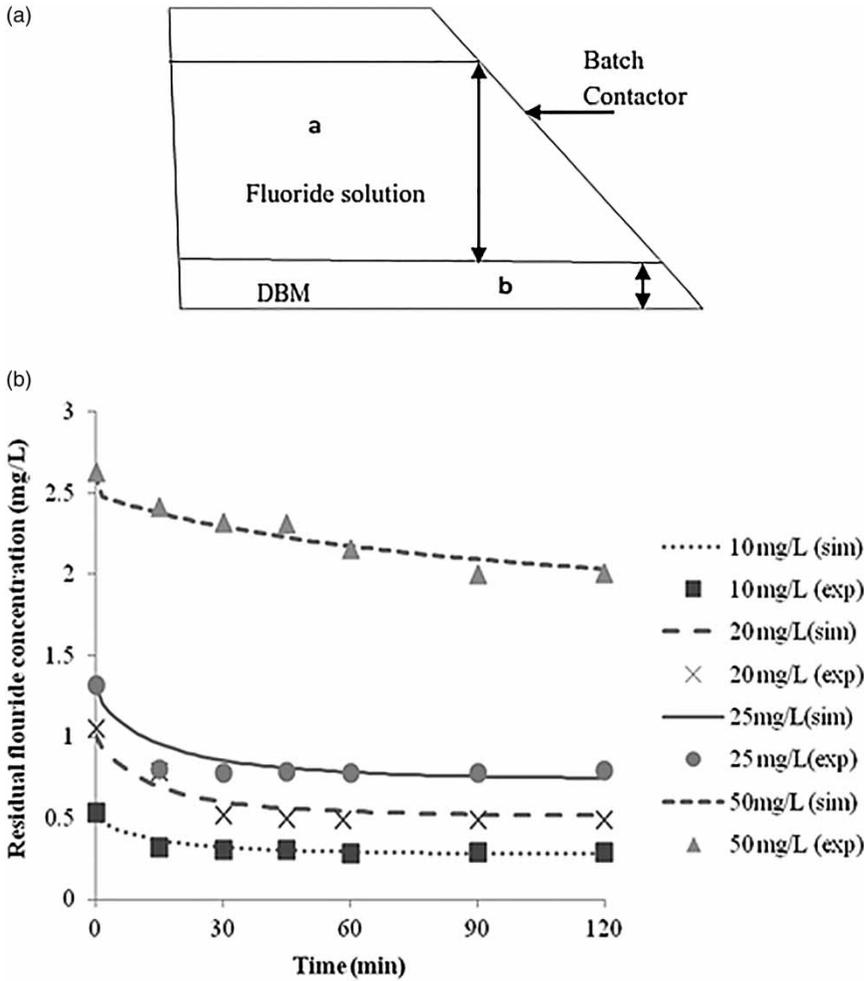


Figure 4 | (a) Schematic diagram of 1/4th of the 250 mL conical flask (a: fluoride solution; b: adsorbent DBM). (b) COMSOL Multiphysics predicted data (line) and the experimental results (point) of residual fluoride concentration for different initial fluoride concentration with time.

From the figure, it is seen that the conductivity of DBM in distilled water 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 confirms 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 the FTIR study (Figure 1(f)). The lower conductivity

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

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

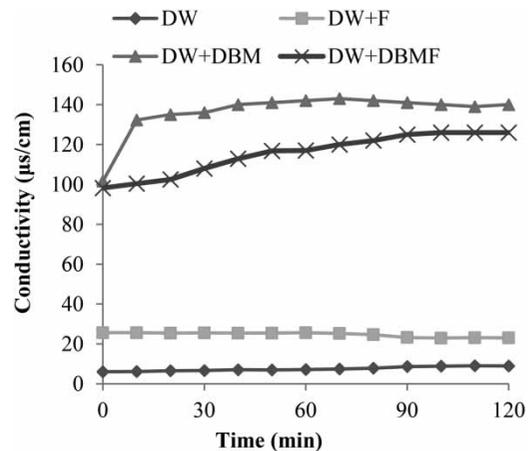


Figure 5 | Conductivity analysis of DBM with time.

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, i.e., pH, AD, IC and temperature, have been varied as the input condition according to CCD (Table 6). Defluoridation by DBM has been considered as

Table 6 | Experimental design and response of fluoride biosorption study

Sl no.	IC (mg/L)	pH	Dose (g/L)	Temperature (°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

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, a quadratic model has been fitted to the responses. 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. Significant model terms are B , D , and BD . Moreover, the 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 the 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

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^2	1.56	1	1.56	0.28	0.6027	
B^2	73.64	1	73.64	13.34	0.0024	
C^2	26.13	1	26.13	4.73	0.046	
D^2	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				

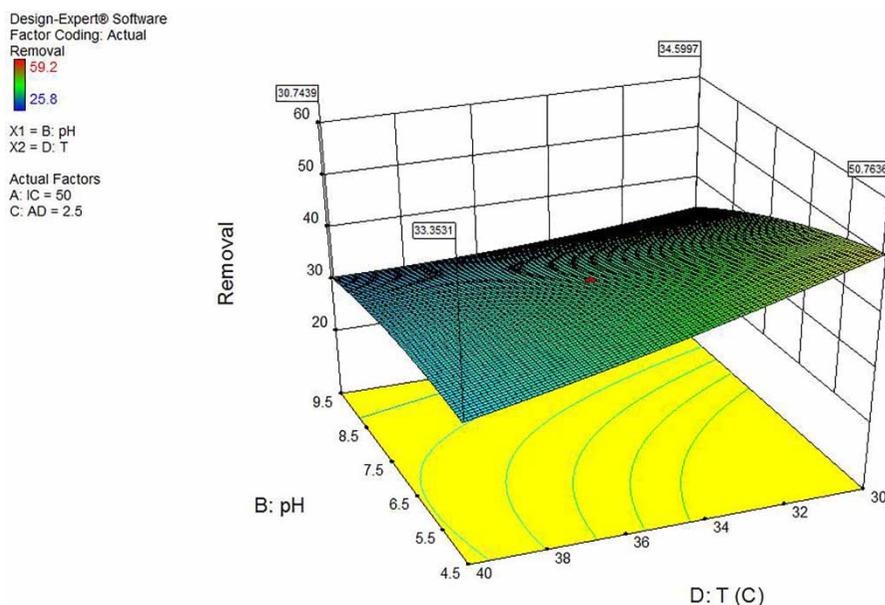


Figure 6 | Effect of pH and temperature on the removal of fluoride.

observed during OFAT analysis (Figure 2(a)). A pH higher than pH_{zpc} leads to a negative charge on the surface of the biosorbent and thus results in lower removal of fluoride. During selection of the 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 removal (58%).

Regeneration study, TCLP test and CHNS study of DBMF

In Figure 7(a), three successive sorption/desorption rounds have been performed with three different desorption conditions. A consistent reduction in adsorption capacity has been noticed for each new cycle after a 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 the 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 the 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 an economical point of view, distilled water can be used as the desorption medium for the present DBM system.

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

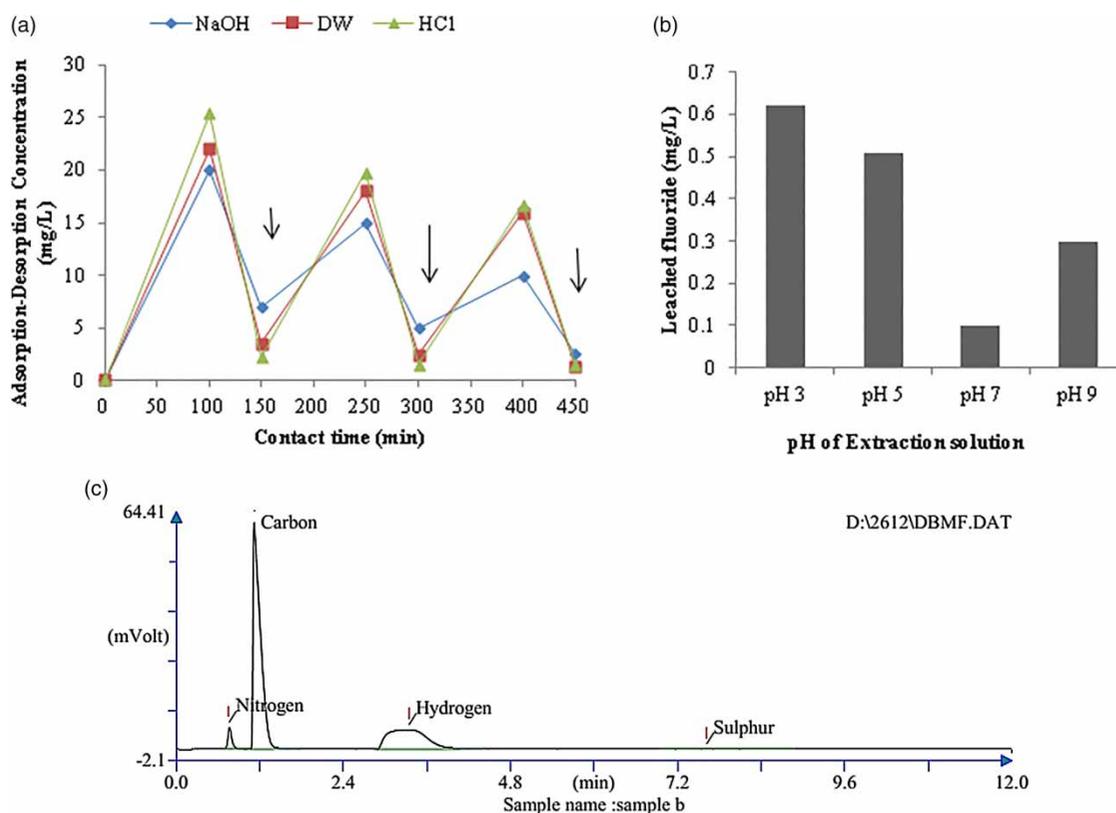


Figure 7 | (a) Pattern of adsorption-desorption of fluoride (represents desorption; represents adsorption). (b) TCLP test of fluoride loaded DBM. (c) CHNS study of fluoride laden DBM.

3.5 g/L AD at two pH conditions, i.e. at the groundwater's 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. The 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 the 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 were obtained after 120 min of contact time from CBM produced water, at pH 8.8, and pH 4.5, respectively (Figure 8). The final concentration of fluoride at pH 4.5 was 2.85 mg/L, which is near the value of the industrial effluent acceptable limit (2 mg/L) as set by EPA (EPA 2017).

Therefore, it can be assured that a higher level of fluoride can be removed from both groundwater and CBM

produced water using DBM under optimum conditions. Since in both 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.

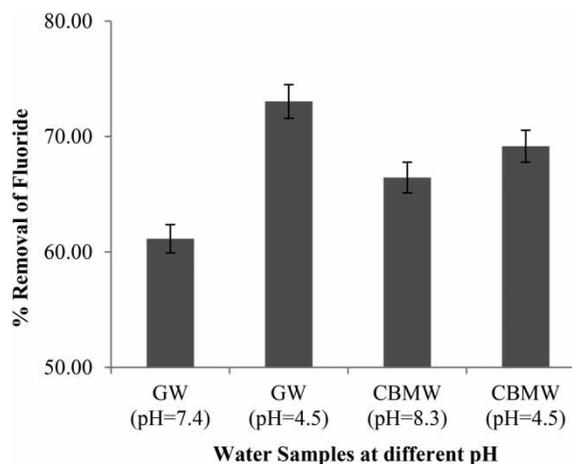


Figure 8 | Removal of fluoride from groundwater (GW) and CBM produced water (CBMW) at different pH.

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 the present DBM in removal of fluoride. The percentage removal decreases from 72 to 36.1% when the 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 is kinetically controlled rather than a mass transfer limited one. Equilibrium data have been found to fit well to the Langmuir isotherm model. The adsorption capacity of DBM has been found to be 34.36 mg/g. RSM has been employed to determine the optimum conditions for fluoride removal. The 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 the 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 analyses of native and fluoride-loaded biomass indicate the binding of fluoride onto biomass and restriction of release of the ionic group from biomass in the latter case. As the fluoride-bearing solid biomass passes the TCLP tests successfully, it can be classified as a non-toxic waste, and disposed of safely. Finally, the groundwater and CBM produced water have been treated at optimum pH (4.5) and at their native pH. In both cases, removal is greater at optimum pH and the final concentration of fluoride meets the 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.

ACKNOWLEDGEMENT

These laboratory works are supported by Department of Chemical Engineering and Earth & Environmental Studies, National Institute of Technology Durgapur, West Bengal, India. The financial grant is funded by Department of Science and Technology, Govt. of West Bengal, India (Sanc. No. 891(Sanc.)/ST/P/S&T/9G-13/2012).

REFERENCES

- Augier, F., Laroche, C. & Brehon, E. 2008 Application of computational fluid dynamics to fixed bed adsorption calculations: effect of hydrodynamics at laboratory and industrial scale. *Separation and Purification Technology* **63**, 466–474.
- Bhatnagar, M., Bhatnagar, A. & Jha, S. 2002 Interactive biosorption by micro algal biomass as a tool for fluoride removal. *Biotechnol Letter*. **24**, 1079–1108.
- Biswas, G., Dutta, M., Dutta, S. & Adhikari, K. 2016 A comparative study of removal of fluoride from contaminated water using shale collected from different coalmines in India. *Environ Sci Poll Res*. **23**, 9418–9431.
- Biswas, G., Kumari, M., Adhikari, K. & Dutta, S. 2017 A critical review on occurrence of fluoride and its removal through adsorption with an emphasis on natural minerals. *Curr Pollution Rep*. **3**, 104–119.
- Bureau of Indian Standard (BIS) 2012 Indian standard specification for drinking water. IS10500: 1–24. *Drinking Water [FAD25: Drinking Water]*. <https://law.resource.org/pub/in/bis/S06/is.10500.2012.pdf> (accessed 28 May 2017).
- Clesceri, L. S., Greenberg, A. E. & Eaton, A. D. 2012 *Standard Methods for the Examination of Water and Wastewater*. 22nd edn. American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF), Washington, DC.
- EPA 1992 Method 1311 Toxicity Characteristic Leaching Procedure. US Environmental Protection Agency Office of Ground Water and Drinking Water Standards and Risk Management Division. Washington, DC (1992). <https://www.epa.gov/sites/production/files/2015-12/documents/1311.pdf> (accessed 12 June 2017).
- EPA 2017 Harmful Algal Blooms. US Environmental Protection Agency Office of Ground Water and Drinking Water Standards and Risk Management Division, Washington, DC. <https://www.epa.gov/nutrientpollution/harmful-algal-blooms> (accessed 10 June 2017).
- Hiremath, P. G. & Binna, P. 2013 First report on biosorption of fluoride on the microalga spirulina platensis: batch studies. *Asian-American Journal of Chemistry* **1**, 1–10.
- Kumar, S. K., Dahms, H. U., Won, E. J., Lee, J. S. & Shin, K. H. 2015 Microalgae – a promising tool for heavy metal remediation. *Ecotoxicol. Env. Safety* **113**, 329–352.
- Kushwaha, D. & Dutta, S. 2017 Experiment, modeling and optimization of liquid phase adsorption of Cu(II) using dried and carbonized biomass of *Lyngbya majuscula*. *Appl. Water Sci*. **7**, 935–949.
- Lagergren, S. 1898 About the theory of so-called adsorption of soluble substances, K. *Svenska Vetenskapsakad. Handl*. **24** (4), 1–39.
- Liu, X., Hu, Z., Zhu, C., Wen, G. & Meng, X. 2013 Removal of fluoride and total dissolved solids from coalbed methane produced water with a movable ultra-low pressure reverse osmosis system. *Desal. Water Treat*. **51**, 4359–4367.
- Mendhe, V. A., Singh, A. P., Mishra, S. & Varma, A. K. 2017 Coalbed methane-produced water quality and its

- management options in Raniganj basin, West Bengal, India. *Appl. Water Sci.* **7**, 1359–1367.
- Myers, R. H., Montgomery, D. C. & Anderson-Cook, C. M. 2005 *Response Surface Methodology: Process and Product Optimization Using Designed Experiments*. 3rd edn. John Wiley & Sons Inc., New Jersey, pp. 49–327.
- Oura, K., Lifshits, V. G., Saranin, A. A., Zotov, A. V. & Katayama, M. 2003 *Surface Science, An Introduction*. Springer, Berlin, Germany.
- Sen, S., Dutta, S., Guhathakurata, S., Chakrabarty, J., Nandi, S. & Dutta, A. 2017 Removal of Cr (VI) using a cyanobacterial consortium and assessment of biofuel production. *Int. Biodet. Biodeg.* **119**, 211–224.
- Veeraputhiran, V. & Alagumuthu, G. 2011 Treatment of high fluoride drinking water using bioadsorbent. *Research Journal of Chemical Sciences* **1**, 49–54.
- Venkata Mohan, S., Ramanaiah, S. V., Rajkumar, B. & Sarma, P. N. 2007 Biosorption of fluoride from aqueous phase onto algal *Spirogyra* IO1 and evaluation of adsorption kinetics. *Bioresource Technology* **98**, 1006–1011.
- Waste Classification Guidelines 2008 *Part 1: Classifying Waste*, Department of Environment and Climate Change NSW, Sydney.
- WBPHEd 2006 Public Health Engineering Department, Government of West Bengal. http://www.wbphed.gov.in/main/images/pdf/Fluoride_Reports/FLVillagewise_A4.pdf (accessed 12 Jun 2017).

First received 9 July 2017; accepted in revised form 11 December 2017. Available online 18 December 2017