

Optimizing the fluoride removal from water using a novel adsorbent prepared from Waste Cerastoderma edule shell with Kinetic, Equilibrium, and Thermodynamic studies

Shreyas Singh

dt26civ001@students.vnit.ac.in

Visvesvaraya National Institute of Technology

Ajay Tembhurkar

Visvesvaraya National Institute of Technology

Research Article

Keywords: Food Waste. Defluoridation. Taguchi optimization. Adsorption. Kinetics. Isotherms. Thermodynamics

Posted Date: October 1st, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10955880/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Optimizing the fluoride removal from water using a novel adsorbent prepared from Waste *Cerastoderma edule* shell with Kinetic, Equilibrium, and Thermodynamic studies

Mr. Shreyas. R. Singh^{1*} and Dr. Ajay. R. Tembhurkar²

¹ *Research Scholar, Department of Civil Engineering, Visvesvaraya National Institute of Technology, Nagpur, 440 010, Maharashtra, India; 9967036622; e-mail: dt26civ001@students.vnit.ac.in*

² *Professor, Department of Civil Engineering, Visvesvaraya National Institute of Technology, Nagpur, 440 010, Maharashtra, India; 9850363905; e-mail: artembhurkar@civ.vnit.ac.in*

Abstract

Conversion of waste materials into useful resource is emerging and development of a low-cost adsorbent from waste materials into useful adsorbent for defluoridation of water is no exception. The present research developed a new chemical-thermal activated adsorbent from calcium carbonate rich marine waste. *Cerastoderma Edule* shell material for defluoridation of water. Taguchi's L16 orthogonal array is applied to optimize the adsorption process for maximum (F-) removal from water. Analysis of mean using S/N ratios, provided optimum values of process parameters as temperature 30°C, initial (F-) concentration 20 ppm, dosage 4 g/L, pH 3, and contact time of 60 minutes for maximum removal efficiency of 94% with adsorbent capacity as 4.8 mg/g. Analysis of variance revealed the percentage contribution of parameters as Temperature 5.24%; Initial F concentration 16.78%; pH 25.49%; Dose 18.81%; and contact time 11.45%, showing pH as the most contributing parameter. For better understating of adsorption process using waste *Cerastoderma Edule* shell adsorbent, equilibrium, kinetics and thermodynamic studies are also conducted on optimum conditions. Equilibrium studies revealed it better fit to Freundlich isotherm signifying that the process involved multilayer adsorption on a heterogeneous surface. Best fitting kinetic model pseudo-second order and the thermodynamic analysis revealed that the process was spontaneous, endothermic, and entropy driven, favouring higher temperatures. For adsorbent material characterization, SEM and EDS tests indicate the adsorption (F-) on the adsorbent material, while FTIR test revealed that the other surface functional groups remained similar through adsorption process. The present adsorbent developed from marine waste *Cerastoderma Edule* shell is effective for defluoridation.

Keywords: Food Waste. Defluoridation. Taguchi optimization. Adsorption. Kinetics. Isotherms. Thermodynamics

1. Introduction

Finding suitable defluoridation method for fluoride (F⁻) contamination water especially from ground source is always a major concern [7, 24]. Excessive presence of (F⁻) in water poses a significant health risks like skeletal and dental fluorosis, and socio-economic disruptions [3, 7, 20, 24, 40]. The WHO guidelines suggest (F⁻) in drinking water should not exceed more than 1.5 mg/L of [13]. Several defluoridation techniques are investigated and employed but each have their own limitations like high cost, complexity, toxicity etc [18, 22, 27, 30, 36, 39]. Among them the adsorption method stands out as superior as it is simple cost effective, flexible, environmentally compatible and easy to operation [38]. In the recent years, developing new adsorbents through exploration of waste-to-resource pathways is highly emerging.

Historically, a wide range of materials have been used to develop adsorbents including alumina and aluminium based adsorbents, biosorbents, ion-exchange resins, calcium based compounds, carbon based materials, and polymer based sorbents for removing (F⁻) ions from aqueous environment [41]. Recently, the research interest has shifted toward utilizing waste-derived materials that are available in abundance, low-cost, affordable and environmentally sustainable alternatives to conventional adsorbents [11, 31]. Waste materials rich in calcium like Chitosan are preferably used for developing adsorbents for fluoride removal as they have high affinity towards fluoride ions. [8].

Cerastoderma Edule shells is one of the marine wastes is hydroxyapatite-like materials with approximately 96-99% CaCO₃ provide good potential to adsorb (F⁻) from aqueous solutions because calcium has high affinity toward (F⁻) ion [28]. Moreover, this marine waste is biocompatible, generated in abundance and is often dumped in landfill or the sea [19]. It provides an excellent opportunity to be get converted into useful adsorbent through simple, energy efficient and low-cost process for remote rural areas [42].

As such, the present research envisages to use waste *Cerastoderma Edule* shells to convert it into new adsorbent suitable for (F⁻) removal. A chemical and thermal technique is used to activate this adsorbent to provide enhance (F⁻) removal. An in-depth laboratory scale investigation is done to have proper insight of the adsorbent developed through material characterization. SEM, FTIR and EDS was utilized to know the composition and analyse for

it's elemental composition before and after adsorption. The process optimization is done using Taguchi's L16 (4^5) orthogonal array to provide accurate results with minimum runs of experimentation. Moreover, batch experiments studies are also conducted to understand equilibrium, kinetics, and thermodynamic behaviour and the important constants are determined.

2. Materials and Methodology

2.1. Reagents and Adsorbent preparation

The fluoride stock solution of 100 mg/L concentration was prepared by dissolving 221 mg of anhydrous sodium fluoride of Analytical Reagent (AR) grade and double distilled water (DDW). Further, dilutions yielded the required working concentrations. The reference solution and Acid Zirconyl-SPADNS reagent were prepared following the standard spectrophotometric method (SPADNS) [14].

Cerastoderma Edule shells, were crushed and sieved to particle size of 180-500 μm . The sieved material was washed with DDW, then oven-dried at 100°C for 3 hours. The dried powder was then mixed with 0.1 N H_3PO_4 in a 1:5 (w/v) ratio and stirred at 80 RPM for 10 minutes using a jar test apparatus. Subsequently, the pH was raised to 10 with 1 N NaOH, and the mixture was left standing for 24 hours. The solid particles were filtered, washed with DDW to neutral pH, and dried again at 100°C for 3 hours in oven (LABIX LBX-102 Make). Finally, the material was calcined at 800°C for 3 hours in muffle furnace (I-THERM Make) to produce the final adsorbent (Fig. 1).

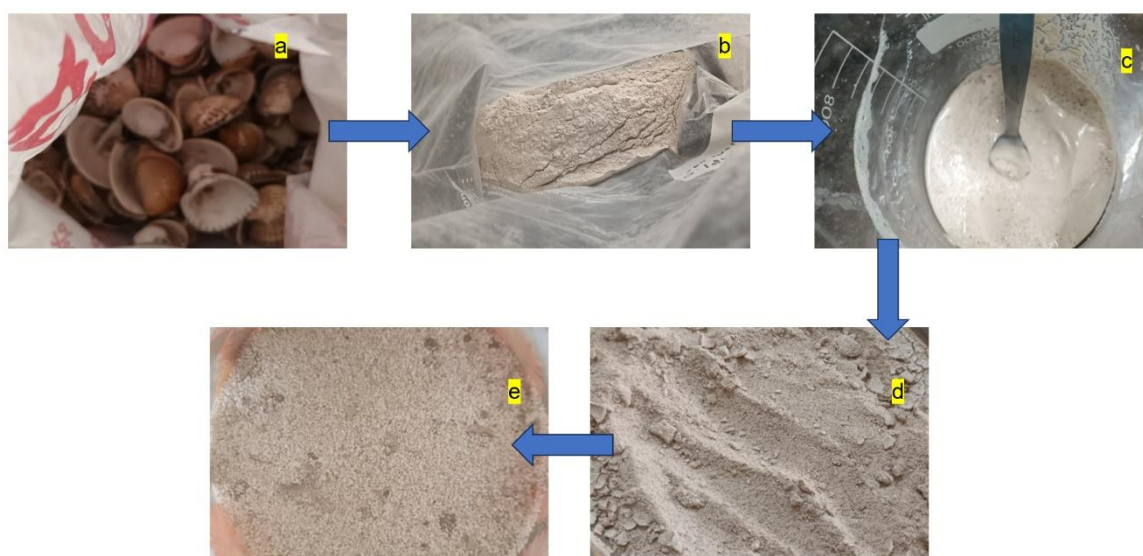


Fig. 1 (a) Cerastoderma Edule shell, (b) powered and washed shell, (c) chemical treatment, (d) post drying, (e) thermal treatment.

2.2. Batch Adsorption Experiments

Batch adsorption experiments were carried out in standard conical flasks of volume 250 mL containing 100 mL of (F-) solution and the adsorbent, placed in an orbital shaker (LABIX LBX-107 Make). SPADNS method was used to determine (F-) concentration by using UV-VIS spectrophotometer (LABINDIA UV 3200TS Make).

The percentage of (F-) removal was calculated using the Equation (1) :

$$R\% = \frac{(C_o - C_e)}{C_o} \times 100\% \quad \dots(1)$$

Where, C_o and C_e represent the initial and equilibrium concentrations, respectively.

Equation (2) was used to determine the amount of fluoride (F-) adsorbed per unit mass of adsorbent.

$$qe = \left(\frac{V}{m}\right) \times (C_o - C_e) \quad \dots(2)$$

Where, V is the volume of solution in Liters. m is the mass of adsorbent in grams.

Further separate batch experimentation was done to determine equilibrium, kinetic, and thermodynamic parameters under optimum conditions.

2.3. Taguchi Approach for Optimization of Process Parameters

Adsorption experiments were conducted according to the L16 orthogonal array design. For each of the 16 runs, a 250 ml conical flask containing 100 ml of (F-) solution and the prepared adsorbent was agitated in an orbital shaker. The parameters/Factors and the levels are given in Table 1.

Table 1 Process Parameters and their Levels.

Factors	Levels			
	1	2	3	4
A (Temperature)	10 °C	20 °C	30 °C	40 °C
B (Initial concentration)	5 ppm	10 ppm	15 ppm	20 ppm
C (pH)	3	4.5	6	7.5
D (Dose)	1 g/L	2 g/L	3 g/L	4 g/L
E (Contact time)	30 min	60 min	90 min	120 min

3. Results & Discussion

3.1. Adsorbent Characterization

The Scanning Electron Microscope is used to analyse the material's surface, grain size, morphology and chemical composition. Fig. 2(a) and 2(b) show the SEM images of the adsorbent before/after adsorption, respectively. 5 microns at x5000 magnification. In Fig. 2(a) jagged, a cracked surface with voids can be observed. In Fig. 2(b) the surface has become uniform and filled.

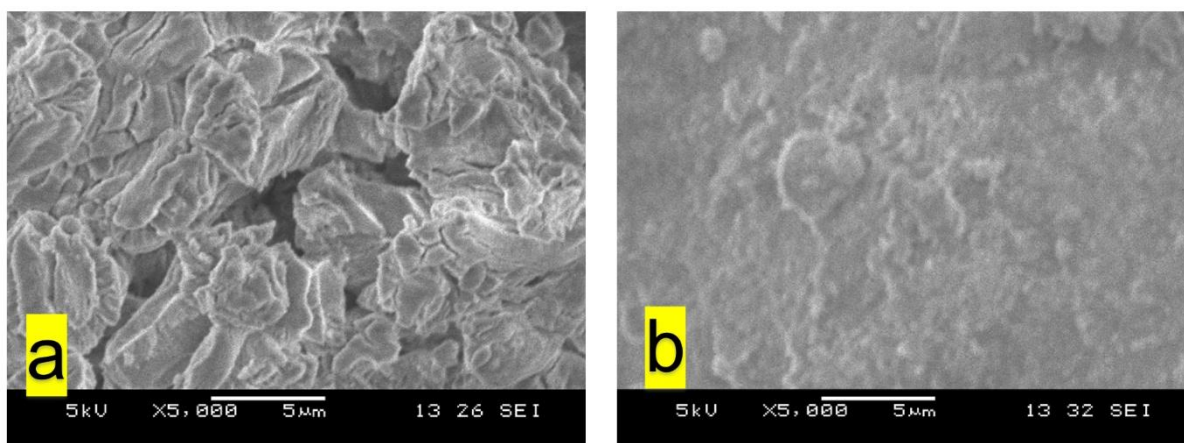


Fig. 2 Scanning Electron Microscope Images: (a) Before Adsorption, (b) After Adsorption

In order to better understand the elemental composition of the adsorbent, the Energy Dispersive Spectroscopy was done. Figures 3(a) and 3(b) show EDS of adsorbent before/after adsorption, respectively. The appearance of (F-) after adsorption confirms the (F-) removal. Calcium,

Oxygen, Sodium, Carbon and Silicon were detected in the sample with some changes in their percentage by weight contribution. The percentage by weight contribution after adsorption clearly increased from 0% to 1.76%, displaying (F-) adsorption.

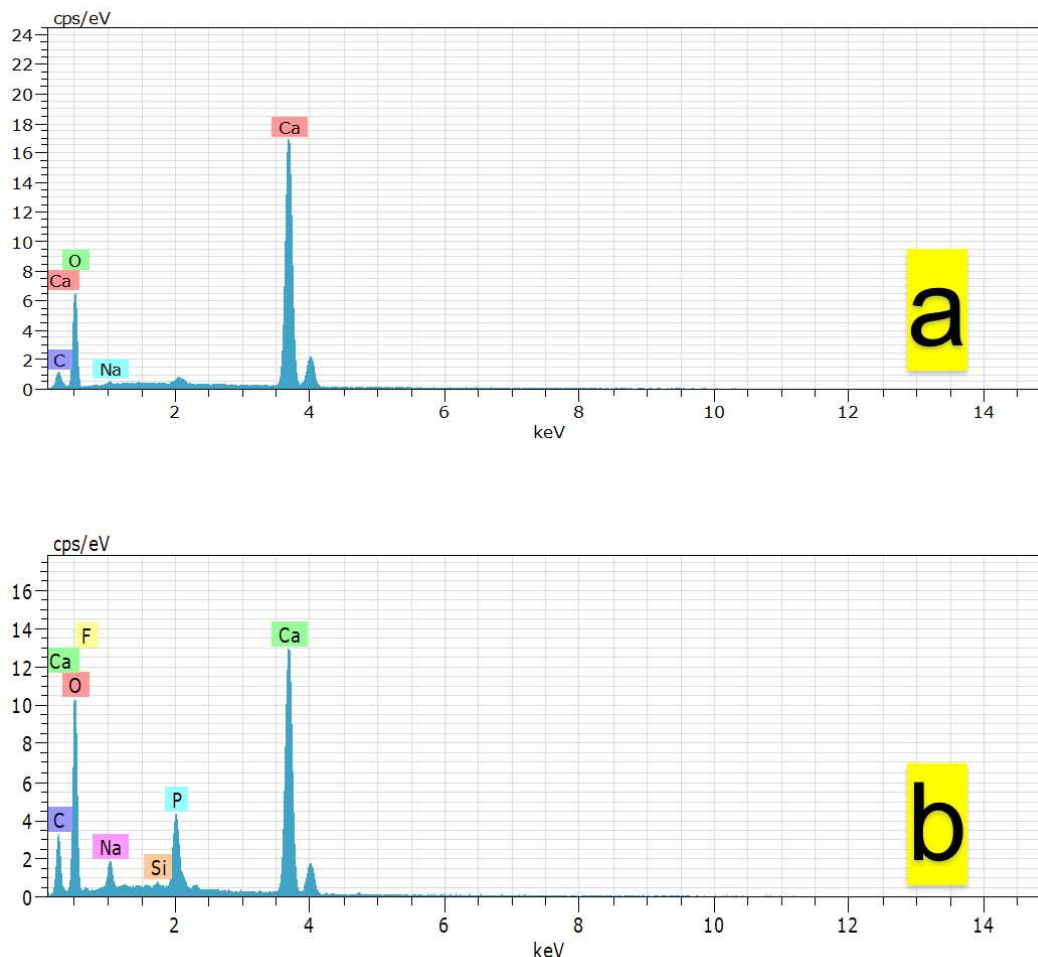


Fig. 3 Energy Dispersive Spectroscopy: (a) Before adsorption, (b) After adsorption

The FTIR spectrum of the adsorbents were recorded before/after adsorption to obtain the information regarding the vibrations (stretching and bending) of the functional groups which are likely to be involved in the sorption of the adsorbate molecules. Fig. 4 shows the FTIR spectra before/after adsorption.

The similarity of the FTIR spectra before and after adsorption confirms the structural integrity of the adsorbent. Hydroxyl groups may be from a sharp peak at 3643 cm^{-1} . Bands at 2984 cm^{-1} and 2870 cm^{-1} seem to suggest that C-H stretches that may be from organic impurities. Carbonate related bands appeared at 2511 , 1795 , and 712 cm^{-1} , though their intensity shifts

following adsorption seem to point to (F-) induced changes. More displays of carbonate alteration may include a peak intensity change at 1487 cm^{-1} and shifts in associated bands from 1403 to 1053 , then 1068 to 1051 , and 875 to 874 cm^{-1} . A shift in the metal-oxygen (which is likely to be Ca-O) band from 583 to 568 cm^{-1} further indicating the effect of adsorption on the lattice structure [1, 29].

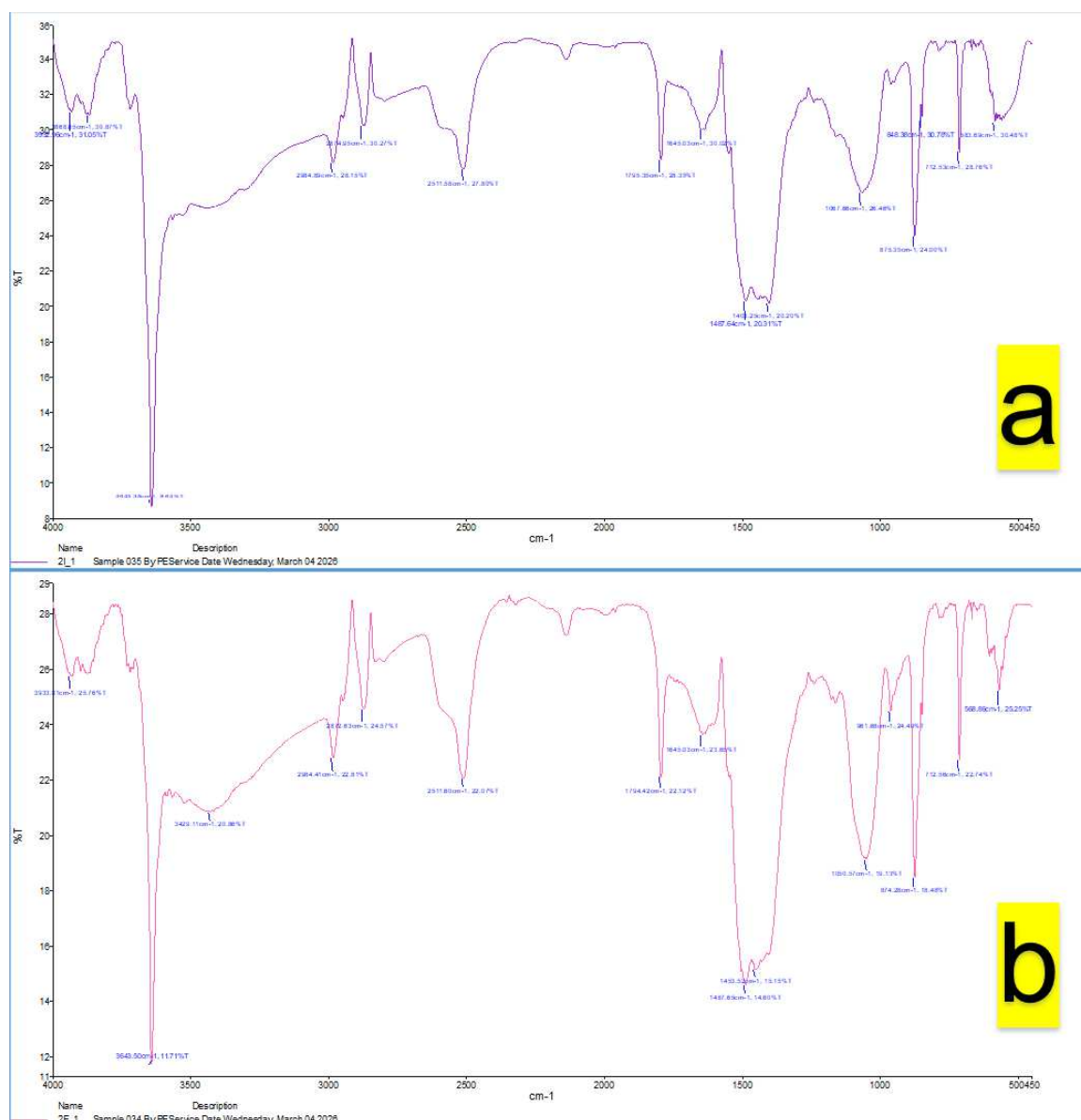


Fig. 4 Fourier Transform Infrared Spectroscopy spectra: (a) Before adsorption (b), After adsorption

3.2. Optimization of Process Parameters

3.2.1. Mean S/N values estimation

L16 orthogonal array was used to maximize the (F-) removal. 16 experimental runs, with 3 replicates were done to obtain the experimental responses (% average removal and S/N), as shown in Table 2. There are 3 categories of formulas to calculate the S/N ratio. Among them, ‘Larger the better’ was selected, since the goal of the study is (F-) removal.

The Signal to Noise S/N ratio is calculated using Eq. 3.

$$\frac{S}{N} = -10 * \log \left[\left(\frac{1}{n} \right) * \sum \left(\frac{1}{Ri^2} \right) \right] \quad \dots\dots\dots(3)$$

Where, n is the number of replicates and Ri is the removal percentages for that given experimental run.

Table 2 Flouride Removal & Corresponding S/N Ratios

Run	Combinations					Trial runs			avg Removal %	S/N Values
	A	B	C	D	E	R%1	R%2	R%3		
1	1	1	1	1	1	63.32	59.77	65.54	62.88	35.95
2	1	2	2	2	2	70.79	72.35	71.68	71.61	37.09
3	1	3	3	3	3	65.58	62.37	64.10	64.02	36.12
4	1	4	4	4	4	84.53	86.56	87.49	86.19	38.70
5	2	1	2	3	4	68.64	66.43	65.54	66.87	36.50
6	2	2	1	4	3	92.08	88.09	90.31	90.16	39.09
7	2	3	4	1	2	63.61	58.43	95.36	72.47	36.64
8	2	4	3	2	1	66.98	73.07	69.19	69.75	36.85
9	3	1	3	4	2	80.62	75.29	78.40	78.10	37.84
10	3	2	4	3	1	65.92	61.04	70.79	65.92	36.33
11	3	3	1	2	4	88.49	90.21	90.95	89.89	39.07
12	3	4	2	1	3	76.03	73.26	71.78	73.69	37.34
13	4	1	4	2	3	58.00	57.11	56.67	57.26	35.15
14	4	2	3	1	4	58.38	60.82	60.59	59.93	35.54

15	4	3	2	4	1	72.23	69.52	70.75	70.83	37.00
16	4	4	1	3	2	90.07	89.33	89.52	89.64	39.05

3.2.2. Analysis of Mean Method (ANOM)

ANOM approach was used to optimize the process parameters of the adsorption process. The S/N values from Table 2 were used to calculate the mean S/N value for every factor at every level. Equation 3, was used for this purpose.

$$M_{pi} = \frac{1}{n_{pi}} * \left[\sum \left(\frac{S}{N} \right)_{pi} \right] \quad \dots(3)$$

Where, M_{pi} is the mean S/N ratio for parameter p at the i -th level and $\sum (S/N)_{pi}$ is the sum of S/N value of parameter p at i -th level for all appearances of that parameter-Level combination during the 16 runs in Table 1.

From Fig. 5, the value with the highest mean for each parameter was identified as the optimal value. A validation test was performed to confirm validity of the predicted combination of ANOM. As per the results of ANOM analysis, temperature 30°C, initial (F-) concentration 20 ppm, dosage 4 g/L, pH 3, and contact time of 60 minutes, was the optimized combination. This combination was experimentally verified, giving a removal percentage of 94%. Table 3 shows the mean of the S/N values and mean of removal percentages, for every appearance of the parameter-Level combination.

The mean at Level 1 (Fig. 5(C)), pH 3 showed maximum removal efficiency. As the pH increased, the removal efficiency and S/N ratios reduced. This is attributed to H^+ ions enhancing surface protonation and neutralizing OH^- groups on the adsorbent [21]. This is similar to many Hydroxyapatite-like materials like Hydroxyapatite synthesized from marine shell waste and Hydroxyapatite-Modified Zeolite [6, 37]. Adsorption capacity rose with increased adsorbent dose, owing to a greater number of available sites, until equilibrium was reached. Beyond this point, further dosage increases were ineffective due to site overlap and competition [32]. The Dose determines the trade-off between removal efficiency and adsorption capacity [32].

Table 3 S/N ratio Response Table

Combination	Appearance			
	1	2	3	4
A1	35.95	37.09	36.12	38.70
A2	36.50	39.09	36.64	36.85
A3	37.84	36.33	39.07	37.34
A4	35.15	35.54	37.00	39.05
B1	35.95	36.50	37.84	35.15
B2	37.09	39.09	36.33	35.54
B3	36.12	39.07	36.64	37.00
B4	38.70	36.85	37.34	39.05
C1	35.95	39.09	39.07	39.05
C2	37.09	36.50	37.34	37.00
C3	36.12	36.85	37.84	35.54
C4	38.70	36.64	36.33	35.15
D1	35.95	36.64	37.34	35.54
D2	37.09	36.85	39.07	35.15
D3	36.12	36.50	36.33	39.05
D4	38.70	39.09	37.84	37.00
E1	35.95	36.85	36.33	37.00
E2	37.09	36.64	37.84	39.05
E3	36.12	39.09	37.34	35.15
E4	38.70	36.50	39.07	35.54

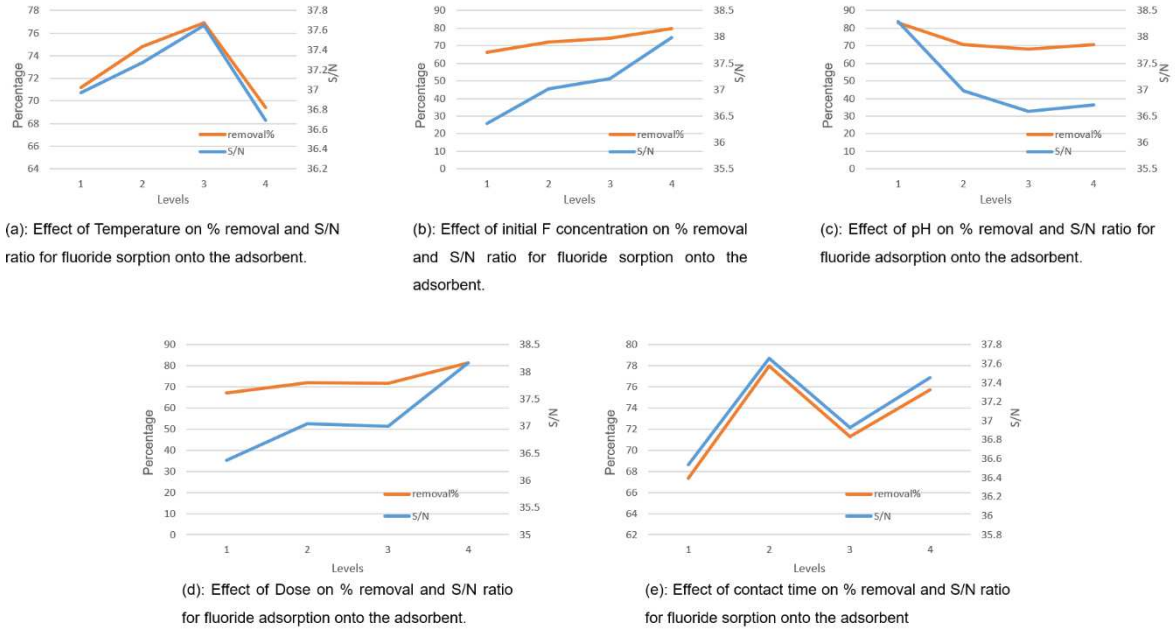


Fig. 5 Effect of Process Parameters on % removal and S/N ratio for fluoride adsorption onto the adsorbent.

3.3. ANOVA Method for Parameter Contribution

The ANOVA statistical method of analysis of variance was applied to determine the contributions of parameters on adsorption of (F-) on the present adsorbent. Equation 5 was used to determine the percentage of contribution of the five factors on the adsorbent.

$$\%Contribution = \frac{SSFp - ((N-1) * VER)}{SST} * 100 \quad \dots(5)$$

Where, N is the number of levels for each parameter, VER is the variance of error.

VER is estimated by Equation 6

$$VER = \frac{SST - \sum_{p=A}^{p=E} SSFp}{m * (n-1)} \quad \dots(6)$$

Where, $SSFp$ is the sum of squares for parameter p , estimated by the Equation 7

$$SSFp = \left(m * \frac{n}{L} \right) * \left(\sum_{k=1}^{k=L} (R_k^{-p} - Rt)^2 \right) \quad \dots(7)$$

$$Rt = \frac{\sum_{j=1}^{j=m} \left(\sum_{i=1}^{i=n} Ri \right)}{m*n} \dots\dots(8)$$

$$SST = \sum_{j=1}^{j=m} \left(\sum_{i=1}^{i=n} Ri^2 \right) - \left(\sum_{j=1}^{j=m} \left(\sum_{i=1}^{i=n} Ri \right) \right)^2 \dots\dots(9)$$

Where, Rt indicates the cumulative mean of (F-) removal of all 48 runs, m is the total number of trials in the for the L16 experiments, n is the number of replicates of each trial (3) and Ri is the removal percentage of each iteration i . R_k^{-p} is the cumulative average percentage of (F-) removal for a particular parameter p , at a given level k , for all appearances of that parameter-level combination. SST is the difference between total sum of squares and square of total sum for all removal percentages of (F-), at every trial and for every replicate.

The ANOVA summary for the individual contribution of process parameters towards (F-) adsorption is given in Fig. 6. The percentage contribution of different process parameters obtained from the ANOVA analysis were calculated as; Temperature 5.24%; Initial F contribution 16.78%; pH 25.49%; Dose 18.81%; and contact time 11.45%.

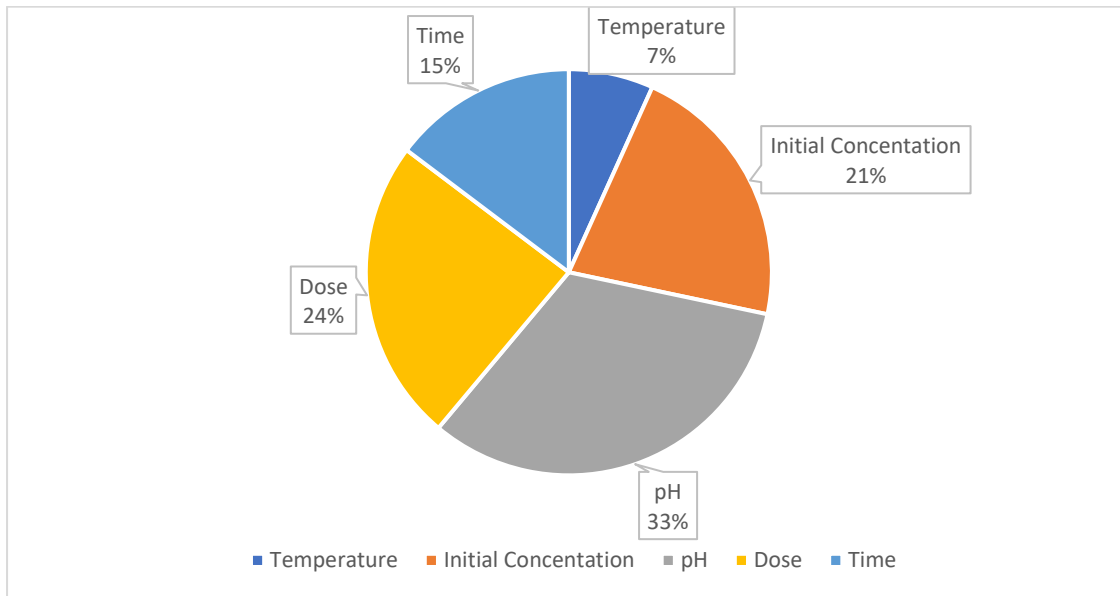


Fig. 6 Percentage Contribution of Each Process Parameter

3.4. Adsorption Isotherms

For the purpose of evaluation of the adsorption mechanism and to study the interactions between the adsorbate and adsorbent for the (F-) uptake, an equilibrium study was conducted. Under the conditions of 30°C with an initial (F-) concentration ranging from 5 to 15 mg/L, at a mixing speed of 150 rpm, with pH 3 and an adsorbent dose of 4 g/L and contact time of 60 minutes. The (F-) removal capacity, and adsorption capacity (q_e) are shown in Fig. 7. As observed, the removal efficiency decreases and adsorption capacity increases, as the initial (F-) concentration increases. In Fig. 7, at 5 mg/L, the adsorption capacity was 1.24 mg/g, which later increased to 3.64 mg/g at 15 mg/L of (F-) concentration. This is a highlight that concentration gradient plays a role in driving (F-) adsorption [25]. This is linked by past studies to the greater availability of (F-) ions at higher concentrations, enhancing the interactions with active sites [12]. Under the optimized conditions (levels temperature 30°C, initial (F-) concentration 20 ppm, dosage 4 g/L, pH 3, and contact time of 60 minutes), the adsorption capacity reached ~4.8 mg/L. This is better than many adsorbents like Modified Crushed Oyster Shells, and less than Bivalve shells (Table 4).

Fitting was done for several isotherm models by linearizing the models and linear regression. The Freundlich isotherm model appeared to be the best fit with R^2 value of 0.9874. This alignment with Freundlich isotherm suggests that the adsorption happens in multilayer, on a heterogeneous surface. This aligns with the drastic change observed in Fig. 2. Table 4 gives a comparison with various other adsorbents. The present adsorbent aligns with HMCTSP [43]. The Freundlich Isotherm constant K_f was estimated to be 0.0147 and n was estimated to be 0.38.

Table 4 Isotherm parameters for adsorption of (F-) onto various sorbents

Adsorbent	Isotherm Model	Maximum Capacity (mg/g)	Reference
Bivalve shells derived	Langmuir	27.31	[16]
Ai-Modified Natural Pumice	Langmuir	0.0399	[2]
HSMSW	Langmuir	19.19	[37]
Hydroxyapatite-Modified Zeolite	Langmuir	39.38	[6]

Hydroxyapatite modified Corbula trigona shell powder	Freundlich	-	[43]
Carbon supported Ce-Al oxides	Langmuir	31.65	[15]
Activated carbon derived from fish scale	Freundlich	-	[25]
Cellulose/Hydroxyapatite Nanocomposite	Langmuir	23.02	[26]
Eggshell Powder	Langmuir	-	[5]
Bone char from cattle bones	Langmuir	-	[35]
Laterite soil	Langmuir	0.8461	[33]
Modified Crushed Oyster Shells	Freundlich	1.5	[23]
SIFHAA	Freundlich	2.42	[9]
Zirconium Impregnated Coconut Fiber Carbon	Langmuir	1.95	[34]
CMNSCES	Langmuir	2.3	[17]
Chemically and thermally treated <i>Cerastoderma Edule</i> shell	Freundlich	4.8	Present adsorbent

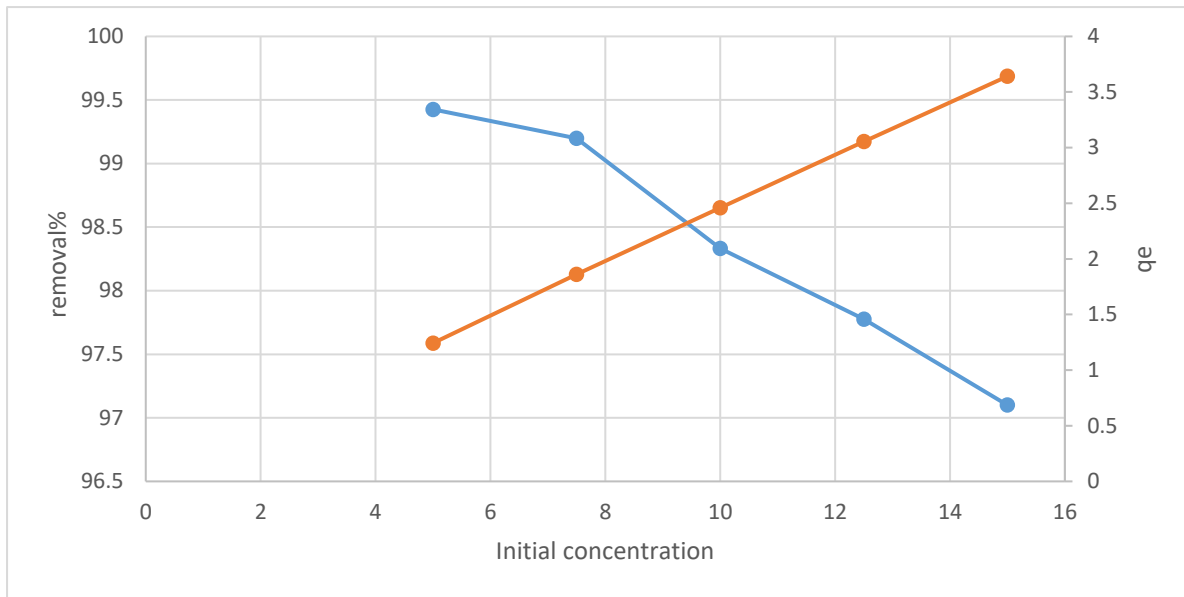


Fig. 7 Fluoride Uptake at Varying Initial F Concentration during Isotherm Study

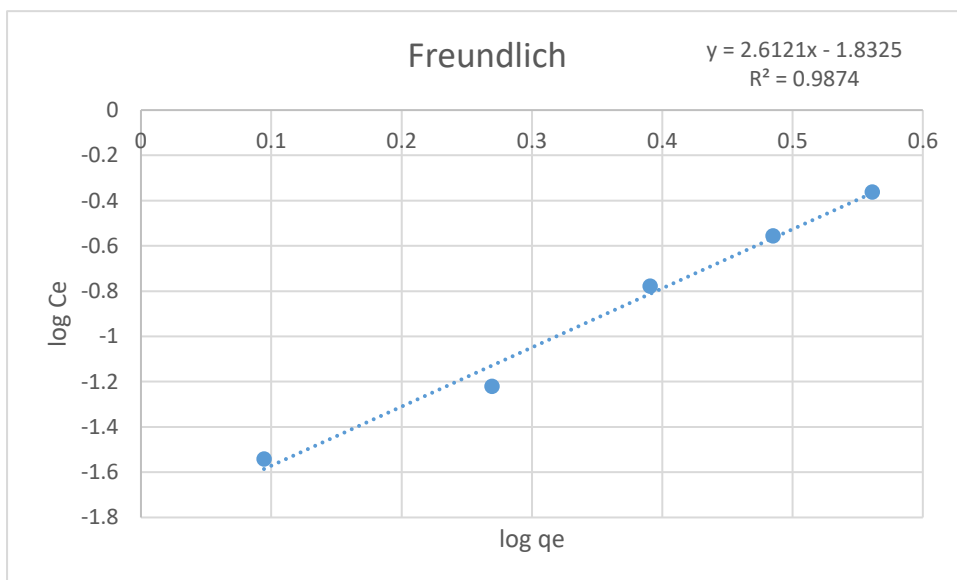


Fig. 9 Freundlich Isotherm Plot for Adsorption of Fluoride on The Adsorbent

3.5. Adsorption Kinetics

In order to study the mechanism of adsorption, a study was performed by varying contact times from 15 minutes to 90 minutes. The other parameters were set at temperature: 30°C, initial (F-) concentration: 20mg/L, pH: 3, Dose: 4g/L and contact time: 60 minutes. From Fig. 12, it can be observed that upto 60 minutes, the (F-) removal percentage and adsorptive capacity increase, and then reach an equilibrium. The further increase in (F-) concentration does not increase removal due to less availability of sites [4]. With the occupation of adsorption sites, the sorption

rates gradually slow down due to occupation of the energy sites [6]. This is similar to Activated carbon derived from fish scale and Ai-Modified Natural Pumice [5, 25]. This equilibrium time is better than many adsorbents listed in Table 5.

The (pfo) pseudo-first order and (pso) pseudo-second order kinetic models have been used to study the experimental data. The regression value of pso is higher than the pfo, with R^2 being 0.99. pso predicted the capacity at equilibrium to be 4.62 mg/g, which is close to the experimental 4.8 mg/g. The pso constant K2 was estimated to be 0.0282.

The present adsorbent appears to align with many shell based adsorbents like Bivalve shells derived, Hydroxyapatite modified Corbula trigona shell powder, and Modified Crushed Oyster Shells, (Table 5).

Table 5 Comparison of Kinetic Parameters with other Adsorbents

Adsorbent	Equilibrium Time (min)	Kinetic Model	Reference
Bivalve shells derived	85	pso	[16]
Ai-Modified Natural Pumice	60	pso	[2]
HSMSW	540	pso	[37]
Hydroxyapatite-Modified Zeolite	240	pfo	[6]
Hydroxyapatite modified Corbula trigona shell powder	175	pso	[43]
Carbon supported Ce-Al oxides	120	pso	[15]
Activated carbon derived from fish scale	60	pso	[25]
Cellulose/Hydroxyapatite Nanocomposite	77	pso	[26]
Eggshell Powder	120	pso	[5]

Bone char from cattle bones	1440	pso	[35]
Laterite soil	-	-	[33]
Modified Crushed Oyster Shells	1440	pso	[23]
SIFHAA	240	pso	[9]
Zirconium Impregnated Coconut Fiber Carbon	360	pfo	[34]
CMNSCES	-	-	[17]
Chemically and thermally treated <i>Cerastoderma Edule</i> shell	60	pso	Present adsorbent

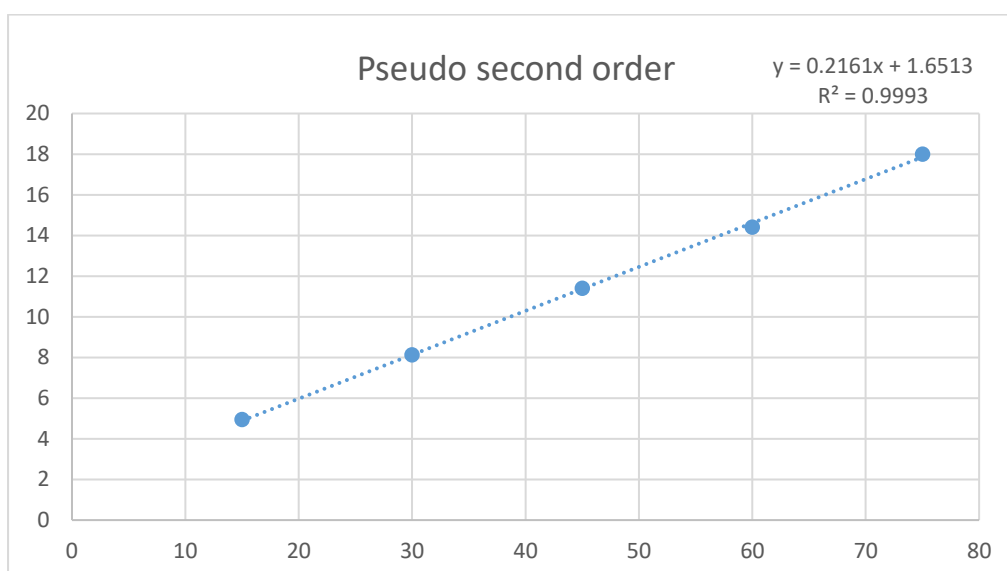


Fig. 11 Pseudo second order plot of the adsorbent

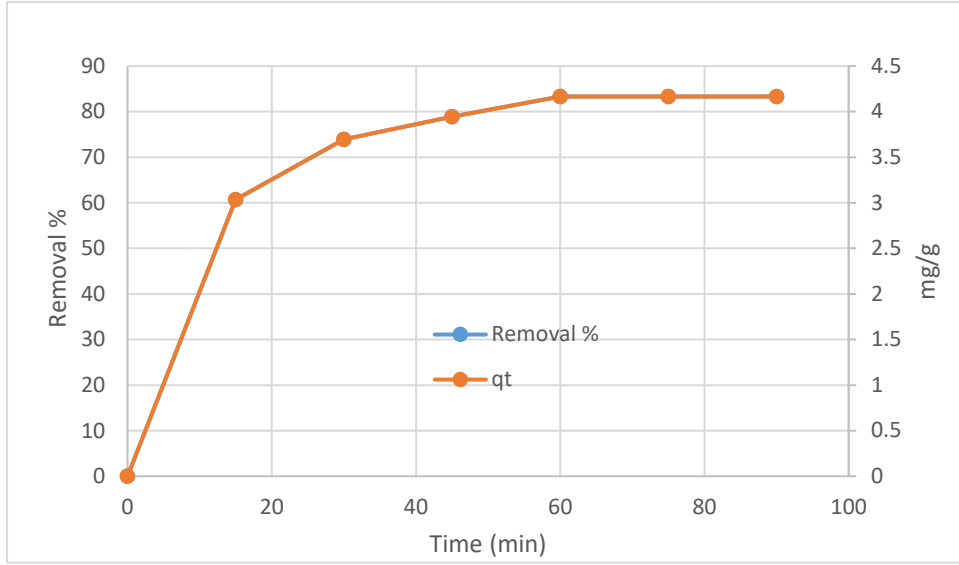


Fig. 12 Fluoride Uptake at Varying Contact Time during Kinetic Study

3.6. Adsorption Thermodynamics

Adsorption Thermodynamics Study was conducted across a range of 10 to 50°C, with initial (F-) concentration of 20 mg/L, adsorbent dose of 4 g/L, pH 3, contact time of 60 minutes and agitation speed of 150 rpm. Thermodynamic parameters viz. Changes in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) was obtained as follows:

$$\Delta G = \Delta H - T\Delta S \quad \text{.....(10)}$$

$$\Delta G = -RT \ln Kc \quad \text{.....11)}$$

$$\ln Kc = \Delta S/R - \Delta H/RT \quad \text{.....(12)}$$

where Kc (C_a/C_e) is the equilibrium sorption constant, T is the temperature in Kelvin, qe (mg/g) is the equilibrium adsorption capacity, C_e (mg/L) is the equilibrium concentration of the adsorbate and R ($8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) is universal gas constant. The values of ΔH and ΔS were derived from the Van't Hoff plot, $\ln Kc$ versus $1/T$ (Fig. 13).

As observed in Fig. 14, the values of ΔG , which became more negative with rising temperature, and hints that (F-) adsorption onto the treated shells is spontaneous and becomes more favourable at higher temperatures [10]. This makes the adsorbent perform better in higher ambient temperature. Both, ΔH and ΔS are positive, with values being $291.56 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ and $79.45 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. This shows that the process is endothermic, and needs external energy for adsorption, and also causes an increase in randomness or disorder at the solid-solution interface during adsorption [10]. Thus, the thermodynamic parameters describe a process which is

spontaneous, endothermic and entropy-driven. This behaviour is similar to HSMSW and HMCTSP, listed in Table 6 [37, 43].

The mechanism of adsorption appears to be similar to HSMSW, where the positive entropy change and positive enthalpy change with the magnitude greater than $40 \text{ J.k}^{-1}.\text{mol}^{-1}$ indicates that the adsorption is related to chemisorption, and there is a release of water molecules during the substitution of OH on the adsorbent surface with (F-) in acidic conditions [37].

Table 6 Comparison of thermodynamic parameters of the adsorbent with various adsorbents

Adsorbent	Nature	Reference
Bivalve shells derived	Spontaneous, Exothermic. Favoured at lower temperatures.	[16]
Al-Modified Natural Pumice	Spontaneous, Exothermic. Favoured at lower temperatures.	[2]
HSMSW	Spontaneous, Endothermic, Entropy-driven. Favoured at higher temperatures; increased disorder at the solid-solution interface.	[37]
Hydroxyapatite-Modified Zeolite	-	[6]
HMCTSP	Spontaneous, Endothermic, Entropy-driven. Favoured at higher temperatures; increased disorder at the solid-solution interface.	[43]
Carbon supported Ce-Al oxides	Spontaneous, Endothermic. Favoured at higher temperatures.	[15]

Activated carbon derived from fish scale	Spontaneous, Exothermic. Favoured at lower temperatures.	[25]
Cellulose/Hydroxyapatite Nanocomposite	Spontaneous, Endothermic, Entropy-driven. Favoured at higher temperatures.	[26]
Eggshell Powder	Spontaneous, Exothermic. Enthalpy-driven.	[5]
Bone char from cattle bones	-	[35]
Laterite soil	-	[33]
Modified Crushed Oyster Shells	-	[23]
SIFHAA	-	[9]
Zirconium Impregnated Coconut Fiber Carbon	Endothermic, spontaneous	[34]
CMNSCES	-	[17]
Chemically and thermally treated <i>Cerastoderma Edule</i> shell	Spontaneous, Endothermic, Entropy-driven. Favours higher temperatures.	Present adsorbent

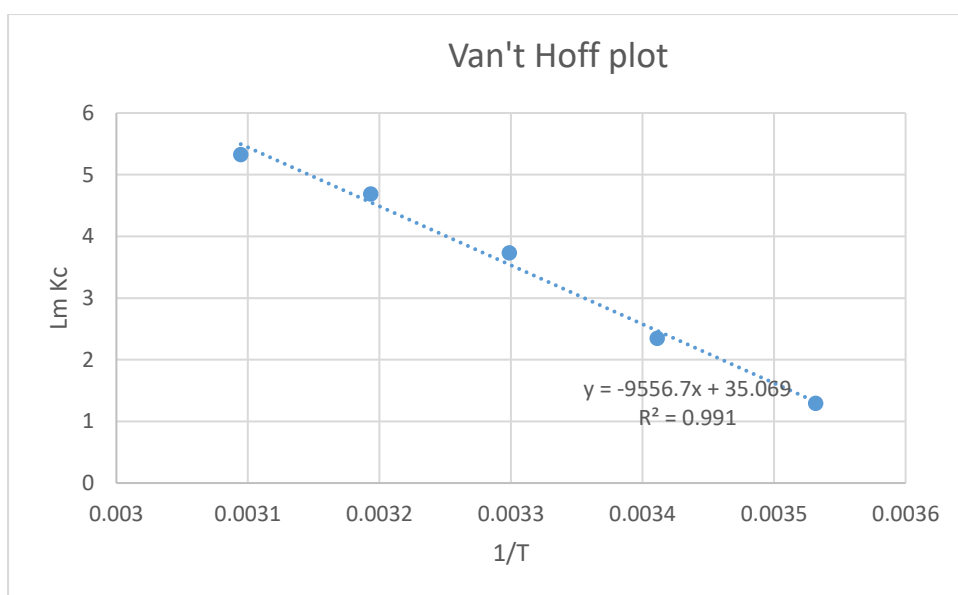


Fig. 13 Van't Hoff plot

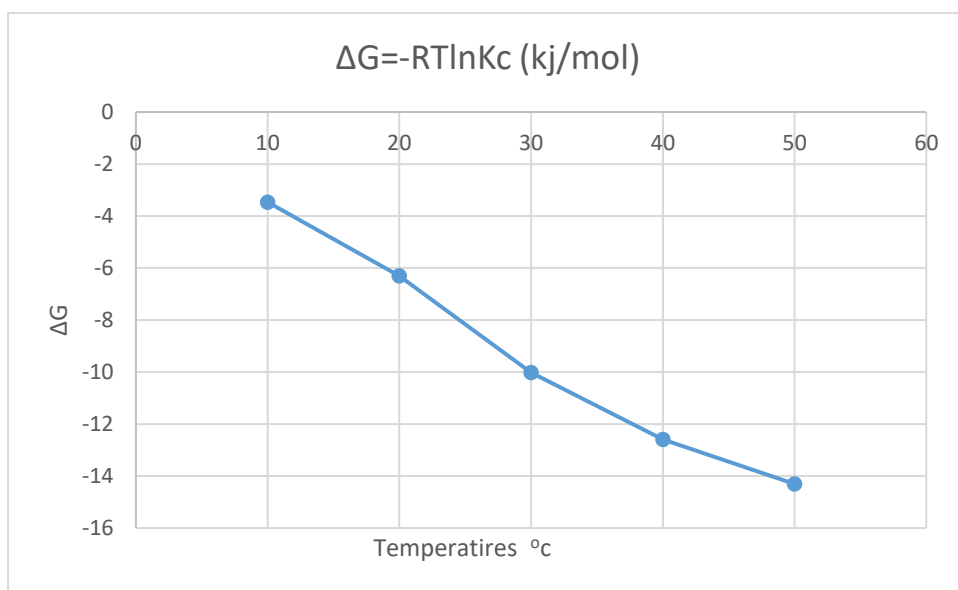


Fig. 14 Temperature effect on Gibbs free energy

4. Conclusion

Overall, the study demonstrated that *Cerastoderma Edule* shell adsorbent is feasible and effective for adsorption of the (F⁻). Under the optimized conditions obtained by ANOM, (pH 3, dose 4 g/L, contact time 60 minutes, 30°C, initial F concentration 20 mg/L, the adsorption capacity was ~94%, with the adsorption capacity of about 4.8 mg/g. The factor contributions of process parameters for (F⁻) adsorption are adsorbent dose (18.81%), initial concentration (16.78%), contact time (11.45%), temperature (5.24%) and finally pH (25.49%), suggesting that pH plays an important role in adsorption. Through the equilibrium studies, it is revealed that Freundlich isotherm is the best fit, which can be linked to multilayer adsorption on a heterogeneous surface, which is shown through SEM images. The adsorbent aligns better to pseudo-second order kinetic model. The thermodynamic parameters indicate that the sorption process is spontaneous, endothermic, and causes an increase in entropy, being favourable at higher temperature and releasing water molecules. SEM and EDS showed the structural changes, while FTIR indicated that the surface itself is similar after adsorption.

Thus, the chemically and thermal treated *Cerastoderma Edule* shell proved to be an adsorbent with good potential for the purpose of (F⁻) removal, being environmentally friendly, low cost and granting a pathway for waste to resource conversion.

Credit authorship contribution statement

Shreyas. R. Singh: Conceptualization, Methodology, Formal Analysis, Investigation, Data Curation, Writing – Original draft preparation.

Dr. Ajay. R. Tembhurkar: Conceptualization, Methodology, Investigation, Writing - Original draft preparation & reviewing.

Declarations

Competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Data availability

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Ethics approval and consent to participate

This study did not involve human participants or animals; therefore, ethical approval was not required. Not applicable. This study did not involve human participants.

Consent for publication

Not applicable. The manuscript does not contain any individual person's data in any form.

References

1. Al-Amin, K., Kawsar, Md., Mamun, M. T. R. B., Hossain, Md. S.: Fourier transform infrared spectroscopic technique for analysis of inorganic materials: a review. *Nanoscale Adv.* **7**, 6677–6702 (2025). <https://doi.org/10.1039/d5na00522a>
2. Al-Hamadi, M. M., Alnedhary, A. A., Quria'a, H. A., Al-Mutawakel, G. M.: Adsorption isotherm, kinetic and thermodynamic studies for removal of fluoride ions from drinking water using modified natural pumice. *Sana'a Univ. J. Appl. Sci. Technol.* **2**, 403–412 (2024). <https://doi.org/10.59628/jast.v2i5.1151>
3. Ali, S., Fakhri, Y., Golbini, M., Thakur, S. K., Aadil, M. T., Khan, A. A., Bhattacharya, P.: Concentration of fluoride in groundwater of India: a systematic

- review, meta-analysis and risk assessment. *Groundwater Sustain. Dev.* **9**, 100224 (2019). <https://doi.org/10.1016/j.gsd.2019.100224>
4. Araga, R., Soni, S., Sharma, C. S.: Fluoride adsorption from aqueous solution using activated carbon obtained from KOH-treated jamun (*Syzygium cumini*) seed. *J. Environ. Chem. Eng.* **5**, 5608–5618 (2017). <https://doi.org/10.1016/j.jece.2017.10.023>
 5. Bhaumik, R., Mondal, N. K., Das, B., Roy, P., Pal, K. C., Das, C., Banerjee, A., Datta, J. K.: Eggshell powder as an adsorbent for removal of fluoride from aqueous solution: equilibrium, kinetic and thermodynamic studies. *J. Chem.* **9**, 1457–1480 (2012). <https://doi.org/10.1155/2012/790401>
 6. Boteju, R., Zheng, L., Wasana, H. M. S., de Alwis, A.: Hydroxyapatite-modified zeolite for fluoride removal from drinking water: Adsorption mechanism investigation and column study. *Water* **17**, 908 (2025). <https://doi.org/10.3390/w17060908>
 7. Bundschuh, J., Maity, J. P., Mushtaq, S., Vithanage, M., Seneweera, S., Schneider, J., Bhattacharya, P., Khan, N. I., Hamawand, I.: Medical geology in the framework of the sustainable development goals. *Sci. Total Environ.* **581–582**, 87–104 (2017). <https://doi.org/10.1016/j.scitotenv.2016.12.164>
 8. de Carvalho Costa, L. R., Jurado-Davila, I. V., Oliveira, J. T. D., Nunes, K. G. P., Estumano, D. O., de Oliveira, R. A., Carissimi, E., Féris, L. A.: Exploring key parameters in the development of alternative adsorbents for fluoride removal from water: A review. *J. Water Process Eng.* **60**, 105174 (2024). <https://doi.org/10.1016/j.jwpe.2024.105174>
 9. Dhanasekaran, P., Sahu, O.: Arsenate and fluoride removal from groundwater by sawdust impregnated ferric hydroxide and activated alumina (SFAA). *Groundwater Sustain. Dev.* **12**, 100490 (2021). <https://doi.org/10.1016/j.gsd.2020.100490>
 10. Ebelegi, A. N., Ayawei, N., Wankasi, D.: Interpretation of adsorption thermodynamics and kinetics. *Open J. Phys. Chem.* **10**, 166–182 (2020). <https://doi.org/10.4236/ojpc.2020.103010>
 11. Ergović Ravančić, M., Habuda-Stanić, M., Škrabal, S., Marčetić, H., Obradović, V.: Fluoride adsorption from water on waste materials. *Kem. Ind.* **72**, 567–572 (2023). <https://doi.org/10.15255/KUI.2022.057>
 12. George, A. M., Tembhurkar, A. R.: Analysis of equilibrium, kinetic, and thermodynamic parameters for biosorption of fluoride from water onto coconut (*Cocos nucifera* Linn.) root developed adsorbent. *Chin. J. Chem. Eng.* **27**, 92–99 (2019). <https://doi.org/10.1016/j.cjche.2018.03.004>
 13. Ghosh, M. K., Patel, S.: An overview of removal of fluoride from potable water in Chhattisgarh. *Int. J. Futuristic Innov. Eng. Sci. Technol.* **2**(2), 158 (2023). <https://doi.org/10.59367/ek4ceq94>
 14. Greenberg, A. E., Clesceri, L. S., Eaton, A. D. (eds.): Standard methods for the examination of water and wastewater, 20th edn. APHA/AWWA/WEF, Washington, DC (1998). <https://www.scirp.org/journal/paperinformation?paperid=78573>
 15. Guo, S., Zhang, L., Wang, Y., Liu, X., Zhao, H.: Enhanced fluoride removal from drinking water by activated carbon supported Ce-Al oxides: performance and mechanism. *RSC Adv.* **15**, 14363–14374 (2025). <https://doi.org/10.1039/D5RA00397K>
 16. Hashemkhani, M., Ghalhari, M. R., Bashardoust, P., Hosseini, S. S., Mesdaghinia, A., Mahvi, A. H.: Fluoride removal from aqueous solution via environmentally friendly adsorbent derived from seashell. *Sci. Rep.* **12**, 9655 (2022). <https://doi.org/10.1038/s41598-022-13756-3>
 17. Hernández-Montoya, V., Ramírez-Montoya, L. A., Bonilla-Petriciolet, A., Montes-Morán, M. A.: Optimizing the removal of fluoride from water using new carbons

- obtained by modification of nut shell with a calcium solution from egg shell. *Biochem. Eng. J.* **62**, 1–7 (2012). <https://doi.org/10.1016/j.bej.2011.12.011>
18. Hu, T., Zhai, Z., Tang, W.: Metal-organic framework-derived diatomic catalysts for environmental remediation: Synthesis, applications and improvement strategies. *Coord. Chem. Rev.* **526**, 216357 (2025). <https://doi.org/10.1016/j.ccr.2024.216357>
 19. Jović, M., Mandić, M., Šljivić-Ivanović, M., Smičiklas, I.: Recent trends in application of shell waste from mariculture. *Stud. Mar.* **32**, 47–62 (2019). <https://doi.org/10.5281/zenodo.3274471>
 20. Kanwal, F., Devrajani, S. K., Hashmani, S. A. K.: Removal of fluoride from aqueous solution using biochar derived from brown macroalgae (*Sargassum polycystum*) impregnated with nanoparticles. *Phycology* **5**, 37 (2025). <https://doi.org/10.3390/phycology5030037>
 21. Khamis, F., Hegab, M. M., Banat, F., Arafat, H. A., Hasan, S. W.: Comprehensive review on pH and temperature-responsive polymeric adsorbents: Mechanisms, equilibrium, kinetics, and thermodynamics of adsorption processes for heavy metals and organic dyes. *Chemosphere* **349**, 140801 (2024). <https://doi.org/10.1016/j.chemosphere.2023.140801>
 22. Khatibikamal, V., Torabian, A., Janpoor, F., Hoshyaripour, G.: Fluoride removal from industrial wastewater using electrocoagulation and its adsorption kinetics. *J. Hazard. Mater.* **179**, 276–280 (2010). <https://doi.org/10.1016/j.jhazmat.2010.03.001>
 23. Kim, W., Singh, R., Smith, J. A.: Modified crushed oyster shells for fluoride removal from water. *Sci. Rep.* **10**, 5759 (2020). <https://doi.org/10.1038/s41598-020-60743-7>
 24. Kimambo, V., Bhattacharya, P., Mtalo, F., Mtamba, J., Ahmad, A.: Fluoride occurrence in groundwater systems at global scale and status of defluoridation—state of the art. *Groundwater Sustain. Dev.* **9**, 100223 (2019). <https://doi.org/10.1016/j.gsd.2019.100223>
 25. Kishor, R., Sharma, A., Parmar, R., Kumari, S., Malik, M. M.: Removal of fluoride from aqueous solution using high surface area activated carbon derived from fish scale solid waste. *Environ. Sci. Pollut. Res.* **32**, 15929–15941 (2025). <https://doi.org/10.1007/s11356-025-36638-3>
 26. Majamo, S. L., Amibo, T. A., Gebremeskel, B. M., Konopacka-Lyskawa, D.: Process optimization and modeling research for the defluoridation of water using a novel adsorbent of cellulose and hydroxyapatite nanocomposite. *Sci. Rep.* **15**, 28798 (2025). <https://doi.org/10.1038/s41598-025-13594-z>
 27. Mameri, N., Yeddou, A. R., Lounici, H., Belhocine, D., Grib, H., Bariou, B.: Defluoridation of septentrional Sahara water of North Africa by electrocoagulation process using bipolar aluminium electrodes. *Water Res.* **32**, 1604–1612 (1998). [https://doi.org/10.1016/S0043-1354\(97\)00357-6](https://doi.org/10.1016/S0043-1354(97)00357-6)
 28. Mukkanti, V. B., Tembhurkar, A. R.: Defluoridation of water using adsorbent derived from *Labeo rohita* (rohu) fish scales waste: optimization, isotherms, kinetics, and thermodynamic study. *Sustain. Chem. Pharm.* **22**, 100520 (2021). <https://doi.org/10.1016/j.scp.2021.100520>
 29. Nandiyanto, A. B. D., Oktiani, R., Ragadhita, R.: How to read and interpret FTIR spectroscopy of organic material. *Indones. J. Sci. Technol.* **4**, 97–118 (2019). <https://doi.org/10.17509/ijost.v4i1.15806>
 30. Ndiaye, P. I., Moulin, P., Dominguez, L., Millet, J. C., Charbit, F.: Removal of fluoride from electronic industrial effluent by RO membrane separation. *Desalination* **173**, 25–32 (2005). <https://doi.org/10.1016/j.desal.2004.07.037>
 31. Olejarczyk, M., Rykowska, I., Urbaniak, W.: Management of solid waste containing fluoride, A review. *Materials* **15**, 3461 (2022). <https://doi.org/10.3390/ma15103461>

32. Rasheed, A. A., Muhammad, H. S., Jakada, Y., Salahudeen, N.: Effect of adsorbent dosage on the kinetics and isotherms of lead(II) removal from aqueous solution using corn husk. *Arid Zone J. Eng. Technol. Environ.* **21**, 702–716 (2025). <https://doi.org/10.63958/azojete/2025/21/3/003>
33. Sarkar, M., Banerjee, A., Pramanick, P. P.: Kinetics and mechanism of fluoride removal using laterite. *Ind. Eng. Chem. Res.* **45**, 5920–5927 (2006). <https://doi.org/10.1021/ie060016j>
34. Sathish, R. S., Sairam, S., Raja, V. G., Rao, G. N., Janardhana, C.: Defluoridation of water using zirconium impregnated coconut fiber carbon. *Sep. Sci. Technol.* **43**, 3676–3694 (2008). <https://doi.org/10.1080/01496390802222541>
35. Shahid, M. K., Kim, J. Y., Choi, Y. G.: Synthesis of bone char from cattle bones and its application for fluoride removal from the contaminated water. *Groundwater Sustain. Dev.* **8**, 324–331 (2019). <https://doi.org/10.1016/j.gsd.2018.12.003>
36. Shen, J., Schäfer, A.: Removal of fluoride and uranium by nanofiltration and reverse osmosis: A review. *Chemosphere* **117**, 679–691 (2014). <https://doi.org/10.1016/j.chemosphere.2014.09.090>
37. Singh, S., Murugesan, G., Vinayagam, R., Varadavenkatesan, T., Selvaraj, R.: Adsorptive removal of fluoride from water using hydroxyapatite synthesized from marine shell waste. *Sci. Rep.* **15**, 25598 (2025). <https://doi.org/10.1038/s41598-025-11132-5>
38. Tan, T. L., Krusnamurthy, P. A., Nakajima, H., Rashid, S. A.: Adsorptive, kinetics and regeneration studies of fluoride removal from water using zirconium-based metal organic frameworks. *RSC Adv.* **10**, 18740–18752 (2020). <https://doi.org/10.1039/D0RA01268H>
39. Tomar, V., Kumar, D.: A critical study on efficiency of different materials for fluoride removal from aqueous media. *Chem. Cent. J.* **7**, 51 (2013). <https://doi.org/10.1186/1752-153X-7-51>
40. Veneri, F., Iamandii, I., Vinceti, M., Generali, L., Giannone, M. E., Mazzoleni, E., Birnbaum, L. S., Consolo, U., Filippini, T.: Fluoride exposure and skeletal fluorosis: a systematic review and dose-response meta-analysis. *Curr. Environ. Health Rep.* **10**, 417–441 (2023). <https://doi.org/10.1007/s40572-023-00412-9>
41. Wang, T., Yan, L., He, Y., Alhassan, S. I., Gang, H., Wu, B., Jin, L., Wang, H.: Application of polypyrrole-based adsorbents in the removal of fluoride: a review. *RSC Adv.* **12**, 3505–3517 (2022). <https://doi.org/10.1039/D1RA08496H>
42. Wei, Y., Wang, L., Li, H., Yan, W., Feng, J.: Synergistic fluoride adsorption by composite adsorbents synthesized from different types of materials—A review. *Front. Chem.* **10**, 900660 (2022). <https://doi.org/10.3389/fchem.2022.900660>
43. Yapo, N. S., Aw, S., Briton, B. G. H., Adouby, K.: Removal of fluoride in groundwater by adsorption using hydroxyapatite modified *Corbula trigona* shell powder. *Chem. Eng. J. Adv.* **12**, 100386 (2022). <https://doi.org/10.1016/j.ceja.2022.100386>