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Low-Cost Fluoride Adsorbent Prepared from Renewable Bio-Waste: Synthesis, Characterization and Optimization Studies

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ABSTRACT

Elevated level of fluoride (> 1.0 mg/L) in drinking water leads to both dental and skeletal fluorides. Present research is dedicated to check the efficacy of duck shell dust towards removal of fluoride. Various analytical tools (XRF, XRD, SEM-EDAX and zero point charge) were used to characterize the present adsorbent. The entire batch mode study results were further optimized by Response Surface Methodology (RSM). The results revealed that Langmuire isotherm is best fitted (R2 = 0.819) with adsorption capacity 4.894 mg/g. However, kinetic study suggest that the fluoride adsorption followed pseudo-second-order kinetic equation (R2 = 0.956). Similarly, thermodynamic study revealed that the fluoride adsorption by duck shell dust is endothermic and entropy driven process. Finally, optimization study demonstrated the optimized condition such as initial concentration, adsorbent dose, contact time and pH are 89.29 mg/L, 1.112 g/100 mL, 42.5 min and 9.91, respectively. Therefore, it may be concluded that duck shell dust could be a promising adsorbent for decontamination of fluoride from contaminated body.

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INTRODUCTION

Fluoride is a strong electronegative inorganic anion (Chiavola et al. 2022). It is considered as one of the most dangerous contaminant (Ghalhari et al. 2021; Mondal 2017; Mondal et al. 2012). The main minerals are fluorspar (CaF_2) and cryolite (Na_3AlF_6) and these are insoluble in water. However, excessive application of phosphatic fertilizer leads to discharge of fluoride from mineral (Pandey and Pandey 2011). Excessive ingestion of fluoride leads to dental caries, bone fluorosis, impairment of thyroid gland, endocrine gland, malfunctioning of human brain etc. (Chen et al. 2010).

Higher level of fluoride in groundwater was reported from twenty develop and developing countries including India where at least nineteen states are severely affected from fluorosis (Iizuka et al. 2022; Mondal and Kundu 2016). Both dental and skeletal fluorosis will accelerate when fluoride concentration in drinking water ranges from 3 – 6 mg/L (Cheng et al. 2014). However, very low level of fluoride (0.7 – 1.2 mg/L) could be helpful to prevent dental fluorosis (Nasr et al. 2011). Again, World Health Organization (WHO, 2011) clearly revealed that maximum

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permissible limit of fluoride is 1.5 mg/L in potable water. Previous report highlighted that the fluoride level in some parts of India are as high as 30 mg/L including some villages of China where groundwater fluoride level is greater than 8 mg/L (Handa, 1975). Cursory review of current literature indicate that more than 60 million people are seriously affected by high loaded of fluoride in the drinking water in India (Akuno et al. 2019). Many analytical technologies are their to treat the excess fluoride congaing water such as precipitation (Fan et al. 2003); nanofiltration (Tahaikt et al. 2007); ion exchange (Grzegorzek et al. 2020) etc.

However, all the above mentioned technologies have some limitations with respect to operating cost, expensiveness, easy handling etc. (Chen et al. 2014). But adsorption technology is one of the attractive technique commonly used for defluodation of water (Chiavola et al. 2022; Wang et al. 2022; Fan et al. 2003). A remarkable number of adsorbents are successfully used for defluoridation such as seashell (Hashemkhani et al. 2022), banana peel (Bhaumik and Mondal 2016); fish scale (Bhaumik et al. 2017); However, all the above adsorbents are worked properly under highly acidic condition and low fluoride contaminated water (< 2 mg/L) (Nasr et al. 2011).

In this study duck egg shell dust was used. Egg shell mainly consists calcium carbonate including uronic acid, sialic acid, glycine, alanine and nitrogen (Nakano et al. 2003; Blumenkrantz and Asboe-Hansen 1973; Baker and Balch 1962).

Traditional optimization technique required large number of experiments and huge time which makes its limited use (Bhaumik and Mondal 2016). However, this limitation was removed by using multivariate optimization process (Roy et al. 2014) in order to achieve both maximum adsorption capacity and removal performance (Sugashini 2013). In this study response surface methodology (RSM) was used. This methodology has three important steps: firstly, statistical design experiment; secondly, estimation of coefficient by using mathematical model and thirdly, response prediction and checking of model adequacy (Mondal et al. 2017).

The main objective of the present study was to explore the efficacy of duck shell dust towards decontamination of fluoride from laboratory made fluoride solution by using various operating variables under batch mode study. The experimental results were used for isotherms, kinetics and thermodynamics studies. Finally, optimization was done by response surface methodology (RSM) (Design expert, 8.0.6.1, USA).

MATERIALS AND METHODS

Chemicals and analytical instruments

All chemicals were purchased from Merck India Ltd. (Mumbai-400018). The instruments like pH meter (LCD Display, power: 4 X 1.5 V "A76" Micro alkaline batteries, IP67 Waterproof) and Ion selective electrode was procured from Deneb Instruments (Kolkata, West Bengal).

Preparation of fluoride solution

The stock solution of fluoride was prepared by dissolving by dissolving 0.22g sodium fluoride (MERCK, Germany) in 1L double distilled water. The intermediate concentration of fluoride solution was prepared by dilution method.

Adsorbent preparation

Duck egg shell

The shell Duck egg shells was collected from the Restaurant of Burwan town. Then collected egg shells are primarily washed by tap water followed by double distilled water. These egg shells are brought to the lab for further processing. Then the egg shells was taken in a tray and the tray is kept in the hot air oven for drying the egg shell for 48 hrs. After drying this the egg shell was grounded with the help of mixer-grinder and also the mortar and pestle. After grinding the egg shell their dust is taken in to a 70 μm sieve for sieving it. Then the final 70 μm dust of duck

Zero point charge (pHzpc)

pH_{ZPC} is an analytical technique by which the neat zero charge on the surface of the adsorbent will determine at a particular pH of the medium (Mondal, 2010). For the above purpose, 0.1(M) KNO_3 solution (50 mL) was take in a number of containers (100 mL) and pH of the solution was adjusted from 1.0 to 10.0 by 0.1 (N) potassium hydroxide or nitric acid. Finally, 1.5 g solid adsorbent was taken in each container and shaking the entire solutions for 24 h and final pH was recorded by using digital pH meter.

SEM-EDX, XRF, and XRD Study

The prepared adsorbent was characterized by varieties of analytical tools such as Scanning Electron Microscopy (SEM EDX JEOL JSM-6390LV), XRF ((Bruker, ARTAX), and XRD (Bruker D5005).

Experimental work

After synthesis of the required adsorbent, batch adsorption was performed. Initially, a set of 250 mL conical flasks were taken and each conical containing 100 mL different concentration fluoride solution with fixed amount of adsorbent dose and constant pH, contact time, temperature, agitation speed etc. Finally, percentage of removal and adsorption capacity were calculated.

Adsorption study

Percentage of fluoride was estimated by using the following equation (Eq. 1):

$$Removal(\%) = \frac{(C_0 - C_e)}{C_f} \times 100 \tag{1}$$

Similarly, adsorption capacity of the adsorbent was evaluated by using the following equation (Eq. 2):

$$Adsorptioncapacity = \frac{(C_0 - C_e)}{m} \times V \tag{2}$$

Where C_0 and $C_{f\,are}$ the initial and final concentration of fluoride solution, m is the mass (g) the adsorbent and V is the volume in litres (L).

Modelling study (RSM)

Normally a 3D response curve was used modelling of the optimization study. This particular curve indicate a relationship between various operating variables (x_1, …..x_n) and the response (Y) (Sadhukhan et al. 2014). The relationship can be represented as (Eq. 3):

$$Y = f(x_1 ....x_n) + \varepsilon \tag{3}$$

Where ε is an error term.

The entire modelling was done by using a software, Design Expert (8.0.17, Minneapolis, USA).

The quadratic expression by which response can be evaluated as (Eq. 4):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ij} x^2 + \sum_{i=1}^{k=1} \sum_{j=2}^{k} \beta_{ij} x_i x_j + \varepsilon \tag{4}$$

Where Y = Response, β_0 = intercept, β_j = linear effect, β_{ij} = interaction effect and ε = error term (Chattaraj et al. 2013). The goodness of fit of the model was evaluated by R^2 value (Sadhukhan et al. 2014).

Desorption study

The exhausted adsorbent was regenerated for further use. For the regeneration, the exhausted adsorbent was treated with NaOH solution maintaining various pH (6 to 14) (Mondal et al. 2015).

RESULTS AND DISCUSSION

Characterization

XRF study

Present adsorbent, duck shell was characterized by X-ray Fluorescence (XRF) study and the results displayed in Figure 1. From the Figure 1 it is clear that duck shell has four strong peaks. Among the four peaks, peaks of Sn, Ca and Fe are very prominent and significant. The overall area coverage of the different elements as 55517 for calcium which much higher than background value (499) ($\chi^2 = 93.94$). This information clearly suggested that calcium may be present as CaO and $CaCO_3$ in the egg shell (Bashir and Manusamy 2015; Freire and Holanda 2006). Similarly, the value for iron 939 and tin 261. The corresponding background values are 71 and 1872. The χ^2 values are 4.51 and 0.84 for iron and tin respectively (Table not supplied).

XRD study

Present results revealed that duck egg shell dust has mine sharp peaks with different intensities. Similarly, the XRD of duck egg shell presented in Figure 2. From Figure 2 it showed the tall and sharp peak at the 2q value of 29.44 with 602 count number. Except this there are other peaks at 2q values are 48.52, 47.48, 39.37, 22.90, 57.68, and 43.30 with count number 138, 109, 91, 55, 46, and 73, respectively. The duck egg shell showed nine sharp peaks with one long and sharp peak (Fig. 2). This information clearly revealed the high degree of crystallinity(Hamidi et al. 2017). Moreover, the prominent peaks are due to existence of CaO and $Ca(OH)_2$ in duck shell dust (Zaman et al. 2018).

pH_{ZPC}

Zero point charge of the adsorbent is a valuable parameter for adsorption study. At certain pH, the adsorbent surface showed no net charge, that particular pH of that adsorbent is known as zero

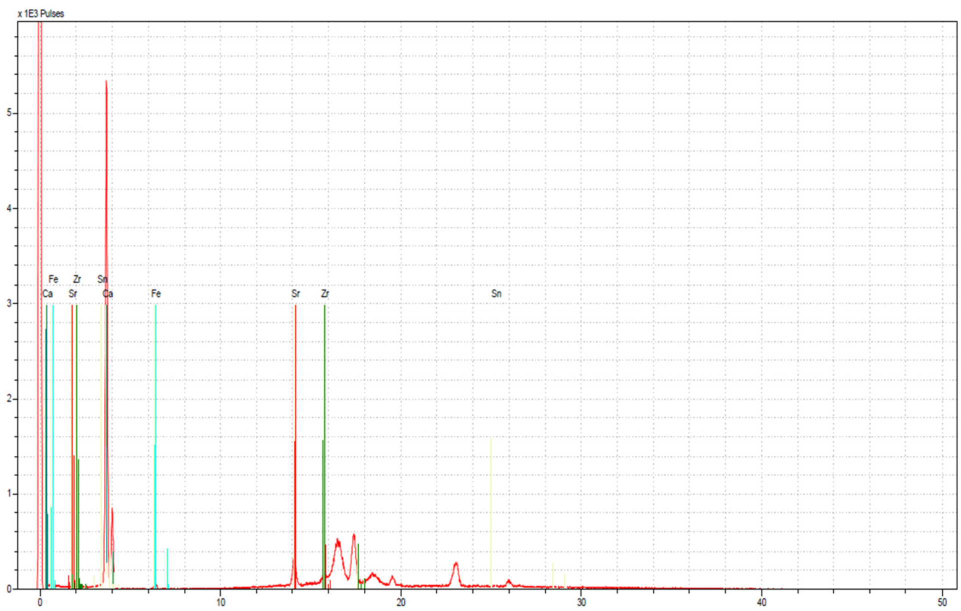


Fig. 1. XRF study of duck shell dust

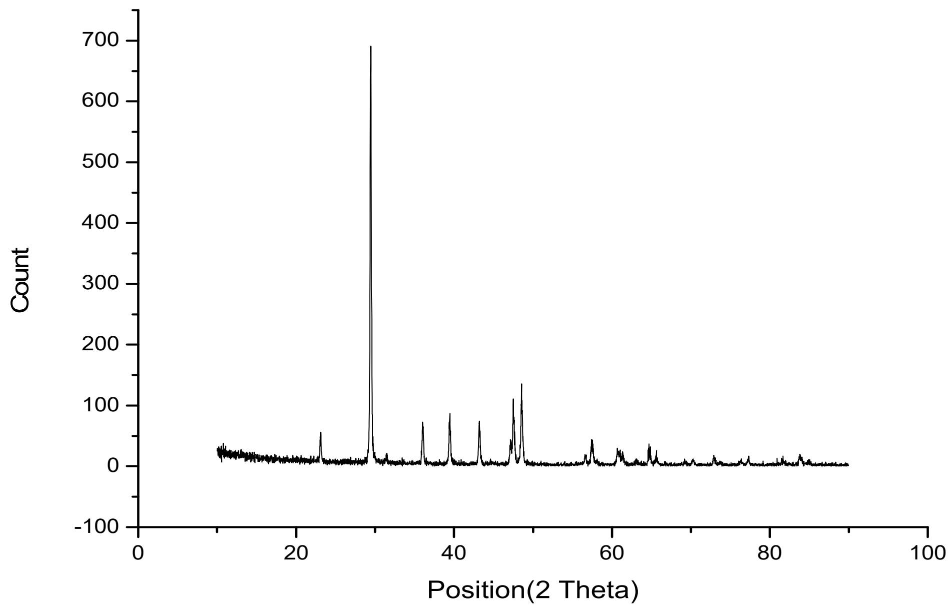


Fig. 2. XRD study of duck egg shell dust

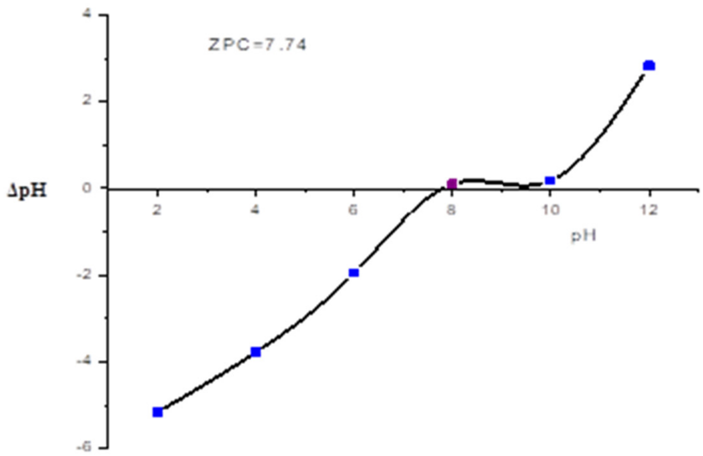


Fig. 3. Zero point charge of duck egg shell dust (DESD)

point charge. Moreover, during adsorption, if we ascertain the pH where charge on the surface is zero, then it can be easily understood that above the pH of zero point charge, the surface of the adsorbent will be negative in charge and below the zero point charge, the surface of the adsorbent will positive charge. In case of duck shell dust, the pH_{ZPC} was observed at pH 7.74, that means above this particular pH, surface of the duck shell dust will be negative and below this particular pH, the surface of duck shell dust is positive (Fig. 3). As duck egg shell dust showed maximum adsorption at pH 2.0 that means it is below the ZPC pH. This may be due to positive surface of duck shell dust attracted negative fluoride ions at that pH (Bhaumik et al. 2012). However, very recently, Shao et al. (2021) highlighted that the decrease of fluoride adsorption on to $CaSO_4 \cdot 2H_2O$ nanorods at acidic pH (pH < 5) is due to increase of calcium fluoride solubility.

SEM-EDX study

The surface morphology of the duck shell dust was assessed by SEM-EDAX study (Fig.

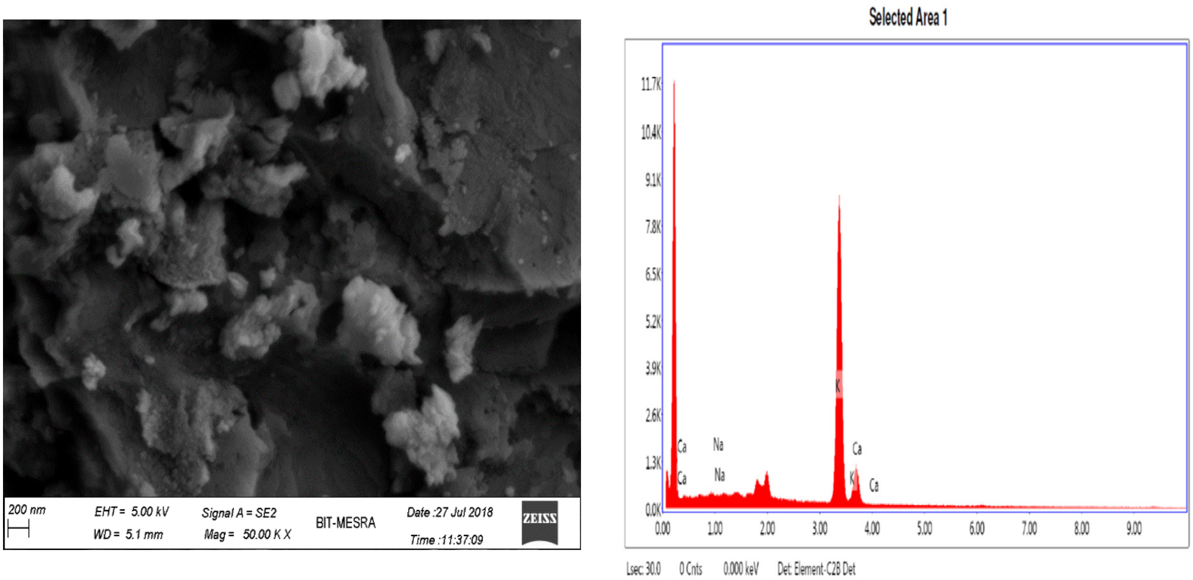


Fig. 4. SEM-EDX study of duck egg shell dust after passing fluoride solution

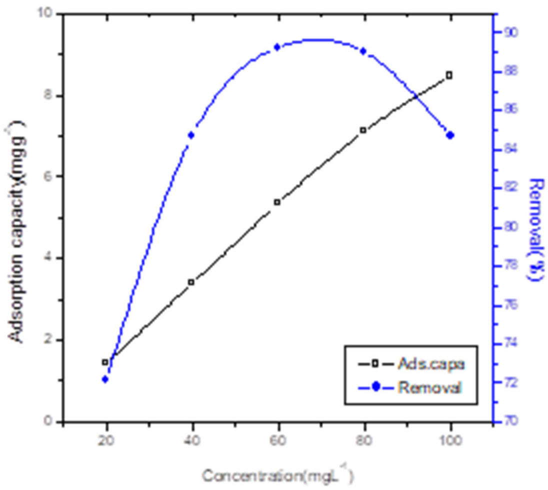


Fig. 5. Effects of Concentration (pH 4, RPM 150, Dose 0.5/50ml, Time 3+0min, Temp. 40^{o}C)

4). From the figure 4 it was observed that SEM of duck shell dust is heterogeneous in nature with some bright areas. SEM study also indicate the presence ofnumerous micropores (Ok et al. 2011). This may be presence of some metals which was again proof from XRF study. From the EDAX spectra it was recorded that intensive peak as potassium peak according to their availability in the egg shell dust (Fig. 4).

Batch study

Effect of Initial concentration

Effect of initial concentration on fluoride removal was assessed by varying the concentration from 20 to100 mg/L and the result was presented in Figure 5. From the figure 5 it is clear that percentage of fluoride removal gradually increased from 72.15% to 89.26% when concentration increased from 20 to 160 mg/L. However, further increased of concentration, fluoride removal gradually decreased and reached to 84.68% when concentration increased to 100 mg/L. At higher initial concentration, the concentration gradient of fluoride is higher near the adsorbent surface (Mondal et al. 2022). Liu et al. (2014) reported almost similar results for removal of fluoride by using Titanium (V) hydrate based chitosan.

Effect of pH

Duck egg dust showed highly pH sensitive that means, it only support the strong acidic environment. The entire pH of the medium changed from 2 to 10 and the percentage of fluoride removal ranges from 90.2% to 85.81 % (Fig. 6). These results clearly indicate that the maximum adsorption occurred at pH 2. This is due to strong electrostatic attraction between positive charge of the adsorbent and negative charge of the fluoride ions (Wang et al. 2022; Mondal and Roy 2018). Our results showed good agreement with the findings of Tchomgui-Kamga et al. (2010). On the other hand, at higher pH, fluoride adsorption decreased to 5.5%. However, very recently, Shao et al. (2021) highlighted that acidic pH (pH < 5) is not favorable towards adsorption of fluoride onto $CaSO_4 \cdot 2H_2O$, due to higher solubility of calcium fluoride in acidic condition.

Effect of Adsorbent dose

Effect of fluoride removal under the influence of adsorbent dose in presented in Figure 7. From

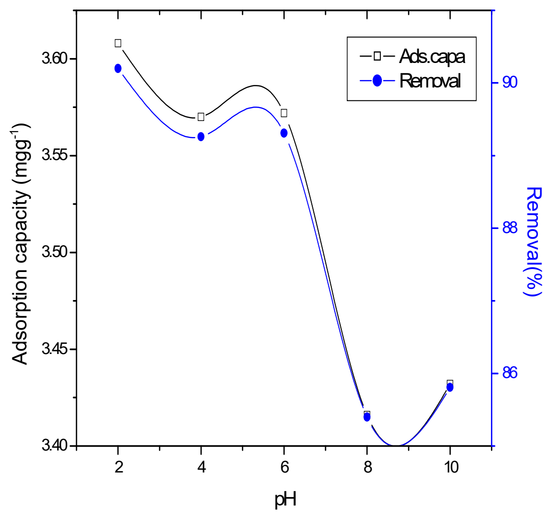


Fig. 6. Effects of pH (Concentration 60ppm, RPM 150, Dose 0.5/50ml, Time 30min, Temp. 40°C)

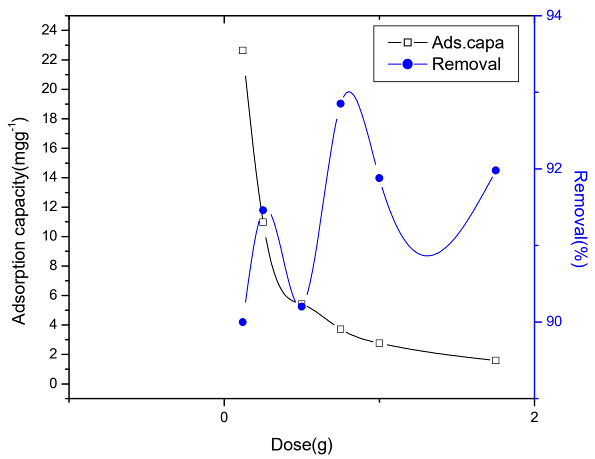


Fig. 7. Effects of Dose (Concentration 60ppm, pH 2, RPM 150, Time 30min, Temp. 40°C)

the figure 7 it in clear that 0.13 g increment of adsorbent dose, the percentage of removal increase only 1.46%. However, further has been increased of adsorbent dose to 0.75 g. The net removal increased to 92.85%. But, further increased of adsorbent dose does not support the removal of fluoride. These results are consistent with an expansion of available active site where fluoride can adsorbed (Shao et al. 2021; Iriel et al. 2018). Similar results were reported by earlier researchers for the various absorbent (Chaudhary and Maiti 2019; Tomar et al. 2013, 2014).

Effect of Time

The effect of contact time by varying time from 5 to 60 min under constant initial concentration (60mg/L), pH (2.0), adsorbent dose (0.75g/50ml), temperature (40°C) and shaking speed (150 rpm) and the outcome of the entire results presented in Figure 8. Results revealed that the gradual increment of percent removal from 85.4% to 92.85%, with increasing the contact time from 5 to 30 min. However, further increase of contact time percent removal shows decreased. This is perhaps due to active participation of surface functional groups (Mondal et al. 2022). Presents results corroborated with earlier findings where fluoride was removal by lateritic soil (Iriel et al. 2018). Almost similar results reported by Bhaumik et al. (2017) for removal of fluoride by fish scale dust.

Effect of Temperature

Temperature has tremendous effect on the absorption reaction (Zhao et al. 2021). In this study, temperature was varied from 25°C to 55°C and the results are depicted in the Figure

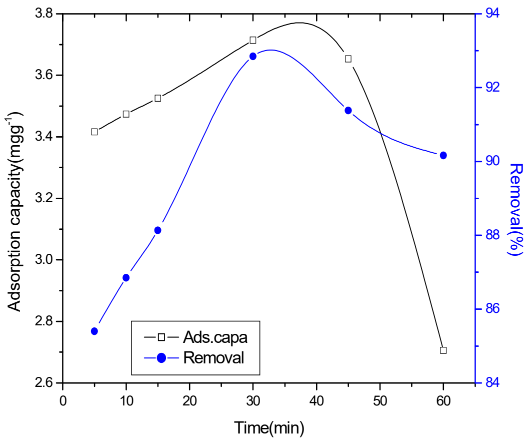


Fig. 8. Effects of Time (Concentration 60ppm, pH 2, Dose 0.75/50ml, RPM 150, Temp. 40°C)

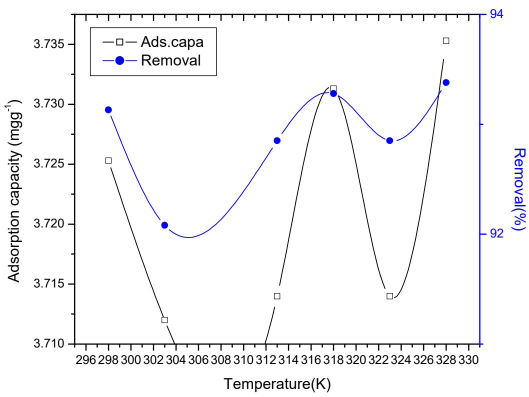


Fig. 9. Effects of Temperature (Concentration 60ppm, pH 2, Dose 0.75/50ml, Time 30min, RPM 150)

9. Figure 9 clearly demonstrated that at lower temperature, 25°C, the percentage of fluoride removal is 93.13% again at 30°C, removal slight decreased to 92.08%. But at 40°C and 45°C, the removal increased to 92.85 and 93.85%, respectively. Further increase of temperature, the removal again shows irregular variation ultimately at higher temperature (55°C) the percentage of removal is 93.38 which is not significantly higher than the results obtained at 45°C. Similar temperature effect on the removal of anion from aqueous medium was reported by previous researchers (Ghosh and Mondal 2019; Paradelo et al. (2017).

Effect of Agitation rate

The effect of shaking speed on fluoride removal was studied by varying the shaking speed from 100 to 300 rpm and the results is depicted in Figure 10. From the figure 10 it is recorded that at 150 rpm, the maximum (92.85%) removal of fluoride occurred. But at higher shaking speed does not support towards removal of fluoride. This is probably due to at higher shaking speed the attached / adsorbed fluoride detouched from the surface of duck egg shell dust (Bhaumik et al. 2012) or initial fluoride monolayer formation on the surface of the adsorbent (Suneetha et al. 2015). Almost similar observation was recorded from the earlier studies (Bhaumik et al. 2013).

Isotherm study

Fluoride adsorption isotherm on to duck egg shell dust (DESD) was investigated by using Freundlich, Langmuir and D-R isotherms. The linear form of Freundlich, Langmuir and D-R isotherms are presented as (Eq. 5, 6 and 7):

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{5}$$

$$\frac{1}{t_e} = \frac{1}{q_{\max} K_L C_e} + \frac{1}{q_{\max}} \tag{6}$$

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{7}$$

The symbols are their usual meaning. The experiment data were fitted in the above equation and the entire results are depicted in Table 1. From the Table 1 it is clear that it is best fitted with Langmuir isotherm.

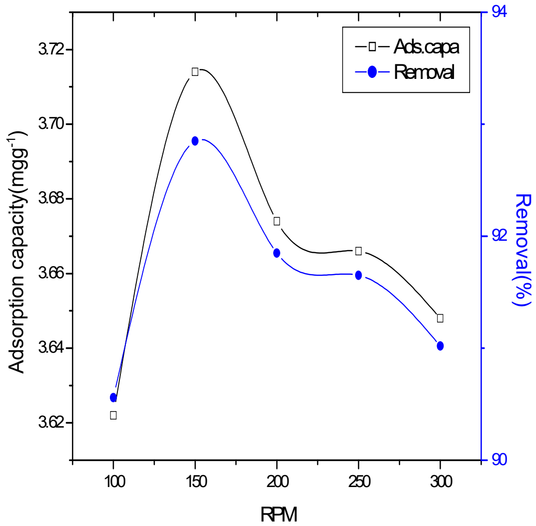


Fig. 10. Effects of RPM (Concentration 60ppm, pH 2, Dose 0.75/50ml, Time 30min, Temp. 40°C)

Table 1. Isotherm model parameters for the adsorption of fluoride on DESD

Isotherm	Parameters	Values
Langmuir	q_m (mg/g)	4.894
	K_L (L/mg)	0.056
	R^2	0.819
Freundlich	K_f	4.256
	1/n	0.71
	R^2	0.597
Dubinin- Radushevich	Q_m (mg/g)	13.677
	E (kj/ml)	233.71
	R^2	0.742

Langmuir isotherm

Langmuir model is also applicable to calculate the affinity between F- and DSED using Langmuir parameter which can be presented by the following way (Eq. 8):

$$R_L = \frac{1}{1 + bC_0} \tag{8}$$

Where, C_o is the initial F- concentration (mg/L) and is the Langmuir isotherm constant. From the above value of RL, the entire adsorption can be described as: $R_L > 1$ unfavourable, $R_L = 1$ linear, $0 < R_L < 1$ favourable, $R_L = 0$ irreversible. In the present study, the calculated R_L value for adsorption of F- onto DESD using above expression were found to be 0.4717, 0.3086, 0.2294, 0.1825, 0.1515 at initial concentration range 20 to 100 mg/L.

Freundlich isotherm

Freundlich adsorption isotherm is a value isotherm which is used to describe the data for heterogenous adsorbents. The general form of Freundlich equation is presented as (Eq. 9 and 10):

$$q_F = K_F C_F^{\ 1/n} \tag{9}$$

The linear form is: $log(q_F) \ = \ log \ K_F + 1/n \ log \ C_F$ (10)

Where, K_F =Freundlich adsorption capacity parameter, (mg/g) $(L/mg)^{1/n}$

1/n = Freundlich adsorption intensity parameter.

A graphical presentation between log(qF) and log KF is presented in figure (Figure not supplied) . The adsorption capacity, adsorption intensity, values are presented in a Table 1.

D-R isotherm

The Dubinin-Radushkenich (D-R) isotherm model is used to ascertain whether a adsorption reaction is proceed through physical or chemical process (Mungapati and Kim 2017). D-R is also used to determine the free energy of adsorption. The non-linear form of D-R equation is presented in the following way (Eq. 11 and 12):

$$q_e = Q_m exp\left(-K\left[RT\ ln\ \left(1+1/C_e\right)\right]^2\right) \quad (11)$$

$$q_e = Q_m = exp\left(-K\varepsilon^2\right) \quad (12)$$

where, Q_m is the maximum amount of fluoride ions that can be sorbed onto perg of DESD, ε is the Polanyi potential which is equal to *RT ln(1/1+* C_e*).*

Isotherm study clearly says that adsorption is favourable, because both K_F and n i.e, adsorption capacity and the adsorption intensity are 4.256 and 0.71, respectively are quite high (Table 1). The condition of adsorption was assessed from Freundlich constant, 1/n (Munagapati and Kim 2017). When $0 < 1/n < 1$, the adsorption is favourable; when $1/n = 1$, the adsorption is irreversible; and when $1/n>1$, the adsorption is unfavorable (Chem and Zhang 2014). On the other hand Langmuir isotherm suggest that the adsorption capacity of DESD is 4.894 which is really promising adsorbent towards adsorption of fluoride and it is much better than the previous adsorbents such as Tealeaf ash, lemon leaf, sugarcane baggase ash and banana peel dust (Mondal et al. 2012; Bhaumik et al. 2013; Mondal et al. 2013; Bhaumik and Mondal 2013; Mondal and Roy 2016). Similarly, Langmuir isotherm could be predicted based on whether the adsorption is favourable or unfavourable in terms of equilibrium parameter or dimensionless constant factor R_L which is represented in Eq. 13.

$$R_L = \frac{1}{1+K_L C_0} \quad (13)$$

Where, K_L is the Langmuir constant and C_O is the initial concentration of fluoride. The condition of favourable adsorption is $0 < R_L$, but if $R_L>1$ or $R_L = 0$ is linear or unfavourable, respectively. In the present study R^2 values were recorded as 0.4717, 0.3086, 0.2294, 0.1825, 0.1515 for initial concentration 20, 40, 60, 80, and 100 mg/L, respectively. Moreover, the free energy of sorption E (kj/mol) required for transfer of one make of fluoride from the infinity in the solution to the surface of DESD is only 233.71 KJ/mol. Therefore, it is very small and loss than 16 kj/mol, i.e, the adsorption of fluoride is solely based on physical process (Munagapati and Kim 2017: Mondal et al. 2012).

Kinetic study

Kinetic study is an extremely important study is an extremely important study through which the exact reaction pathways and mechanism of adsorption reaction can be understood (Won et al. 2009). Kinetics of fluoride adsorbed by DESD was assessed by pseudo first-order, pseudo second-order, kinetics and intraparticle diffusion and the entire results is presented in Table 2. Any adsorption process where pollutant adsorbed onto the solid-pores materials will follow the following steps: i) bulk solution transport, ii) external (film) resistance to transport, and iv) adsorption (rapid for physical adsorption) (Adamson and Gast 1997). In this study The Linear form of Lagergren's pseudo first-order model is expressed as (Eq. 10):

$$log\left(q_e - q_t\right) = log\ q_e - K_L t / 2.303 \quad (10)$$

where, q_e is the amount of fluoride adsorbed onto the DESD at equilibrium (mg/g), qt is the amount of fluoride adsorbed at time t onto DESD, and KL is the pseudo first order rate constant for the kinetic model (1/min). The present study results is depicted in Table 2. From the Table 2 it is clear that adsorption fluoride onto DESD is to not follow the pseudo first order kinetics. However, pseudo second order kinetics nicely fitted with experimental results which is reflected

Table 2. Kinetics model of adsorption of fluoride on duck egg shell dust

Kinetics	Parameters	Values
Pseudo-first-order	$q_{e,}$ exp (mg/g)	13.672
	K_1(L/min)	$9.636*10^2$
	R^2	0.742
Pseudo-second-order	$q_{e,}$ cal (mg/g)	0.367
	K_2 (g/mg/min)	1.742
	R^2	0.956
Intraparticles diffusion	K_i	15.02
	I	48.679
	R^2	0.632

Table 3. Thermodynamic parameter of F^- on DESD

Temperature(K)	ΔG (j/mol)	ΔH (j/mol)	ΔS(j/mol K)	R^2
298	-2805.49	0.049	0.117	0.933
303	-2796.71			
313	-2897.57			
318	-3020.97			
323	-2990.15			

from regression coefficient (R^2) value (R^2 = 0.956). Results also indicated that intraparticle diffusion model is not full agreement with the experimental results (Table 2).

Thermodynamic study

The adsorption can be judged whether is thermodynamically feasible or not i.e, exothermic, endothermic or free energy of adsorption reaction can be calculated by the following equation (Pannecrselvam et al. 2011) (Eq. 11-14):

$$K_c = C_{ae} / C_e \tag{11}$$

$$\Delta G^0 = -RT \ ln \ K_c \tag{12}$$

$$\Delta H^0 = RT_2T_1 / T_2 - T_1 ln \ K_2 / K_1 \tag{13}$$

$$\Delta S^0 = \Delta H^0 - \Delta G^0 / T \tag{14}$$

Where, K_c is the equilibrium concentration constant and C_{ae} andC_e are the equilibrium concentration of fluoride ions on the DESD (mg/L) and the equilibrium concentration of fluoride ions in the solution (mg/L), respectively.

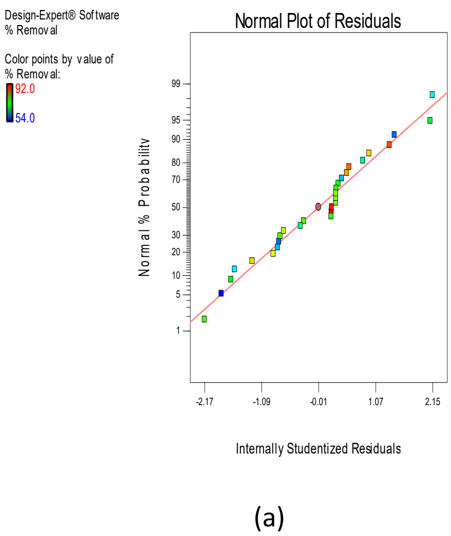
On the other hand, ΔG^0, ΔH^0, ΔS^0 are free energy, enthalpy and entropy of fluoride adsorption at standard state. Present study results indicate that free energy is negative in all studied temperature and negative value of increase with increasing temperature from 298 K to 318 K (Figure not supplied), but further increase of temperature free energy is negative but lower magnitude which suggest that fluoride adsorption is favourable up to 318K (Table. 3). Again positive value of ΔH^0, indicate the adsorption is exothermic in nature at higher temperature. Moreover, the increased randomness at the DESD solution interface during adsorption of fluoride by DESD (Dehghani et al. 2016).

Modelling study (RSM)

Recently most of the researchers used only one factor -at-a-time experiments for evaluating the influence of various operating variables on the outcome of the selected dependent variable in batch mode experiment for removal of heavy metals, dyes or other inorganic pollutants (Al Mesfer et al. 2021; Khataee et al. 2011). But this technique is absolutely time wasting and laborious task. To overcome such difficulties by Response Surface Methodology (RSM), this was introduced by Box and Wilson (1951). RSM is a blending technology where both Mathematics and Statics are combined to build an empirical model to solve various problems by providing respective responses against interaction between various variables (Montgomery 2005). In this study, fluoride removal was assessed by various operating variables such as initial fluoride concentration, pH, adsorbent dose, and contact time. The optimizations of the four variables were screened by applying RSM. The entire experimental data were fitted to a second-order polynomial model (Eq. 4). Based on the experimental data obtained from removal of fluoride by duck shell dust and the second order polynomial regression model presented by equation 15.

Removal (%) = 77.56+6.82 (initial concentration - IC) + 5.69 (adsorbent dose - AD) + 1.80 (contact time- CT) + 10.74(pH) -1.3 IC* AD – 5.4 IC*CT +5.13 IC * pH – 1.46 AD *CT +1.35 AD * pH + 2.19 CT*pH – $3.14(IC)^2$– $0.74(AD)^2$ + $0.31(CT)^2$ – $5.46(pH)^2$ (15)

Removal (%) = 77.56+6.82 (initial concentration - IC) + 5.69 (adsorbent dose - AD) + 1.80 (contact time- CT) + 10.74(pH) -1.3 IC* AD - 5.4 IC*CT +5.13 IC * pH - 1.46 AD *CT +1.35 AD * pH + 2.19 CT*pH - 3.14(IC)2 - 0.74(AD) 2 + 0.31(CT) 2 - 5.46(pH)2 (15) The analysis of variance (ANOVA) for the proposed model and the probability value (p-value) those are less than 0.05 are consider as statistical significant at 95% level of significance (Table 4). From the ANOVA it has been found that ‘F’- value is 47.50 and it is significant at $p < 0.0001$. Similarly, very large p-value ($p < 0.0933$) was recorded for lack of fit that means lack of fit is non-significant. Another significant ratio called adequate ratio is the ratio of predicted responses and average standard deviation. Normally, > 4 is the acceptable value of this particular ratio (El-Din Mohamed et al. 2020). Present study, this ratio war recorded as 22.203 that is signal is acceptable. Similarly, the goodness of fit, R^2 is the indication of the overall acceptability of model and which is very close to 1.0 (0.9794). Therefore, all the above indicators clearly indicate that the model is lightly significant. A plot of the residuals was also used to assess the



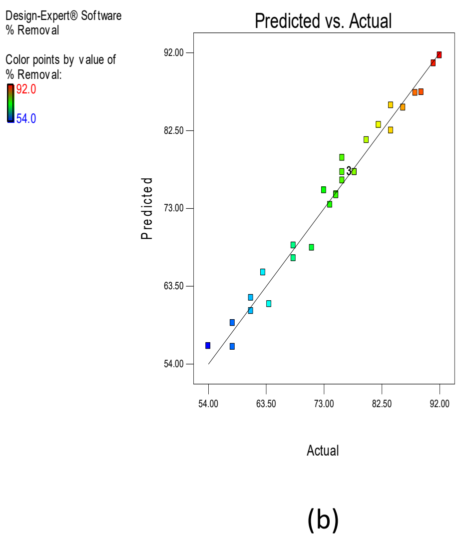


Fig. 11. Assess the adequacy of the model used the plot of the residuals (a) Normal probability of residuals and (b) Predicted versus actual values.

Table 4. ANOVA for Response Surface Quadratic Model for adsorption of fluoride by Duck egg shell dust

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model significant	3021.63	14	215.83	47.50	< 0.0001
A-initial concentration	*523.35*	*1*	*523.35*	*115.18*	*< 0.0001*
B-adsorbent dose	*382.12*	*1*	*382.12*	*84.10*	*< 0.0001*
C-contact time	*36.60*	*1*	*36.60*	*8.05*	*0.0132*
D-PH	*1263.96*	*1*	*1263.96*	*278.18*	*< 0.0001*
AB	*8.45*	*1*	*8.45*	*1.86*	*0.1941*
AC	*98.89*	*1*	*98.89*	*21.76*	*0.0004*
AD	*111.42*	*1*	*111.42*	*24.52*	*0.0002*
BC	*9.31*	*1*	*9.31*	*2.05*	*0.1743*
BD	*5.44*	*1*	*5.44*	*1.20*	*0.2925*
CD	*20.05*	*1*	*20.05*	*4.41*	*0.0543*
A^2	*64.03*	*1*	*64.03*	*14.09*	*0.0021*
B^2	*3.13*	*1*	*3.13*	*0.69*	*0.4204*
C^2	*0.60*	*1*	*0.60*	*0.13*	*0.7222*
D^2	*150.49*	*1*	*150.49*	*33.12*	*< 0.0001*
Residual	63.61	14	4.54		
Lack of Fit	*60.61*	*11*	*5.51*	*5.51*	*0.0933*[NS]
Pure Error	*3.00*	*3*	*1.00*		
Cor Total	3085.24	28			

appropriateness of the model. The normal plot of residuals was presented in Figure 11. Another Figure 12 represent predicted versus actual values. In both the figures Figure 11 and 12 clearly indicate that most of the observed values are in and around of straight line. The output of the model is clearly revealed that the experimental values are well fitted. Similarly, 3D response surface plot (Fig. 12a-f) indicate the interaction effect between the variables. This type of plot are generally represent as the function of two variables at the same time, keeping the third variable at the level (Li et al. 2018). As shown in figure from 12a, it is clear that both adsorbent dose and initial concentration are simultaneously change, and the percent removal increasing with change of both dose and initial concentration of fluoride solution (Alkhatib et al. 2015). Almost similar response surface plot was recorded for the variation of contact time and adsorbent dose (Fig. 12d). But in this case surface plot nicely demonstrate that percentage of removal much steeper with adsorbent dose, but percent removal with contact time is not so steeper (Fig. 12d). The optimum condition (initial concentration 89.29, adsorbent dose 1.112 g/50 mL contact time 42.5 min and pH 9.95) of fluoride removal was extracted from the desirable study (Fig. 13). The most important part of this modeling technique is perturbation plot which is really important to know the importance or most influential operating variables (Fig.14). From the figure 14 it is clearly revealed that the most influential factors are pH followed by adsorbent dose, then initial concentration and least influential factor is contact time.

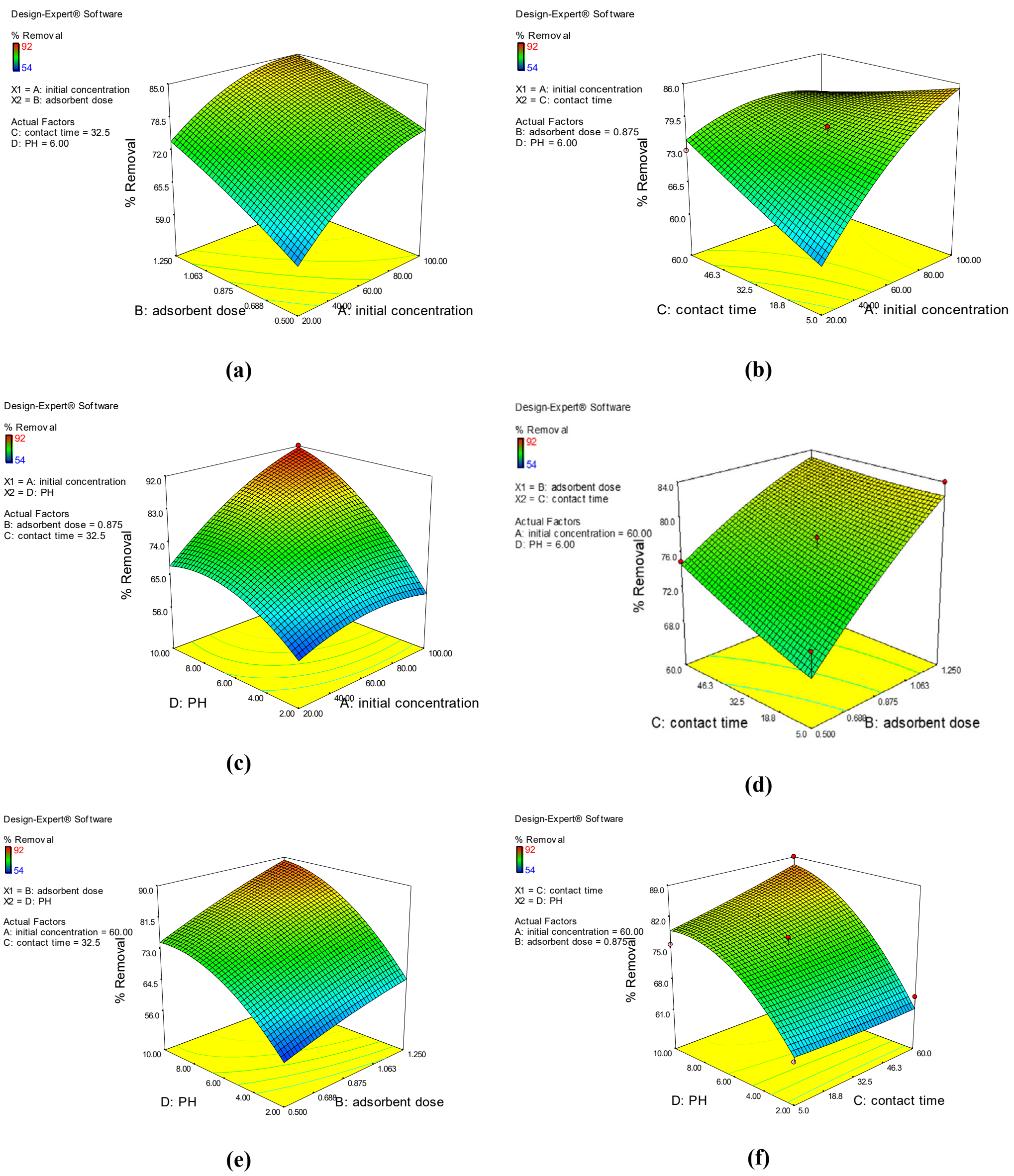


Fig. 12(a-f). Response surface plots showing the effect of independent variables on Fluoride adsorption onto DESD adsorption**.**

Desorption study

Desorption study is an important part of adsorption study where exhausted adsorbent can be regenerated (Yihunu et al. 2020). In this study, desorption was performed with 0.1 (M) NaOH solution. The results revealed that at high pH medium, maximum 97.3% desorption occurred (Fig. 15). This is perhaps due to higher hydroxyl ion concentration replaced accumulated fluoride ions (Mondal et al. 2015; Nur et al. 2014). In previous study, Bhaumik and Mondal (2014) also regenerated the exhausted banana peel with NaOH solution. Almost similar desorption study with various alkaline pH solution was used by earlier researchers (Bhaumik and Mondal 2016; Mondal et al. 2012).

Comparative study

Many previous researchers were reported for removal of fluoride by using low-cost materials. A comprehensive list of low-cost materials was depicted in a Table 5. From the Table 5 it

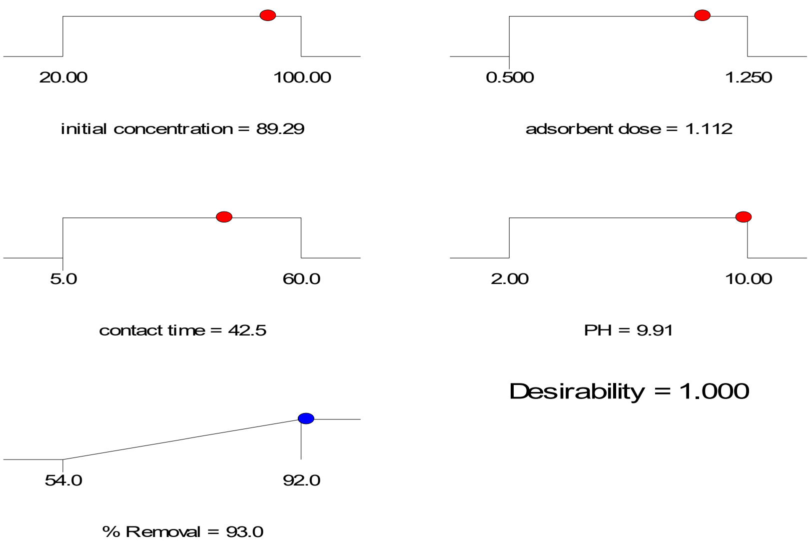


Fig. 13. Desirability ramp of fluoride adsorption by DESD

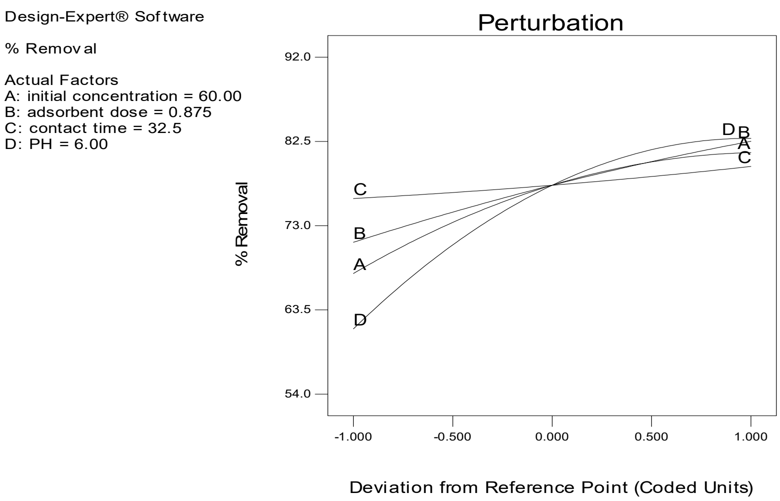


Fig. 14. Perturbation plot of Fluoride adsorption by DESD

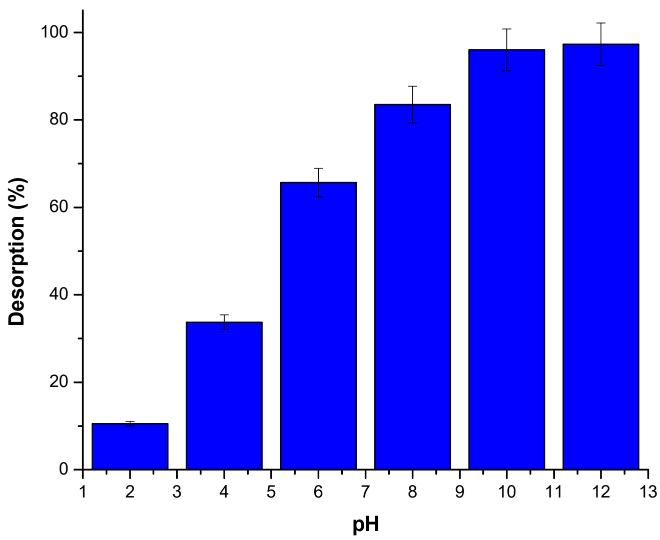


Fig. 15. Desorption of fluoride under various pH medium

Table 5. Comparison of the defluoridation capacities of different biosorbents

Adsorbents	pH	Removal (%)	Adsorption capacity (mg/g)	References
1. Fruit peel (Banana peel)	--	86.5	8.15	Mondal and Roy 2018
2. Natural banana peel (*Musa acuminate*)	--	--	1.212	Mondal 2017
3. Fish scale (*Catla catla*)	6.0	89.21	4.89	Bhaumik et al., 2017
4. Potato plant ash	2.0	62.5	34.5	Ghosh et al., 2016
5. Modified banana peel				
BPD-1				
BPD-2	5.6	95.43	17.43	Bhaumik and
BPD-3	6.1	96.395	26.31	Mondal 2016
	7.2	98.197	39.5	
6. Aluminium impregnated coconut fiber ash	5.0	---	3.192	Mondal et al., 2015
7. Acitivated coconut fiber				Bhaumik and Mondal 2015
CFD-1				
CFD-2	6.0	--	12.66	
CFD-3	6.1	--	25.64	
	6.9	--	38.46	
8. Lemon leaf (*Citrus* sp.)				Bhaumik et al.,
LLD-1	6.0		7.63	2013
LLD-2	6.0	96.9 -98.8	27.03	
LLD-3	6.0		38.46	
9. Sugarcane charcoal	--	--	7.33	Mondal et al., 2013
10. *Aspergillus*	10.0	--	8.09	Mondal et al.,
Ca-impregnated *Aspergillus*	8.0	--	4.80	2013
11. Waste Tea ash	6.0	--	5.59	Mondal et al., 2012
12. Egg shell dust (chicken)	6.0	94.5	1.09	Bhaumik et al., 2012
13. Clay composite	--	91.6	0.093	Gidi et al., 2019
14. Duck shell dust	--	--	4.894	Present work

was found that very high adsorption capacity (12.66 - 39.5 mg/g) of fluoride was reported by Bhaumik et al. (2013); Bhaumik and Mondal (2015). Bhaumik and Mondal (2016); and Ghosh et al. (2016) for the materials such as Lemon leaf (Citrus sp.), activated coconut fibre, modified banana peel, and potato plant ash, respectively. However, moderate adsorption capacity (5.59 - 8.15 mg/g) were also reported by Mondal et al. (2012); Mondal et al. (2013); Mondal et al. (2013); and Mondal and Roy (2018) by using waste tea ash, *Aspergillus* biomass and Ca-impregnated *Aspergillus* biomass, sugarcane charcoal and fruit peel (Banana peel), respectively

(Table 5). Very low level adsorption capacity (0.093 - 4.89 mg/g) were also recorded for the biomass such as clay composite, fish scale (*Catla catla*), aluminium impregnated coconut fiber ash, egg shell dust (Chicken) etc. Present biomass, duck shell dust showed moderate adsorption capacity (4.894 mg/g) and it is much better than natural banana peel (Musa acuminate), clay composite, chicken egg shell dust etc.

CONCLUSIONS

Egg shell dust is an inexpensive material which is also available as waste material. Present study clearly prove that the duck egg shell dust has enough potentiality towards removal of fluoride from aqueous medium. The experimental data nicely fitted with isotherms, kinetics and thermodynamics equations. Both isotherm and kinetics data suggested that the duck egg shell dust has moderately fluoride adsorption capacity and interaction between fluorine and adsorbent surface is absolutely chemical in nature. Moreover, thermodynamics of adsorption results revealed that the adsorption of fluoride on the duck egg shell is favorable at intermediate temperature. Again positive value of enthalpy indicate the adsorption is exothermic in nature at higher temperature. Finally, the experimental data were fitted in response surface methodology model for optimization study. The desorption study clearly indicate the exhausted adsorbent nicely regenerated by dilute solution of sodium hydroxide. Therefore, it may be concluded that duck shell dust could be an efficient adsorbent for removal of fluoride. However, further study can be initiated to remove other anionic species from aqueous medium by using duck shell dust and modification of said egg shell dust to enhance its adsorption capacity.

CONFLICT OF INTEREST

All the authors unanimously declare that they have no conflict of interest.

FUNDING

Not applicable in the system

INFORMED CONSENT

Not applicable in the system

AUTHORS' CONTRIBUTION

N. K. Mondal: Designing the experiment, drafting the MS and overall supervision; **P. Roy**: conduct the experiment and typing the MS; **K. Sen**: characterized the adsorbent and MS checking; **A. Mondal**: Sample preparation and help in instrumentation; **P. Debnath**: characterized the adsorbent and MS checking

ABBREVIATION

XRF: X-ray fluorescence, **XRD**: X-ray diffraction, **SEM-EDAX**: Scanning electron microscopy-energy dispersive X-ray, **RSM**: Response Surface Methodology, CaF_2: Calcium fluoride, Na_3AlF_6: Sodium aluminium fluoride, KNO_3: Potassium nitrate, **CaO**: Calcium oxide, $CaCO_3$: Calcium carbonate, $Ca(OH)_2$: Calcium hydroxide, **NaOH**: Sodium hydroxide, **EDAX**: Energy dispersive X-Ray, R_L: Langmuir parameter, **DESD**: duck egg shell dust

REFERENCES

Al Mesfer, M.K., Danish, M., & Shah, M. (2021). Optimization of fluoride adsorption from aqueous solution over mesoporous titania-alumina composites using Taguchi method. Water Environ. Res. 94, e1663. https://doi.org/10.1002/wer.1663

Akuno, M.H., Nocella, G, Milia, E.P., & Gutierrez, L. (2019). Factors influencing the relationship between fluoride in drinking water & dental fluorosis: a ten-year systematic review & meta-analysis. J. Water Health 17(6), 845-862. https://doi.org/10.2166/wh.2019.300.

Alkhatib, M.F., Mamun, A.A., & Akbar, I. (2015). Application of response surface methodology for optimization of colour removal from POME by granular activated carbon. Inter. J. Environ. Sci. Technol. 12, 1295-1302. https://doi.org/10.1007/s13762-014-0504-4

Adamson, A., & Gast, A. (1997). Physical Chemistry of Surface, Wiley N. Y, 368.

Baker, J.R., & Balch, D.A. (1962). A study of the organic material of hen's eggshell. Biochem. J. 82, 352–361. https://doi.org/10.1042/bj0820352

Bashir, A.S.M., & Manusamy, Y. (2015). Characterization of Raw Egg Shell Powder (ESP) as A Good Bio-filler. J. Eng. Res. Technol. 2(1), 56-60.

Bhaumik, R., & Mondal, N.K. (2014). Optimizing adsorption of fluoride from water by modified banana peel dust using response surface modelling approach. Appl.Water Sci. http://dx.doi.org/ 10.1007/s13201-014-0211-9.

Bhaumik, R., & Mondal, N.K. (2016). Optimizing adsorption of fluoride from water by modified banana peel dust using response surface modelling approach. Appl. Water Sci. 6, 115–135. http://dx.doi.org/10.1007/s13201-014-0211-9

Bhaumik, R., Mondal, N.K., Das, B., Roy, P., Pal, K.C., Das, C., Banerjee, A., & Dutta, JK (2012). Eggshell powder as an adsorbent for removal offuoride from aqueous solution: equilibrium, kinetic & thermodynamic studies. Eur. J. Chem. 9(3), 1457–1480. http://dx.doi.org/10.1155/2012/790401

Bhaumik, R., Mondal, N.K., Chattoraj, S., & Datta, J.K. (2013). Application of response surface methodology for optimization of fluoride removal mechanism by newely developed biomaterial. Am. J. Anal. Chem. 4, 404–419. http://dx.doi.org/10.4236/ajac.2013.48051

Bhaumik, R, Mondal, N.K., & Chattoraj, S. (2017). An optimization study for defluoridation from synthetic fluoride solution using scale of Indian major carp Catla (*Catla catla*): An Unconventional Biosorbent. J. Fluorine Chem. 195, 57-69. https://doi.org/10.1016/j.jfluchem.2017.01.015

Bhaumik, R., & Mondal, N.K. (2015). Adsorption of fluoride from aqueous solution by a new low-cost adsorbent: thermally & chemically activated coconut fibre dust. Clean Technol. Environ. Policy. 17, 2157–2172. doi:10. 1007/s10098-015-0937-6

Blumenkrantz, N., & Asboe-Hansen, G. (1973). New method for quantitative determination of uronic acids. Anal. Biochem. 54, 484–489. https://doi.org/10.1016/0003-2697(73)90377-1

Box, G.E.P., & Wilson, K.B. (1951). On the experimental attainment of optimum conditions. J. R. Stat. Soc. 13(1), 1-45.

Chattoraj, S. Mondal, N.K., Das, B., Roy, P., & Sadhukhan, B. (2013). Biosorption of
carbaryl from aqueous solution onto Pistiastratiotes biomass. Appl. Water Sci. 4, 79-88. http://doi.org/10.1007/s13201-013-0132-z.

Chaudhary, M., & Maiti A. (2019). Defluoridation by highly efficient calcium hydroxide
nanorods from synthetic & industrial wastewater. Colloids Surf, A Physicochem. Eng. Asp. https://doi.org/10.1016/j.colsurfa.2018.10.052

Chen, N., Feng, C., & Li, M. (2014). Fluoride removal on Fe-Alimpregnated granular ceramic adsorbent from aqueous solution. Clean Technol. Environ. Policy 16, 609–617. https://doi.org/10.1007/s10098-013-0659-6

Chen, N., Zhang, Z., Feng, C., Li, M., Zhu, D., Chen, R., & Sugiura N. (2010.) An excellent fluoride sorption behaviour of ceramic adsorbent. J. Hazard. Mater. 183, 460–465. https://doi.org/10.1016/j.jhazmat.2010.07.046

Chiavola, A., D'Amato, E., & Di Marcantonio, C. (2022). Comparison of Adsorptive Removal of Fluoride from Water by Different Adsorbents under Laboratory & Real Conditions. Water 14, 1423. https://doi.org/10.3390/w14091423

Dehghani, M.H., Sanaei, D., Ali, I., & Bhatnagar, A. (2016). Removal of chromium(VI) from aqueous solution using treated waste newspaper as a low-cost adsorbent: Kinetic modeling & isotherm studies. J. Mol. Liq. 215, 671-679. https://doi.org/10.1016/j.molliq.2015.12.057

El-Din Mohamed, W.S., Hamad, M.T.M.H., & Kamel, M.Z. (2020). Application of statistical response surface methodology for optimization of fluoride removal efficiency by Padina sp. alga. Water Environ. Res. 92, 1080–1088.

Fan, X., Parker, D.J., & Smith, M.D. (2003). Adsorption kinetics of fluorideon low cost materials. Water Res. 37, 4929–4937. https://doi.org/10.1016/j.watres.2003.08.014

Freire, M.N., & Holanda, J.N.F. (2006). Characterization of avian eggshell waste aiming its use in a ceramic wall tile paste‖. Cerâmica 52, 240-244. https://doi.org/10.1590/S0366- 69132006000400004

Ghalhari, M.R., Kalteh, S., Tarazooj, F.A., Zeraatkar, A.and Mahvi, A.H. (2021). Health risk assessment of nitrate & fuoride in bottled water: A case study of Iran. Environ. Sci. Pollut. Res. 28, 1–12. https://doi.org/10.1007/s11356-021-14027-w

Ghosh, S.B., Bhaumik, R., & Mondal, N.K. (2016). Optimization study of adsorption parameters for removal of fluoride using aluminium-impregnated potato plant ash by response surface methodology. Clean Technol. Environ. Policy 18(4), 1069-1083. https://doi.org/10.1007/s10098-016-1097-z

Ghosh, S.B., & Mondal, N.K. (2019). Application of Taguchi method for optimizing the process parameters for the removal of fluoride by Al-impregnated *Eucalyptus* bark ash. Environ. Nanotechnol. Monitor. Manage. 11, 100206. https://doi.org/10.1016/j.enmm.2018.100206

Gidi, L.D., Amare, E.Z., & Murthy, H.C.A., & Abebe, B. (2019). Application of Novel Clay Composite Adsorbent for Fluoride Removal. Mater. Sci. Res. Ind. 16(2). doi.org/10.13005/msri/160209

Grzegorzek, M., Majewska-Nowak, K., & Ahmed, A.E. (2020). Removal of fluoride from multicomponent water solutions with the use of monovalent selective ion-exchange membranes. Sci. Total Environ. 722, 137681. doi.org/10.1016/j.scitotenv.2020.137681

Hamidi, A.A., Salimi, M.N., & Yusoff, A.H.M. (2017). Synthesis & characterization of eggshell-derived hydroxyapatite via mechanochemical method: A comparative study. AIP Conference Proceedings 1835; 020045. https://doi.org/10.1063/1.4981867

Handa, B.K. (1975). Geochemistry & genesis of fluoride- containing ground waters in India. Groundwater 13, 275-281. https://doi.org/10.1111/j.1745-6584.1975.tb03086.x

Hashemkhani, M., Ghalhari, M.R., Bashardoust, P., Hosseini, S.S., Mesdaghinia, A., & Mahvi, A.H. (2022). Fluoride removal from aqueous solution via environmentally friendly adsorbent derived from seashell. Sci. Reports 12, 9655 https://doi.org/10.1038/s41598-022-13756-3

Iriel, A., Bruneel, S.P., Schenone, N., & Cirelli, A.F. (2018). The removal of fluoride from aqueous solution by a lateritic soil adsorption: Kinetic & equilibrium studies. Ecotoxicol. Environ. Safety 149, 166-172. https://doi.org/10.1016/j.ecoenv.2017.11.016

Khataee, A.R., Kaisiri, M.B., Alidokht, L. (2011). Application of response surface methodology in the optimization of photocatalytic removal of environmental pollutants using nanocatalysts. Environ. Technol. 32(15), 1669-1684. https://doi.org/10.1080/09593330.2011.597432.

Liu, J., Li, W-Yi., Liu, Y., Zeng, Q., Hong, S. (2014). Titanium (V) hydrate based on chitosan template for defluoridation from aqueous solution. Appl. Surface Sci. 213, 46-54. https://doi.org/10.1016/j.apsusc.2013.12.050

Iizuka, A., Ho, H-J., & Yamasaki, A. (2022). Removal of fluoride ions from aqueous solution by metaettringite. PLoS ONE 17(3), e0265451. https:// doi.org/10.1371/journal.pone.0265451

Mondal, N.K., & Kundu, M. (2016). Biosorption of Fluoride from Aqueous Solution Using Lichen And Its Ca-Pretreated Biomass. Water Conserv. Sci. Eng. 1(3), 143-160. https://doi.org/10.1007/s41101-016-0009-8

Mondal, N.K., Bhaumik, R., Roy, P., Das, B., & Datta, J.K. (2013). Investigation on fixed bed column performance of fluorideadsorption by sugarcane charcoal. J. Environ .Biol. 34, 1059-1064

Mondal, M.K. (2010). Removal of Pb (II) from aqueous solution by adsorption using activated tea waste. Korean J. Chem. Eng. 27(1), 144–151. https://doi.org/10.1007/s11814-009-0304-6

Mondal, N.K. (2017). Effect of fluoride on photosynthesis, growth & accumulation of four widely cultivated rice (*Oryza sativa* L.) varieties in India. Ecotoxicol. Environ. Safety 144, 36-44. https://doi.org/10.1016/j.ecoenv.2017.06.009.

Mondal, N.K. (2017). Natural Banana (Musa acuminate) Peel: an Unconventional Adsorbent for Removal of Fluoride from Aqueous Solution through Batch Study. Water Conserv. Sci. Eng. 1(4), 223-232. https://doi.org/10.1007/s41101-016-0015-x

Mondal, N.K., Samanta, A., Dutta, S., & Chattaraj, S. (2017). Optimization of Cr (VI) biosorption onto *Aspergillus niger* using 3-level Box-Behnken design: equilibrium, kinetic, thermodynamic & regeneration studies. J. Genetic Eng. Biotechnol 15, 151-160. https://doi.org/10.1016/j.

jgeb.2017.01.006
Mondal, N.K., & Roy, S. (2016). Optimization study of adsorption parameters for removal of phenol on gastropod shell dust using response surface methodology. Clean Technol. Environ. policy 18(2), 429-447. https://doi.org/10.1007/s10098-015-1026-6
Mondal, N.K., Bhaumik, R., Banerjee, A., Datta, J.K., & Baur, T. (2012). A comparative study on the batch performance of fluoride adsorption by activated silica gel & activated rice husk ash. Int. J. Environ. Sci. 2(3), 1643–1661. https://doi.org/10.6088/ijes.00202030049
Mondal, N.K., Bhaumik, R., & Datta, J.K. (2015). Removal of fluoride by aluminum impregnated coconutfiber from synthetic fluoride solution & natural water.
Alexandria Eng. J. 54, 1273-1284. https://doi.org/10.1016/j.aej.2015.08.006
Mondal, N.K., Pal, K.C., & Kabi, S. (2012). Prevalence & severity of dental fluorosis in relation to fluoridein ground water in the villages of Birbhum district, West Bengal,India. Environmentalist 32, 70–84. https://doi.org/10.1007/s10669-011-9374-1
Mondal, N.K., Bhaumik, R., Baur, T., Das, B., Roy, P., & Datta, J.K. (2012b). Studies on defluoridation of water by tea ash: an unconventional biosorbent. Chem. Sci. Trans. 1(2), 239–256. https://doi.org/10.7598/cst2012.134
Mondal, N.K., Kundu, M., Das, K., Bhaumik, R., & Datta, J.K. (2013). Biosorption of fluoride from aqueous phase onto Aspergillus & its calcium-impregnated biomass & evaluation of adsorption kinetics. Fluoride 46(4), 239–245
Mondal, N.K., Bhaumik, R., Sen, K., & Debnath, P. (2022). Adsorption of fuoride in aqueous solutions using saline water algae (Rhodophyta sp.): an insight into isotherm, kinetics, thermodynamics and optimization studies. Model. Earth Syst. Environ. 8, 3507–3521 https://doi.org/10.1007/s40808-021-01320-3
Montgomery, D.C. (2005). Design & analysis of experiments: Response surface method & Design. John Wiley & Sons, Inc New York.
Munagapati, V.S., & Kim, D-Su. (2017). Equilibrium isotherms, kinetics, & thermodynamics studies for congo red adsorption using calcium alginate beads impregnated with nano- goethite. Ecotoxicol. Environ. Safety 141, 226-234. https://doi.org/10.1016/j.ecoenv.2017.03.036
Nakano, T, Ikawa, N.I & Ozimek,L. (2003). Chemical Composition of Chicken Eggshell & Shell Membranes. Poultry Sci. 82, 510–514. https://doi.org/10.1093/ps/82.3.510
Nasar, A.B., Walha, K., Charcosset, C., & Amar, R.B. (2011). Removal of fluoride ions using Cuttle fish bones. J. Fluoride Chem. 132, 57–62. https://doi.org/10.1016/j.jfluchem.2010.11.006
Nur, T., Loganathan, P., Nguyen, T.C., Vigneswaran, S., Singh, G., & Kandasamy, J. (2014). Batch & column adsorption & desorption of fluoride using hydrous ferric oxide: Solution chemistry & modelling. Chem. Eng. J. 247, 93-102. http://dx.doi.org/10.1016/j.cej.2014.03.009
Ok, Y.S., Lee, S.S., Jeon, W-T., Oh, S-E., Usman Adel, R.A., & Moon, D.H. (2011). Application of eggshell waste for the immobilization of cadmium & lead in a contaminated soil. Environ. Geochem. Health 33, 31–39. https:// doi.org/0.1007/s10653-010-9362-2
Pandey, J., & Pandey, U. (2011). Fluoride contamination & fluorosis in rural community in the vicinity of phosphate fertilizer factory in India. Bulletin Environ. Conta. Toxicol. 87(3), 245-249. https://doi.org/10.1007/s00128-011-0344-6
Panneerselvam, P., Morad, N., & Tan, K.A. (2011). Magnetic nanoparticle (Fe_3O_4) impregnated onto tea waste for the removal of nickel(II) from aqueous solution. J. Hazard. Mater. 186, 160-168. https://doi.org/10.1016/j.jhazmat.2010.10.102
Paradelo, R., Conde-Cid, M., Arias-Estevez, M., Nóvoa-Muñoz, J.C., Álvarez-Rodríguez, E., Fernández-Sanjurjo, M.J., & Núñez-Del, A. (2017). Removal of anionic pollutants by pine bark is influenced by the mechanism of retention. Chemosphere 167, 139-145. https://doi.org/10.1016/j.chemosphere.2016.09.158
Roy, P., Mondal, N.K., & Das, K. (2014). Modeling of the adsorptive removal of arsenic: a statistical approach. J. Environ. Chem. Eng. 2, 585–597. https://doi.org/10.1016/j.jece.2013.10.014
Sadhukhan, B., Mondal, N.K., & Chattoraj, S. (2014). Biosorptive removal of cationic dye from aqueous system: a response surface methodological approach. Clean Technol. Environ. Policy 16, 1015–1025. https://doi.org/10.1007/s10098-013-0701-8
Shao, S., Ma, B., Chen, Y., Zhang, W., & Wang, C. (2021). Behavior & mechanism of fluoride removal from aqueous solutions by using synthesized $CaSO_4·2H_2O$ nanorods. Chem. Eng. J. 426, 131364. https://doi.org/10.1016/j.cej.2021.131364

Sugashini, S., & Meera, S.B.K.M. (2013). Optimization using central composite design (CCD) for the biosorption of Cr(VI) ions by cross linked chitosan carbonized rice husk (CCACR). Clean Technol. Environ. Policy 15, 293–302. https://doi.org/10.1007/s10098-012-0512-3

Suneetha, M., Sundar, B.S. & Ravindhranath, K. (2015). Removal of fluoride from polluted waters using active carbon derived from barks of Vitex negundo plant. J. Anal. Sci. Technol. 6, 15 https://doi.org /0.1186/s40543-014-0042-1

Tomar, V., Prasad, S., & Kumar, D. (2013). Adsorptive removal of fluoride from water samples Using Zr-Mn composite material. Microchem. J. 111, 116-124. https://doi.org/10.1016/j.microc.2013.04.007

Tomar, V., Prasad, S., Kumar, D. (2014). Adsorptive removal of fluoride from aqueous media using Citrus limonum (lemon) leaf. Microchem. J. 112, 97-103. https://doi.org/10.1016/j.microc.2013.09.010

Tchmgui_Kamga E, Ngameni E, Darchen A (2010). Evaluation of removal efficiency of fluoride from aqueous solution using new charcoals that contain calcium compounds. J. Colloid Interface Sci. 346, 494-499. https://doi.org/10.1016/j.jcis.2010.01.088

Tahaikt, M., El Habbani, R., Ait Haddou, A., Achary, I., Amor, Z., Taky, M., Alami, A., Boughriba, A., Hafsi, M., & Elmidaoui, A. (2007.) Fluoride Removal from Groundwater by Nanofiltration. Desalin. 212(1-3), 46-53. https:// doi.org/10.1016/j.desal.2006.10.003

Wang, T., Yan, L., He, Y., Alhassan, S.I., Gang, H., Wu, B., Jin, L., & Wang, H. (2022). Application of polypyrrole-based adsorbents in the removal of fluoride: a review. RSC Adv. 12, 3505-3517 https://doi.org/10.1039/D1RA08496H

Wang, X., Pfeiffer, H., Wei, J., Wang, J., Hang, J. (2022). Fluoride ions adsorption from water by $CaCO_3$ enhanced Mn-Fe mixed metal oxides. Front. Chem. Sci. Eng. https://doi.org/10.1007/s11705-022-2193-8 WHO (2011). Guideline for drinking-water quality, 4th edn. WorldHealth Organization, Geneva

Zaman, T., Mostari Mst, S., Al Mahmood, Md. A., & Rahman, Md. S. (2018). Evolution & characterization of eggshell as a potential candidate of raw material. Cerâmica 64, 236-241. doi.org/10.1590/0366-69132018643702349

Zhao, Y., Li, X., Liu, L., & Chen, F. (2018). Fluoride removal by Fe() loaded exchange cotton cellulose adsorbent from drinking water. Carbohydr. Polym. 72, 144-150. https://doi.org/10.1016/j.carbpol.2007.07.038