Defluoridation of water using micelle templated MCM-41: adsorption and RSM studies

Inderpreet Kaur, Abhishek Gupta, Bhupinder Pal Singh, Rajeev Kumar and Jyoti Chawla

ABSTRACT

Defluoridation of water using an economic method is important to combat the issue of excessive fluoride content (>1.5 mg/L), which is very detrimental to human health, in drinking water. In the present work, micelle templated mesoporous material, MCM-41, was synthesized and explored as an adsorbent for adsorption of fluoride ions from aqueous media and the process of adsorption was optimized through three levels of Box–Behnken design (BBD) of response surface methodology (RSM). The data obtained were found to be best fitted for Langmuir adsorption isotherm suggesting monolayer adsorption of fluoride ions on the surface of micelle templated MCM-41; Langmuir maximum adsorption capacity was found to be 52.91 mg/g. Optimization through BBD involves approximation of selected input of independent variables, i.e., initial fluoride concentration, solution pH and adsorbent dose with percentage removal of fluoride as the response variable. The quadratic model was suggested to predict the percentage removal of fluoride ions. As per the prediction, maximum removal of 82% can be achieved at initial concentration up to 21 ppm in pH range of 5.4–5.8 and adsorbent dose of 1–1.3 g/L. Experimental and model predicted values of adsorption were found to be in good agreement with each other.

Key words | adsorption, Box–Behnken design, defluoridation, mesoporous material, micelle templated MCM-41, optimization

Inderpreet Kaur (corresponding author)
Abhishek Gupta
Department of Chemistry, Centre for Advanced Studies,
Guru Nanak Dev University,
Amritsar, Punjab 143005,
India
E-mail: inderpreet11@yahoo.co.in

Bhupinder Pal Singh
Centre for I.T. Solutions,
Guru Nanak Dev University,
Amritsar Punjab 143001,
India

Rajeev Kumar
Jyoti Chawla
Manav Rachna International Institute of Research and Studies,
Faridabad, Haryana 121004,
India

INTRODUCTION

Fluoride is present naturally in some groundwater sources and various food items which are grown using fluoride contaminated water. The source of fluoride in groundwater is mainly geogenic and includes fluoride minerals such as fluorite, rock phosphate, felspar and lepidolite in bedrocks (Patel *et al.* 2009; Lapworth *et al.* 2017). Anthropogenic sources of fluoride include urban waste, cow dung, fluoride-based insecticides or rodenticides, phosphatic fertilizers, and cement plants (Colombani *et al.* 2018). The permissible limit for fluoride concentration in drinking water as recommended by the World Health Organization is 1.5 mg/L (Craig *et al.* 2015). Fluoride ions if ingested beyond the permissible limit can cause gastrointestinal problems, interfere with bone formation, dental fluorosis, etc. (Dey & Giri 2015). It can also accumulate in the bone tissues of fish and in the exoskeleton of aquatic invertebrates (Buric *et al.* 2018). There have been extensive records of cases of fluorosis in India and across the world. Consumption of fluoride through water is one of the main routes of exposure. Brindha *et al.* (2011) analysed for fluoride concentration in 45 water samples from different wells in Nalgonda district in Andhra Pradesh and reported fluoride concentration in a range of 0.1 to 8.8 mg/L; 30% of the water samples possessed fluoride content of more than 1.5 mg/L which is a matter of great concern. Kheradpisheh *et al.* (2018) reported that fluoride in drinking water has an

impact on levels of T_3, T_4 and TSH hormones even when present in the standard concentration of less than 0.5 mg/L. The elevated fluoride content may lead to higher TSH values (greater impairment of thyroid function) which cause hypothyroidism in human beings. Due to the health hazards posed by an excess of fluoride content, it is essential to monitor the fluoride content in various sectors of the environment with a special focus on drinking water.

Different techniques may be used for defluoridation of drinking water. The adsorption method is found to be cheap, easy and efficient and can be applied for the removal of fluoride at a wide pH range under different sets of conditions. There is a requirement for cheaper and effective adsorbent materials that can work as efficient defluoridating agents under different sets of conditions. Various adsorbent materials for removal of fluoride ions from water have been reported in the literature (Dey *et al.* 2012; Nagaraj *et al.* 2017; Yang *et al.* 2017; Nagaraj & Rajan 2018; Zhu *et al.* 2018). The most frequently used adsorbents are activated charcoal and activated alumina (Emmanuel *et al.* 2008; Tang *et al.* 2009; Mullick & Neogi 2019). It has been reported in many studies that adsorption efficiency of materials becomes affected due to the variation in characteristics of water such as temperature, pH, adsorbent dose, contact time, etc. It is very important to optimize these variables in order to achieve the maximum defluoridation. Response surface methodology (RSM) may be applied for the optimization of input variables such as pH, adsorbent dose, contact time, initial concentration of target ions, in order to get the desired response in terms of percentage removal (Kaur *et al.* 2018). In the present study, attempts were made to synthesize micelle incorporated mesoporous material, MCM-41, and its application as an adsorbent for defluoridation of water. The variables affecting the adsorption process were further optimized by using Box–Behnken experimental design of RSM in order to achieve maximum defluoridation.

MATERIALS AND METHODS

Chemicals

Analytical grade reagents were used in all experiments. Tetraethylorthosilicate (TEOS) and 3-aminopropyl triethoxy silane (APTES) were purchased from Sigma-Aldrich. The surfactant, cetyltrimethylammonium bromide (CTAB) with 99% purity and standard solution of fluoride (1,000 mg/L) were procured from Merck. Double distilled water was used for preparing stock solutions and other dilute solutions of lower concentrations.

Preparation of MCM-41

A mixture of 2 g of CTAB, 7 mL sodium hydroxide (NaOH) and 80 mL of water was heated for 30 minutes at 80 °C. To the clear solution, 10 mL TEOS and 1.34 mL of 3-APTES were added. White precipitates were formed after 3 minutes stirring at 300 rpm. The reaction temperature was maintained at 80 °C for 2 hr. White precipitates thus obtained were filtered, washed and dried in a hot air oven for 24 hr. These white precipitates possessed template micelles within the framework of MCM-41 and were used as adsorbent without any additional processing, such as acid treatment or pyrolysis at an elevated temperature, which may lead to the loss of template micelles.

SPADNS spectrophotometric method

The SPADNS method was used to estimate the concentration of fluoride ion in aqueous solutions. It involves the use of acid zirconyl sodium-2-(parasulphophenylazo)-1,8-dihydroxy-3,6-naphthalene disulphonate (SPADNS) reagent, which was added to fluoride solutions. The method relies on the fact that when fluoride reacts with zirconium dye (red in colour), a colourless complex anion (ZrF_6^{2-}) and a dye are formed. The concentration of ZrF_6^{2-} complex is proportional to fluoride concentration which tends to bleach the dye and solutions become progressively lighter as the fluoride concentration increases. For construction of the calibration curve, solutions containing different concentrations of fluoride were treated with SPADNS and the resulting coloured complex was measured using Shimadzu UV-Visible Spectrophotometer Model UV 1800 at 580 nm and a plot was made between absorbance and concentration of fluoride solutions (in ppm).

Batch studies

Batch studies were conducted to arrive at the optimum conditions, such as contact time, dose of adsorbent, pH and temperature, to achieve the best performance of adsorbent, as described by Kaur *et al.* (2016). The distribution of adsorbate fluoride ions between solution and micelle templated MCM-41 was investigated using Langmuir, Freundlich and Temkin isotherm equations (Kumar *et al.* 2015; Kaur *et al.* 2016).

Response surface methodology

Optimization of experimental conditions was carried out to investigate the interactive effects of three independent variables on the percentage removal of fluoride using the Box–Behnken design (BBD) matrix. In the present study, the three independent variables used were initial concentrations of fluoride ion, pH, and adsorbent dose. The experiment was designed on the basis of results obtained from batch studies.

RESULTS AND DISCUSSION

Preliminary adsorption studies

The adsorption potential of micelle templated MCM-41 for the removal of fluoride ions from aqueous solution was investigated at different experimental conditions, such as contact time, pH, adsorbent dose, initial fluoride ion concentration and temperature, in order to select the range of parameters for the design of experiments through BBD and for isotherm studies. The results so obtained are discussed in the following sections.

Effect of contact time

The contact time strongly influences the adsorption process. Thirty mg/L fluoride solutions were taken with 1 g/L micelle templated MCM-41 for this study. The resulting solutions were shaken in a shaker for different times of contact (20 min–180 min). After the respective shaking, the solutions were filtered and analysed for fluoride ion

concentration. It was observed that the removal of fluoride first increases with an increase in contact time, then it becomes constant after 2 hr. This can be explained on the basis of the fact that initially all vacant sites on the adsorbent were unoccupied but as the time passes vacant sites decrease gradually and, ultimately, at equilibrium most of the vacant sites were occupied. Thus, the optimized contact time for fluoride ion removal was considered as 2 hr (Figure 1(a)).

Effect of adsorbent dose

The effect of adsorbent dose on the removal of fluoride was studied by using various doses of adsorbent (0.2–1.4 g/L). These doses were added to 30 mg/L solution of fluoride ion and after shaking for 2 hr the contents were filtered and analysed for remaining fluoride content in the solution. It was found that removal of fluoride first increases as the dose was increased from 0.2 g/L to 1 g/L then it become constant on further increasing the dose to 1.2 g/L and 1.4 g/L. This can be explained on the basis of the fact that as the dose was increased from 0.2 g/L to 1.0 g/L the availability of active sites keeps on increasing and resulted in an increase in fluoride removal. However, saturation of fluoride removal at 1 g/L suggested that there may be enough active sites available for fluoride adsorption on further increasing dose, but the active sites may remain vacant which may be attributed to overlapping of sorption sites as a consequence of overloading of adsorbent particles (Kaur *et al.* 2016). Thus, the optimum dose was taken as 1 g/L (Figure 1(b)).

Effect of pH

The effect of pH on the removal of fluoride ions using micelle templated MCM-41 was studied with 30 mg/L fluoride ion solutions of different pH ranging from 2 to 9. One g/L of adsorbent was added into fluoride solutions of different pH and the solutions were shaken for 2 hr in a shaker and the resulting solutions analysed for fluoride content. It was found that the removal of fluoride first increases from pH 2 to 6 followed by a gradual decrease from pH 6 to 9. At low pH, the protons are available in high concentrations and may combine with fluoride
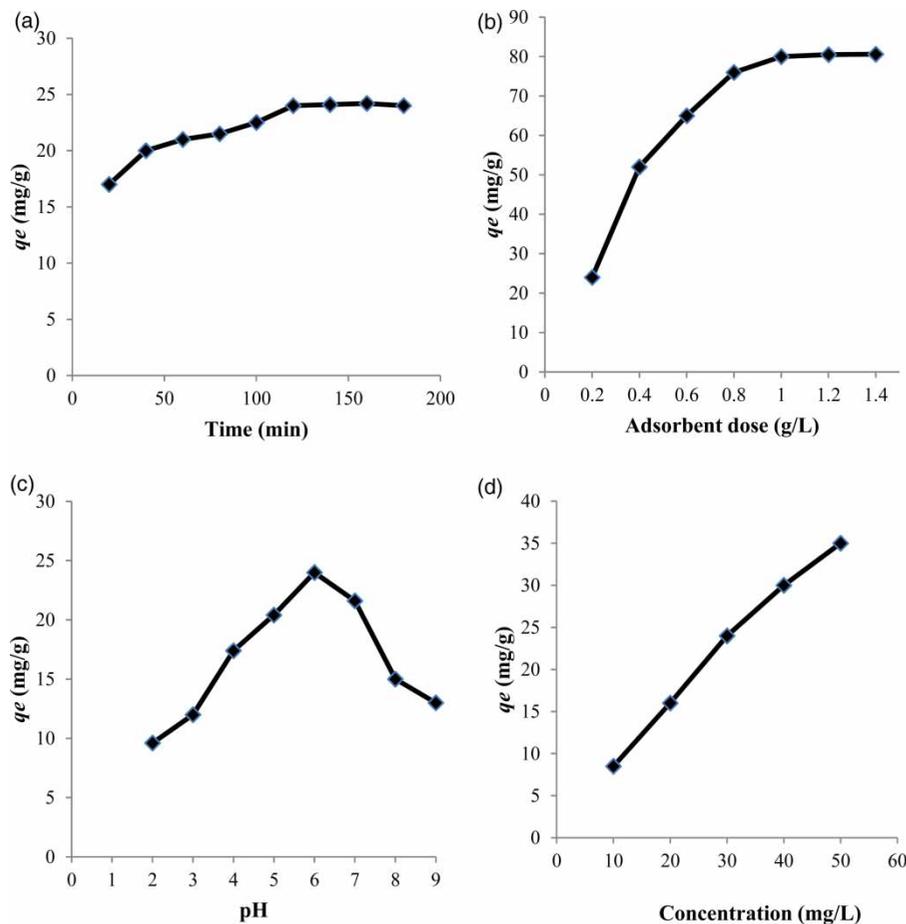
Figure 1 │ Effect of (a) contact time, (b) adsorbent dosage, (c) pH and (d) initial fluoride ions concentration, on adsorption of fluoride using micelle templated MCM-41 as adsorbent.

anions and provide hindrance towards their adsorption on the adsorbent via ion formation between fluoride and ammonium head groups in micelle templated MCM-41 framework. As the pH increases from 2 to 6, the concentration of protons decreases gradually, which led to an increase in probability of fluoride adsorption on the surface of adsorbent (Figure 1(c)). On the other hand, at pH > 6, hydroxyl anions may compete for cationic head groups of micelles and result in poor defluoridation. Thus, the optimum pH for the removal of fluoride ion was found to be 6 (Figure 1(c)).

Effect of initial fluoride concentration

The effect of initial fluoride ion concentration was studied by conducting batch experiments with various concentrations of fluoride ion solution ranging from 10 mg/L to 50 mg/L with optimum adsorption conditions: adsorbent dose 1 g/L and contact time 2 hr (Figure 1(d)). It can be seen that as the initial concentration of fluoride (C_o) increased from 10 mg/L to 50 mg/L, the equilibrium adsorption capacity of micelle templated MCM-41 for fluoride uptake increased from 8.5 mg/g to 35.0 mg/g, which indicated that the initial concentration of adsorbate strongly affected adsorption capacity and resulted in increased q_e with an increase in initial fluoride concentration (C_o). The C_o provides the necessary driving force to overcome the mass transfer resistance between adsorbate in the aqueous phase and adsorbent and also boosts the chances of interaction between adsorbate and the vacant sorption sites (ammonium head groups) on the surface of adsorbent (Suresh *et al.* 2011). Therefore, an increase in C_o enhances the adsorptive uptake of fluoride ions by micelle templated MCM-41.

Adsorption isotherm studies

An adsorption isotherm is characterized by certain parameters that express the surface properties and affinity of adsorbent for adsorbate. Equilibrium data can be analysed using different models for characterization of the adsorption process as well as feasibility of an adsorbent's application for pollutant removal from aqueous solution. Correlation among the concentration of pollutant and its binding on the surface of adsorbent at constant temperature can be determined. In the present study, Langmuir, Freundlich and Temkin isotherm models were used for the description of defluoridation using micelle templated MCM-41 at various temperatures: 298 K, 308 K, 318 K and 328 K.

Langmuir adsorption isotherm

The Langmuir isotherm model analyses the uptake of adsorbate on adsorbent surface and predicts whether adsorption is favourable or unfavourable. The Langmuir equation is given by:

$$C_e/q_e = 1/(q_{max}.K_L) + C_e/q_{max} \tag{1}$$

where C_e and q_e are equilibrium concentration and amount of adsorbate at equilibrium (mg/g), respectively, q_{max} and K_L are maximum adsorption capacity (mg/g) and equilibrium constant or Langmuir constant of adsorption. Langmuir adsorption isotherm was obtained by plotting C_e/q_e versus C_e at 298 K (Figure 2(a)). Maximum adsorption capacity for adsorption of fluoride ions using micelle templated MCM-41 and Langmuir constant were evaluated from slope and intercept, respectively, of the Langmuir adsorption isotherm. As shown in Table 1, the Langmuir isotherm confirmed better fit to experimental data than the Freundlich and Temkin isotherms for defluoridation. The Langmuir maximum adsorption capacity was found to be 52.91 mg/g and the equilibrium constant K_L was calculated as 0.131 L/mg.

The feasibility of the adsorption can be expressed in terms of separation factor (R_L):

$$R_L = 1/(1 + K_L C_o) \tag{2}$$

where K_L and C_0 are Langmuir constant and initial fluoride ion concentration (mg/L), respectively. Separation factor indicate the feasibility of adsoprtion. Separation factor calculated by the Langmuir model at a selected concentration of fluoride ions (30 mg/L) was found to be 0.202, which indicated that the process is favourable.

Freundlich adsorption isotherm

The Freundlich isotherm is appropriate for non-ideal adsorption on heterogeneous surfaces. The Freundlich equation is given by:

$$ln \; q_e = ln \; K + 1/n \; ln \; C_e \tag{3}$$

where C_e and q_e are equilibrium concentration and amount of adsorbate at equilibrium (mg/g), respectively. K_F and $1/n$ are Freundlich constant and heterogeneity factor of adsorption, respectively, n is measure of deviation from linearity of adsorption. Freundlich adsorption isotherms were obtained by plotting lnq_e versus lnC_e at different temperatures (Figure 2(b)). The Freundlich isotherm was found to be linear and results are summarized in Table 1. K_F indicated the adsorption capacity of the adsorbent and its value was calculated as 7.18 (mg/g) $(L/g)^{1/n}$. The value of n varies from 1 to 10 for favourable adsorption (Chantawong *et al.* 2003). For defluoridation using micelle templated MCM-41, the value of n was found to be 1.62, indicating favourable adsorption. Micelle templated MCM-41 showed high adsorptive tendency towards fluoride that can be also explained on the basis of $1/n$ value of the Freundlich equation (Ding *et al.* 2016). The value $1/n < 1$ indicates normal adsorption and greater heterogeneity (Li *et al.* 2004; Madannejad *et al.* 2018). In the present study, the value of $1/n$ is 0.61, which indicated normal adsorption and greater heterogeneity.

Temkin adsorption isotherm

The Temkin isotherm is based on the assumption that the free energy of adsorption is a function of surface coverage. The Temkin adsorption isotherm equation is given by:

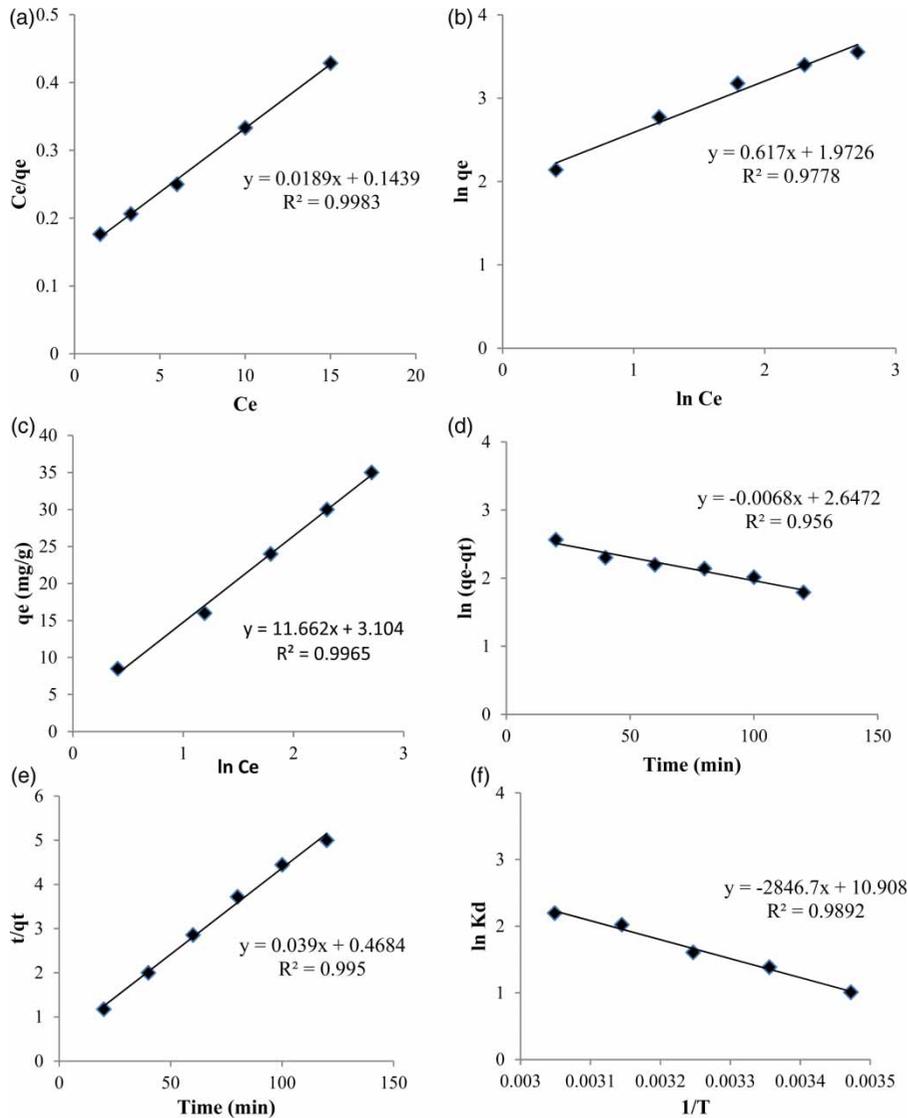$$q_e = B \; ln \; A + B \; ln \; C_e \tag{4}$$

Figure 2 │ Isotherm and kinetic models: (a) Langmuir, (b) Freundlich, (c) Temkin, (d) pseudo-first order kinetic model, (e) pseudo-second order kinetic model, (f) Van't Hoff equation, for adsorption of fluoride on micelle templated MCM-41.

Table 1 │ Isotherms models for adsorption of fluoride ions on micelle templated MCM-41

Adsorbent	Langmuir			Freundlich			Temkin			
	q_{max} (mg/g)	K_L (L/mg)	R^2	n	K_F (mg/g)(L/g)$^{1/n}$	R^2	B (J/mol)	b	A (L/min)	R^2
Micelle templated MCM-41	52.91	0.131	0.998	1.62	7.18	0.977	11.66	212.38	1.303	0.996

where A and B are Temkin isotherm constants. The value of B (slope) is equal to (RT/b) and related to heat of sorption. R is the gas constant (8.314 J/mol K) and T is the absolute temperature. C_e and q_e are equilibrium concentration and amount of adsorbate at equilibrium, respectively. Temkin adsorption isotherms were obtained by plotting q_e versus lnC_e (Figure 2(c)). The intercept is represented by $B\ ln\ A$ and can be calculated by linear

plot of the Temkin adsorption isotherm (Figure 2(c)). A is the equilibrium binding constant (L/min) corresponding to the maximum binding energy. The calculated parameters are summarized in Table 1. Heat of adsorption (B) obtained from the Temkin isotherm was found to be 11.66 J/mol, which was less than 40 kJ/mol and indicated physical adsorption of fluoride on the surface of micelle templated MCM-41.

Kinetic study

Adsorption of fluoride ions on the surface of micelle templated MCM-41 was studied by pseudo-first order and pseudo-second order kinetics. The linear equation of pseudo-first order can be expressed as:

$$ln(q_e - q_t) = ln(q_e) - k_1 t \qquad (5)$$

where q_e and q_t are amount adsorbed at equilibrium time (mg/g) and any time t, respectively. k_1 is the rate constant for first order adsorption (Figure 2(d)).

The linear equation of pseudo-second order can be expressed as:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \qquad (6)$$

where q_e and q_t are amount adsorbed at equilibrium time (mg/g) and any time t, respectively. k_2 is the rate constant for second order adsorption (Figure 2(d)).

The value of square of regression correlation coefficient (R^2) was used to identify the close agreement between predicted and experimental value. The value of R^2 of pseudo-second order kinetics was found to be very close to unity compared to pseudo-first order kinetics. Table 2 indicated that model is best explained by pseudo-second order kinetic model. The calculated q_e value (25.64 mg/g) was found to be in excellent conformity with experimental q_e

value (24 mg/g), which confirmed that the kinetics of adsorption of fluoride using micelle templated MCM-41 was best explained by the pseudo-second order model in comparison to pseudo-first order model. Therefore, it can be concluded that the rate-limiting step of fluoride ions adsorption on MCM-41 may be chemical adsorption.

Thermodynamics of adsorption

Adsorption of fluoride ions using micelle templated MCM-41 was studied at different temperatures, i.e., 288 K, 298 K, 308 K, 318 K and 328 K. The thermodynamic parameters, i.e., free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o) were calculated to get information regarding the spontaneity and feasibility of the adsorption phenomenon using the following equation:

$$lnK_D = \Delta S^o/R - \Delta H^o/RT \qquad (7)$$

where K_D ($=q_e/C_e$) is thermodynamic constant, R and T are universal gas constant (8.314 KJ/mol) and absolute temperature (K), respectively. C_e and q_e are equilibrium concentration and amount of adsorbate at equilibrium (mg/g), respectively. The thermodynamic parameters were obtained by plot of lnK_D versus $1/T$ at different temperatures (Figure 2(f)). The slope and intercept of the linear plot represent $\Delta H^o/R$ and $\Delta S^o/R$, respectively. The calculated parameters are summarized in Table 3. The positive entropy change ΔS^o indicated that the randomness increases during the adsorption process. Also, the positive enthalpy change ΔH^o indicated that the adsorption was endothermic. By using the values of ΔS^o and ΔH^o, free energy change (ΔG^o) associated with adsorption of fluoride was obtained and the negative values of ΔG^o at different temperatures indicated the spontaneous nature of the adsorption process.

Table 2 │ Kinetics models for adsorption of fluoride ions on micelle templated MCM-41

Adsorbent	Pseudo-first order kinetics			Pseudo-second order kinetics			q_e, exp. (mg/g)
	q_e (mg/g)	k_1	R^2	q_e (mg/g)	k_2	R^2	
Micelle templated MCM-41	14.11	0.0068	0.956	25.64	0.00325	0.995	24

Table 3 | Thermodynamic parameters for adsorption of fluoride ions on micelle templated MCM-41

| Adsorbent | ΔG^o (kJ/mol) | | | | | ΔH^o (kJ/mol) | ΔS^o (kJ/mol/K) |
| | Temp. (K) | | | | | | |
	288 K	298 K	308 K	318 K	328 K		
MCM-41	−2.27	−3.17	−4.07	−4.97	−5.87	23.65	0.090

Mechanism of adsorption of fluoride by MCM-41

Micelle templated MCM-41 was prepared by co-condensation method. The reaction was stopped at the stage when the MCM-41 framework was formed around the template micelles of the surfactant CTAB. The material used as an adsorbent consisted of template micelles within the pores of MCM-41 (Trofymchuk *et al.* 2016). Adsorption of the fluoride ions from water on MCM-41 could be explained by hydrophilic interactions between the fluoride ions in water and cationic head groups, cetyltrimethyl ammonium of surfactant in the template. The fluoride ions are trapped in the template of CTAB by ion pair formation (Figure 3) which is responsible for defluoridation of water (Zhang *et al.* 2019).

In order to confirm the adsorption of fluoride on the surface of micelle templated MCM-41, FT-IR spectra of adsorbent before and after adsorption were recorded using a Fourier Transform Infrared Spectrometer (Cary 630, Aglient Technologies). The spectra obtained are shown in Figure 4. The band at 3,436 cm^{-1} in IR spectra of micelle templated MCM-41 is a characteristic band of Si-OH vibration. Also, the vibration bands at 2,922 cm^{-1}, 2,855 cm^{-1} and 1,483 cm^{-1} are characteristic bands of asymmetric and symmetric stretching of –CH$_2$ groups in the micelle template. The band at 790 cm^{-1} is due to symmetrical stretching of Si-O-Si vibrations. Considerable changes were observed in frequency bands after adsorption of fluoride ions. The band at 3,436 cm^{-1} becomes significantly broadened after interaction of fluoride ions with quaternary nitrogen of ammonium group resulting in the formation of ion pairs (Dey *et al.* 2012). Moreover, the intensity of bands at 2,922 cm^{-1} and 2,855 cm^{-1} slightly increased, which confirmed the adsorption of fluoride on the surface of micelle templated MCM-41.

In the present study, the results obtained from the Temkin isotherm indicated physical adsorption of fluoride on the surface of micelle templated MCM-41. On the other hand, pseudo-second order kinetic studies support the chemical adsorption process which involves ion-pair formation between fluoride ions and positively charged ammonium head groups. On the basis of the results obtained, it can be concluded that adsorption behaviour of micelle templated MCM-41 for defluoridation involved both physical as well as chemical adsorption. It was also found in the literature that both processes, i.e., physical and chemical adsorption, may occur simultaneously or alternatively (Gisi *et al.* 2016).

Optimization studies

Experiments were designed using the BBD that provide logical information for testing lack of fit with a lesser number of experiments. Information was further used for optimization of three variables (Table 4) and to further understand their interactive effects.

Analysis of variance (ANOVA)

The sufficiency of the model was determined by ANOVA. Table 5 includes the related analysis of variance for adsorption

Figure 3 | Mechanism for defluoridation of water by adsorption on micelle templated MCM-41 through ionic interactions with cationic micelle template.
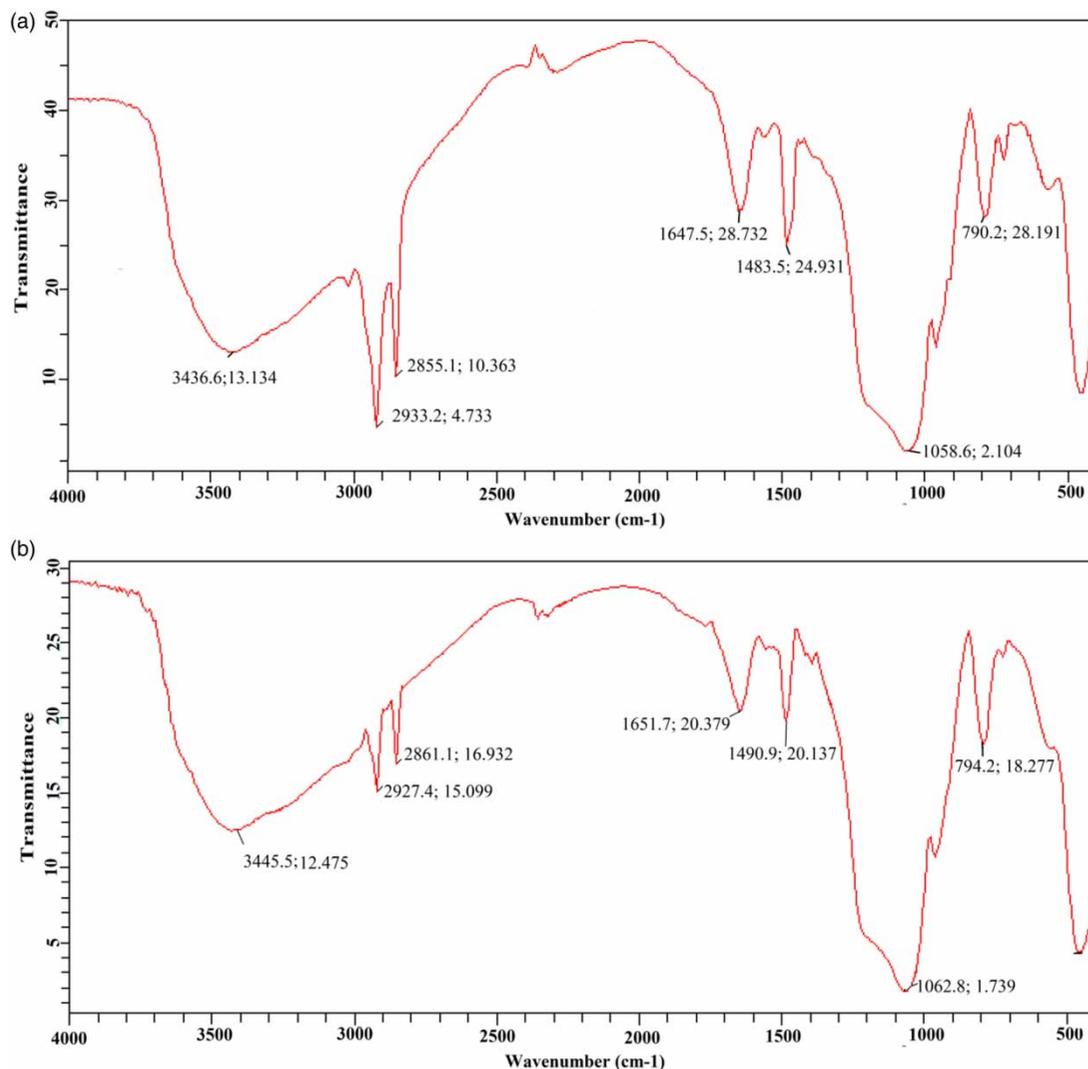
Figure 4 │ FT-IR spectra of micelle templated MCM-41 (a) before and (b) after adsorption of fluoride ions.

capacity with initial concentration (A), pH of medium (B) and adsorbent dose (C). The quadratic model F-value of 8,578.57 confirms the significance of the model where A, B, C, AB, AC, A^2, B^2, C^2 are significant model terms. In model summary statistics (Table 6), 'Pred R-squared' of 0.9985 is in reasonable agreement with the 'Adj R-squared' of 0.9998. The final equation in terms of coded factors is:

$$\% \text{ removal} = -80 - 4.75\ A + 3.875\ B + 2.375\ C - 0.5\ AB$$
$$- 3.5\ AC + 0.25\ BC - 4.88\ A^2 - 42.13\ B^2 - 4.13\ C^2 \quad (8)$$

In each term, coefficients with one independent variable represent the effect of that specific factor, while the term with two coefficients indicates the interaction between those two factors. A positive term signifies a synergistic effect, whereas a negative signifies an antagonistic effect up to a certain value. The predicted removal percentages versus the observed values are shown in Figure 5, which shows that the predicted value of percentage removal per cent is in agreement with the experimental value with a negligible error.

Response surface (RS) plots

The graphical illustration of the response surface of the adsorbed fluoride ions relative to the three variables was used to understand the interactions between variables and

Table 4 | Coded level for independent variables

Factor	Name	Low actual (code − 1)	High actual (code 1)
A	Concentration (ppm)	10	50
B	pH	2	9
C	Adsorbent dose (g/L)	0.6	1.4

validate the optimal level of each variable to the highest removal percentage. The response surface (RS) plots are shown in Figure 5(a)–5(c). It can be seen from Figure 5(a) (at fixed adsorbent dose of 1.4 g/L) that removal percentage was good (approximately 82%) at a lower initial concentration range (10–17 ppm) with pH values in the range of 5.6–5.8. The maximum observed value at this dose was 81.86%. Figure 5(b) analyses the removal percentage at fixed pH value of 5.5. It depicts the maximum removal (82%) within the concentration range of 10–21 ppm and adsorbent dose of 1.1 to 1.34 g/L. It can be observed from Figure 5(c) that at a fixed concentration of 20 ppm, the maximum removal percentage can be obtained at pH 5.4–5.8, keeping adsorbent dose in range (1.1–1.28 g/L). It is important to highlight that all the plots depict the maximum removal of 82% that can be achieved at initial concentration

up to 21 ppm keeping adsorbent dose 1.3 g/L at pH not more than 5.8. Best pH range is 5.4–5.8 corresponding to adsorbent dose 1–1.3 g/L.

Practical implications of current work

It is well known that fluoride is safe for dental health at low concentrations but its consumption in large amounts is very hazardous. An excess of fluoride has been prevalent in the roundwater of India where the soil is heavily loaded with fluoride minerals such as fluorite, rock phosphate, feldspar and lepidolite. In such regions, the drinking water was found to be generally contaminated with fluoride ions beyond permissible limits (Patel *et al.* 2009). The groundwater is also polluted with fluoride due to some anthropogenic sources, i.e., cement plants, aluminium plants, etc. There is an urgent need for cheap and efficient defluoridation methods in order to ensure the safer concentrations of fluoride content in drinking water and aquatic bodies. The present study is very useful for practical application as it provides a very economic method for water treatment.

Attempts were made to compare the performance of micelle templated MCM-41 with other adsorbents already available in the literature to explore its effectiveness as an

Table 5 | ANOVA for response surface quadratic model

Source	Sum of squares	df	Mean square	F value	*p*-value prob > F
Model	8,272.191	9	919.1324	8,578.569	<0.0001
A – Concentration	180.5	1	180.5	1,684.667	<0.0001
B – pH	120.125	1	120.125	1,121.167	<0.0001
C – Adsorbent dose	45.125	1	45.125	421.1667	<0.0001
AB	1	1	1	9.333333	0.0185
AC	49	1	49	457.3333	<0.0001
BC	0.25	1	0.25	2.333333	0.1705
A^2	100.0658	1	100.0658	933.9474	<0.0001
B^2	7,471.645	1	7,471.645	69,735.35	<0.0001
C^2	71.64474	1	71.64474	668.6842	<0.0001
Residual	0.75	7	0.107143		
Lack of fit	0.75	3	0.25		
Pure error	0	4	0		
Cor total	8,272.941	16			

Table 6 │ Model summary statistics

Source	Std. dev.	R-squared	Adjusted R-squared	Predicted R-squared	PRESS
Linear	24.6938	0.041793	−0.17933	−0.66841	13,802.68
2FI	28.06589	0.047867	−0.52341	−2.48942	28,867.76
Quadratic	0.327327	0.999909	0.999793	0.998549	12

adsorbent for defluoridation of water. The adsorbents showing a capacity for water defluoridation that have attracted

Figure 5 │ 3-D surface plots for adsorption of fluoride ions on micelle templated MCM-41.
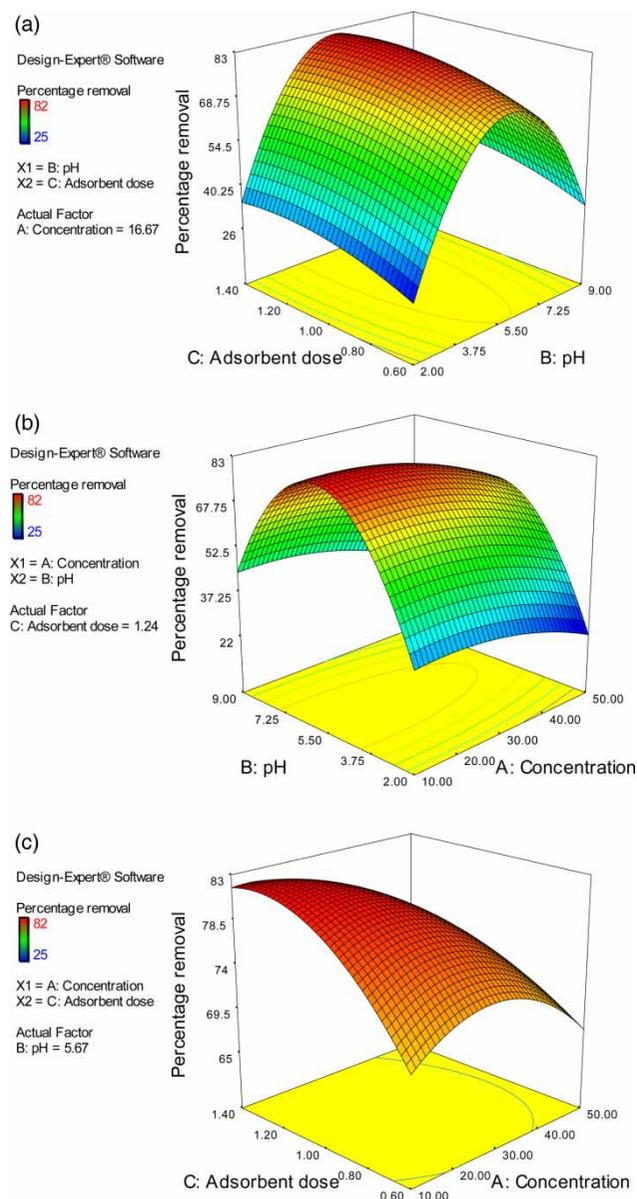
the most attention include hydroxyapatites, montmorillonites, zeolites, ceramics, ferrihydrites, hydrotalcite, palygorskites, boehmite/bauxite (Wambu *et al.* 2015). On the basis of their defluoridation capacities (in mg/g), the various adsorbents may be ordered as:

Ceramics (1.699) < Montmorillonites (3.365) < Zeolites (4.13) < Kaolinite-ferrihydrite (12.83) < Hydroxyapatite (13.268) < Calcium hydroxyapatite (16.38) < Limestone derived apatite (22.22) < Al^{3+}-modified calcium hydroxyapatite (32.57) < Micelle templated MCM-41 (52.91) (Present work)

It can be seen that all the above-mentioned adsorbents show inferior adsorption capacity in comparison to micelle templated MCM-41 and also involve high costs of synthesis. Hence, it can be concluded that due to the presence of micelle in pores which allow the formation of ion pairs between positively charged ammonium head groups and fluoride anions, micelle templated MCM-41 could serve as an effective and economic defluoridating agent.

CONCLUSION

Defluoridation of water using micelle templated MCM-41 through adsorption of fluoride ions via ion-pair formation between fluoride ions and ammonium head groups of surfactant present in the pores of MCM-41, provides as an effective water treatment method. Removal of fluoride ion from aqueous solution (10–21 ppm) was observed as maximum under optimized conditions: pH 5.4–5.8, adsorbent dose 1.0–1.34 g/L and contact time 2 hr. The best fitted isotherm was the Langmuir adsorption isotherm, thus suggesting monolayer adsorption of fluoride ion onto mesoporous material (MCM-41). The maximum Langmuir adsorption capacity was 52.91 mg/g. The results obtained

from batch mode and RSM studies showed that micelle templated MCM-41 can be used as a viable and economic adsorbent for the removal of fluoride ions from aqueous solution.

ACKNOWLEDGEMENTS

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