

ASSESSMENT ON THE DEFLUORIDATION USING NOVEL ACTIVATED CARBON SYNTHESIZED FROM TEA WASTE: BATCH, STATISTICAL OPTIMIZATION AND MATHEMATICAL MODELING

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(Received 05 May, 2016; accepted 24 September, 2016)

Key words: Fluoride, Activated carbon from tea waste, Adsorption isotherm and kinetics, Equilibrium, Response surface methodology

ABSTRACT

This present study is highlighted on defluoridation onto activated carbon prepared from tea waste (ACTW). Tea waste (TW) is cheap, easily available and waste materials. In this present study, activated carbon was prepared from tea waste in a high temperature tubular reactor and activated by chemical activation using dilute H_2SO_4 . This experiment was performed to investigate the interaction of process parameters using response surface methodology (RSM). The two level three factor (2^3) central composite design (CCD) with the help of design expert software was applied to optimize process parameters. The higher correlation coefficient (R^2) value of 0.9952 indicates the well-fitted to response surface quadratic model. The optimum removal efficiency of activated carbon for fluoride adsorption is 99.59% at optimum condition. The Langmuir and Freundlich adsorption isotherm were used to explain adsorption between the liquid and solid phases in batch studies. The mechanism of sorption process was described by calculating Gibbs free energy, enthalpy and entropy from thermodynamic studies.

INTRODUCTION

Fluorine is a naturally available element that does not exist in the elemental state in nature as its more reactivity. It exists in the form of fluorides in various minerals (Lounici, *et al.*, 1997) such as fluorspar, cryolite and fluorapatite. Inorganic fluorine compounds are used in industry for different purposes such as ceramic, nano-technology industries.

Fluorosilicic acid, sodium hexafluorosilicate and sodium fluoride are used in water fluoridation. In several studies, it is revealed that daily fluoride uptake widely varied according to the various sources of exposure. As elevation of fluoride intake in drinking water is significantly higher, so after oral uptake, water-soluble fluorides are almost absorbed in the gastrointestinal tract and then it is transported through the blood. Due to prolonged intake of fluoride (Bell, *et al.*, 1970) from water, there is same concentrations of fluoride in the blood and in drinking water, it is safe up to 10 mg/l. As the distribution of

fluoride is very fast process, so it is accumulated into teeth and bones, also into skeletal tissues. Fluoride intake can seriously effect skeletal tissues. When water contains 3 mg/l to 6 mg/l fluoride, then skeletal fluorosis occurs. There was statistically significant trend of an increased incidence of osteosarcomas in animal with increasing exposure to fluoride. Fluoride exposure significantly affected bladder cancer, mainly among workers exposed to excess fluoride. Thyroid activity is affected by fluoride. The toxicological effect of fluoride on human health drives urgent need to find out an effective method for the removal of excess fluoride from drinking water. According to the national standards (APHA, AWWA, WEF, 2012) in evaluating the possible health consequences of exposure to fluoride, it is essential to consider the uptake of fluoridated water from food and air. The RSM (Garg, *et al.*, 2009) has graphic representing a response surface method in three dimensions. Actually this is four-dimensional space, which is represented since the three factors are in 3-dimensional space and the response is the 4th dimension.

The present study is highlighted on the preparation of activated carbon from tea waste (Hu, *et al.*, 1999; Amarasinghe, *et al.*, 2007; Wasewar, *et al.*, 2010) as an adsorbent for fluoride removal from water. Various process parameters such as effect of adsorbent dose, contact time, reaction temperature were experimented to study the effect of these parameters on the removal efficiency. The adsorption isotherm and adsorption capacity of ACTW in batch studies were also investigated and its advantages for the removal of fluoride over other contaminants were also studied.

MATERIALS AND METHODS

Preparation of adsorbent

The raw material used for preparation of activated carbon is tea waste (Malkoc and Nuhoglu, 2006). Tea waste (González, *et al.*, 1997) was taken from the waste tea leaves after tea making process. The tea waste (Awoyale, *et al.*, 2013) was washed several times with distilled water to remove surface impurities and then dried at 373 K. This tea waste is then dried and digested by using dilute sulphuric acid (Ademiluyi and David-West, 2012) which is followed by carbonization in muffle furnace. The complete carbonization at 723 K took place and at 823 K the material was converted into complete ash form. Then it was cooled to room temperature and washed with distilled water until their pH equal to 7 which indicates no trace acid. Then it was dried, cooled and stored in an air-tight container. On sieve analysis below and above 300 mesh sizes particle were separated.

Physicochemical properties

The physicochemical properties (Sricharoenchaikul, *et al.*, 2008; Jun, *et al.*, 2010; Evbuomwari, *et al.*, 2013) of the produced activated carbons such as the oil yield, bulk density, porosity, moisture content, ash content and pH were estimated using standard procedures (Rodriguez-Reinoso, *et al.*, 1982; Hu, *et al.*, 1995). All the experiments were performed thrice and results are given in Table 1.

Yield of carbon

After carbonization (Budinova, 2006) followed by cooling, the activated carbon was weighed. Then the percentage yield of carbonizing is achieved by applying this formula:

$$\% \text{ yield of carbon} = \frac{\text{weight of char}}{\text{weight of raw material}}$$

Determination of bulk density

The dry empty 10 ml centrifuge tube was cleaned and weighed (W1) and then the centrifuge tube was filled with the prepared activated carbon powder and then weighed (W2). The difference in the weights denotes the weight of the activated carbon powder in tube. The bulk density was estimated using the following equation:

$$\text{Bulk Density} = \frac{W2 - W1}{\text{volume of centrifuge tube}}$$

Porosity determination

The porosity of the activated carbon was estimated using the formula:

$$\text{Porosity} = \frac{\text{pore volume}}{\text{total volume}}$$

The pore volume of prepared activated carbon was achieved using the formula:

$$\text{Pore volume} = \frac{\text{Bulk density of activated carbon}}{\text{density of water}}$$

$$\text{Hence, porosity} = \frac{\text{Bulk density of activated carbon}}{\text{density of water} \times \text{Total volume}}$$

Determination of moisture content

The empty crucible was dried at 110°C and then cooled in a desiccator and weighed (W1). Then the prepared known weight of activated carbon powder with crucible were weighed (W2) and dried in an oven at 110°C. This weight was taken constantly at 30 min interval until the weight became constant. Then activated carbon with crucible was cooled in a desiccator and reweighed (W3). The weight difference of the activated carbon is used to measure the moisture content (X_o) of the activated carbon from tea waste

$$X_o = (W2 - W3) / (W2 - W1) \times 100$$

Determination of ash content

The empty crucible was oven dried at 110°C and cooled in a desiccator and weighed (W1). The known weight of prepared dried activated carbon powder was put the crucible and weighed (W2) and then kept in the muffle furnace at 800°C for 1 hour and then allowed to cool.

Table 1. Physicochemical analysis of ACTW

| Activated carbon prepared from Tea waste | Yield (%) | Bulk Density | Porosity | Moisture content | Ash content | pH |
|--|-----------|--------------|----------|------------------|-------------|------|
| | 74 | 0.8 | 0.79 | 6.9 | 12.5 | 7.03 |

Finally the crucible was reweighed (W_3). The percentage ash content of activated carbon sample was obtained from the following equation:

$$\text{Ash\%} = \frac{W_{\text{ash}}}{W_0} \times 100 = \frac{W_3 - W_1}{W_2 - W_1} \times 100$$

Where Wash=weight of ash (g)

Determination of pH

1 g activated carbon from lemon shell and wheat bran was weighed. Then it was dissolved in 3 ml distilled water. The mixture was heated and stirred for few minutes. Then it was filtered and pH was determined using a digital pH meter.

Preparation of synthetic fluoride solutions

Sodium fluoride (Merck, Germany) was used in this study. Stock fluoride ion solution (1000 mg L^{-1}) was prepared by dissolving accurately weighed quantity in double-distilled water. Experimental fluoride solution of different concentrations was prepared by diluting the stock solution with suitable volume of double- distilled water.

EXPERIMENTAL PROCEDURE

Batch experiment

In this experiment, 100 ml fluoride solutions of concentration 50 mgL^{-1} were taken in 250 ml PTFE conical flasks. The particular weighed amount of adsorbent was added to each solution. Then the flasks were agitated at 150 rpm in an incubator shaker at different temperatures. The effects of contact time, adsorbent dose and reaction temperature on the adsorption of fluoride were investigated by using batch studies.

Experimental set up

Experiments were conducted in temperature controlled incubator shaker (INNOVA 4430, New Brunswick Scientific, Canada). Temperature fluctuations in the reactor were negligible. After shaking for particular time intervals those samples were collected from the flasks for analysis of fluoride concentration in the solution. The residual amount of fluoride in each conical flask was estimated by using ion-meter (Thermo Scientific Orion ion-meter, USA).

Adsorption isotherm

•Freundlich isotherm: The Freundlich isotherm constants are estimated using the following equation:

$$\ln Q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (1)$$

Where Q_e is the amount of fluoride adsorbed at equilibrium, and K_F and n are Freundlich constants indicates adsorption capacity and adsorption intensity respectively

•Langmuir isotherm: In this case the following equation is used as follows:

$$\frac{C_e}{Q_e} = \frac{C_e}{q_m} + 1 \frac{1}{K_L q_m} \quad (2)$$

Where Q_e is the amount of fluoride adsorbed at equilibrium (mg/l), C_e is the concentration of fluoride in the aqueous phase at equilibrium (mg/l). K_L and q_m are the Langmuir constants related to energy of adsorption and the adsorption capacity.

Adsorption kinetics

The adsorption process is carried out at various temperatures to determine the optimum temperature for maximum adsorption efficiency and for obtaining the reaction rate constant activation energy. 100 ml of fluoride solution of concentration 50 mg/l was taken in PTFE conical flask and 1 g adsorbent is added to it. Then this mixture was agitated at 150 rpm for 1 hr. From this experiment kinetic rate constant at different temperatures is estimated.

•Pseudo first order kinetics: The rate constant is estimated using the following equation:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (3)$$

Where, q_e =fluoride adsorbed at equilibrium/unit weight of adsorbent (mg/g), q_t is the amount of fluoride adsorbed at any instant (mg/g) and k_1 is the rate constant (min^{-1}).

Integrating at these conditions as $t=0$ and $q_t=0$ to $t=t$ and $q_t=q_t$, the final equation is written as given below:

$$\text{Log} (q_e - q_t) = \text{log} q_e - \frac{k_1 t}{2.303} \quad (4)$$

•Pseudo second order kinetics: The model equation is described as follows:

$$\frac{t}{q_t} = + 1/q_e (t) \quad (5)$$

Where k_2 denotes the pseudo-second-order rate constant of adsorption ($\text{g mg}^{-1} \text{ min}^{-1}$) and q_e and q_t are the amounts of fluoride adsorbed (mg/g) at equilibrium and at time t respectively.

•Activation energy:

From the obtained the rate constant, activation energy of the adsorption of fluoride is calculated using Arrhenius Eq (6) given as follows:

$$\ln k_2 = \ln A_0 - \frac{E_a}{RT} \quad (6)$$

Where E_a =activation energy (kJ mol^{-1}); R =gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$); and A_0 =Arrhenius constant.

Adsorption thermodynamics

The thermodynamic parameters of fluoride adsorption is calculated using the following formulas:

$$K_c = \frac{C_a}{C_e} \quad (7)$$

Where, K_c =coefficient of distribution for the adsorption; C_a =fluoride adsorbed per unit mass of the adsorbent (mg L^{-1}); C_e =equilibrium concentration of adsorbate in aqueous phase (mg L^{-1}).

$$\Delta G_0 = -RT \ln K_c \quad (8)$$

Where, G_0 (kJ mol^{-1})=change of Gibb's free energy; R =universal gas constant; and T =absolute temperature (K); and

$$\ln K_c = \frac{\Delta S_0}{R} - \frac{\Delta H_0}{RT} \quad (9)$$

Where ΔH_0 (kJ mol^{-1})=change of enthalpy; ΔS_0 ($\text{J mol}^{-1} \text{K}^{-1}$)=change of entropy.

Statistical analysis

In order to maintain quality assurance, the precision, accuracy, repeatability and reproducibility of the obtained experimental data, all experiments are conducted thrice. Data were analyzed. Mean values and standard deviation (SD) obtained with Design Expert Version 9.1.6 (Stat Ease, USA).

RESULTS AND DISCUSSION

Characteristics of ACTW

XRD (X-ray diffraction) analysis: X-ray diffraction analysis of the adsorbent was carried out using X-ray diffractometer equipment (Bruker, D8 Advance) with a $\text{Cu K}\alpha$ radiation. The XRD pattern of the prepared activated carbon from tea waste was shown in the Fig. 1.

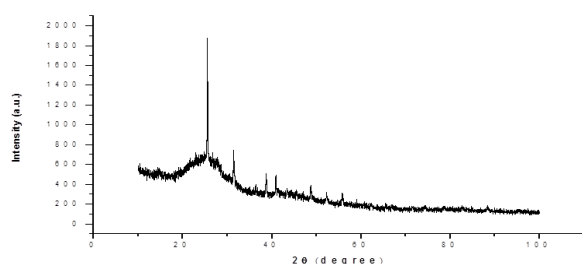


Fig. 1 XRD of ACTW.

Batch adsorption studies

Effect of adsorbent dose: Within the experimental range of adsorbent dose in between 0.2 g to 1.5 g/l, percent removal of fluoride firstly increases (up to 1.0 g/l), then slowly decreases. The adsorbent dose in the range of 0.2 g to 1.0 g/l, defluoridation efficiency increases due to the number of ions

increases on the adsorbent surface as the attraction force between adsorbate ions and adsorbent. While increasing adsorbent dose higher than 1.0 g/l, it shows decrease in removal on the adsorbent surface because surface of adsorbent is saturated by adsorbate ions, and in that case the repulsive force between fluoride ions and adsorbent surface occurs. Comparing two adsorbents (ACTW and TW), the pore size of ACTW is smaller than TW. Additionally, there is one more factor, in acidic medium (in acidic medium the defluoridation efficiency is higher) tea waste was activated for preparing activated carbon. So adsorption capacity is naturally higher than that of TW. From Fig. 2, it was observed that the removal of fluoride increased higher in case of ACTW than using TW, so it can be inferred that ACTW is a better adsorbent for defluoridation than only TW. So this present study was further investigated using ACTW.

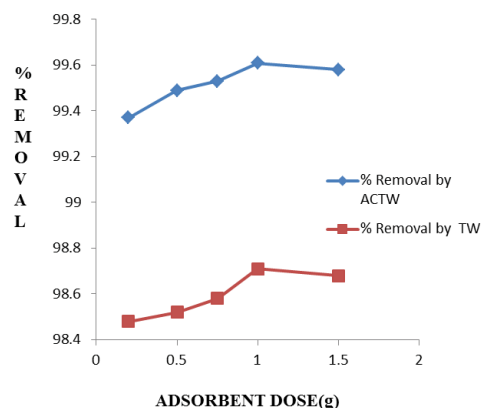


Fig. 2 Effect of adsorbent dose on removal of fluoride by ACTW and TW (experimental conditions: $C_0=50 \text{ mg L}^{-1}$, agitation speed=150 rpm, $T=333 \text{ K}$, contact time: 70 min).

Effect of contact time

It is observed from Fig. 3, the experimental results that on increasing the contact time at particular temperature, defluoridation efficiency increases. As the contact time increases, higher the number of fluoride ions attached on the adsorbent surface. Chemically the accumulation of fluoride ions on adsorbent surface increases due to attraction force which results in increasing the defluoridation in solution. But after certain point (70 min), defluoridation efficiency decreases. The reason behind is that maximum number of the fluoride ions attached on adsorbent surface when reaction time was 70 minutes. Comparing two adsorbents (ACTW and TW), pore size of ACTW is smaller than TW. As a result, in particular contact time, adsorption capacity is higher by ACTW rather than TW. From Fig. 3, it was observed that the removal of fluoride increased higher in case of ACTW than using TW. So further study was carried out by ACTW.

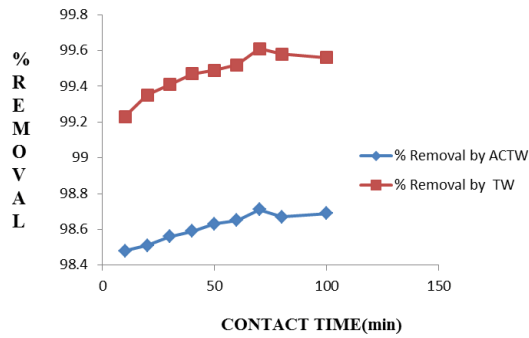


Fig. 3 Effect of contact time on removal of fluoride by ACTW (experimental conditions: $C_0=50 \text{ mg L}^{-1}$, agitation speed=150 rpm, $T=333 \text{ K}$, adsorbent dose=1 g/100 ml).

Effect of temperature

In the above experiment, it is showed that with increasing temperature, the percent removal of fluoride first increases from 308 K to 333 K in both cases. After 333 K, defluoridation efficiency decreases slowly. Following the adsorption process, increasing the number of adsorbate ions which were accumulated on adsorbent surface, the attractive force in between fluoride ions and ACTW as well as TW increases Fig. 4. But as temperature increases beyond 333 K, as charge density of fluoride ions increases, the repulsive force increases in between adsorbate and adsorbent surface. Consequently, the defluoridation efficiency firstly increases, then decreases. As the adsorption capacity by ACTW is higher than that of TW (due to pore size), so at particular temperature the number of adsorbate ions increased on ACTW than TW, so ACTW is the better adsorbent for further experiment than TW.

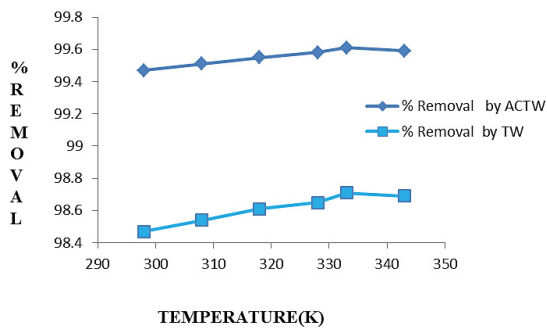


Fig. 4 Effect of temperature on removal of fluoride by ACTW and TW (experimental conditions: $C_0=50 \text{ mg L}^{-1}$, agitation speed=150 rpm, contact time=70 min, adsorbent dose=1.0 g/100 ml).

Thermodynamics and kinetics study of batch experiments

Effect of adsorption isotherms

A graph between C_e vs C_e/Q_e and $\log C_e$ vs $\log Q_e$ between was plotted to obtain Langmuir and Freundlich adsorption isotherms respectively (Fig. 5 and 6).

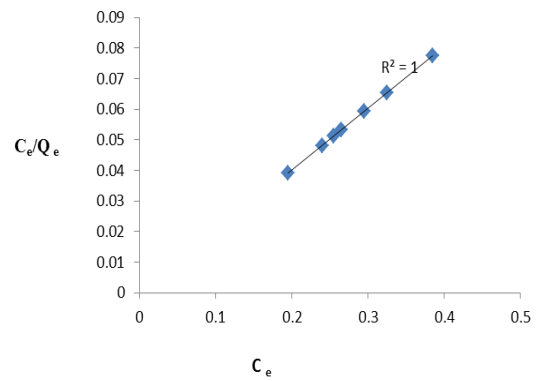


Fig. 5 Langmuir Adsorption Isotherm plots of defluoridation onto ACTW (experimental conditions: $C_0=50 \text{ mg L}^{-1}$, agitation speed=150 rpm, $T=333 \text{ K}$, contact time: 70 min).

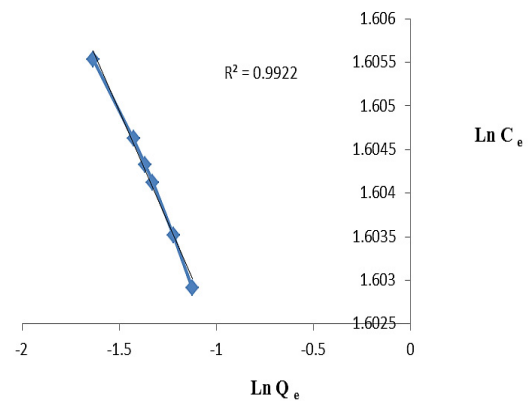


Fig. 6 Freundlich Isotherm plots of defluoridation onto ACTW (experimental conditions: $C_0=50 \text{ mg L}^{-1}$, agitation speed=150 rpm, $T=333 \text{ K}$, contact time: 70 min).

Both Freundlich and Langmuir adsorption isotherms yields a straight line with R^2 values of 0.9922 and 1.000 respectively, confirms the validity of both the isotherms and the suitability of ACTW for the adsorption of fluoride ions from the solution.

Comparisons between R^2 values between these isotherms show that the adsorption of fluoride has a good agreement with Langmuir adsorption model ($R^2=1.000$ versus 0.9922) which suggests the priority for the formation of monolayer on ACTW by fluoride species. Based on equation (1) and (2) and equation curve on Fig. 5 and 6 respectively, the values of K_{Fr} , n , q_m and b were calculated and found to be 0.982, 2.89, 1.598 $\mu\text{g/g}$ and 0.794 $1/\mu\text{g}$ respectively.

Effect of adsorption kinetics and temperature:

The linear plots of t/Q_t vs t is shown in Fig. 7. At 333 K, the rate and the initial adsorption rate is 3.9 $\text{mg g}^{-1} \text{ min}^{-1}$. As a consequence, from experimentally obtained results, it is proved that as temperature increased from 308 K to 333 K, the amount of fluoride adsorption increased. This phenomenon occurred due to increasing mobility of fluoride ions with temperature and so the adsorption capacity also increased with a rise in temperature.

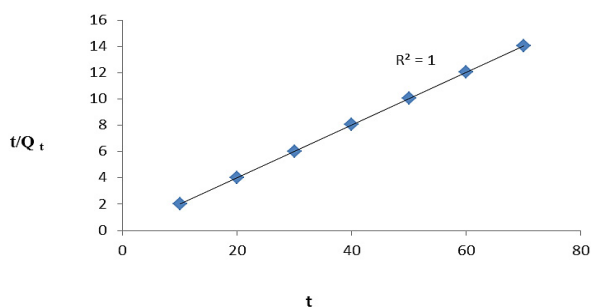


Fig. 7 Pseudo second order kinetic model for adsorption of fluoride by ACTW (experimental conditions: $C_0=50 \text{ mg L}^{-1}$, agitation speed=150 rpm, $T=333 \text{ K}$, contact time: 70 min).

From the pseudo second order rate constant k_2 at different temperatures, the activation energy E_a is estimated using the Arrhenius equation (Eq. 6). The slope calculated from Arrhenius equation is 45.76 kJ/mol .

From the batch experiment studies, it is observed that as time increases, the efficiency of the reduction of fluoride increases as well as the adsorption capacity and after a certain time 99.61% removal of fluoride is obtained. At 333 K (Fig. 7) t/Q_t vs t plot is showing linear plot with regression coefficient 1.0. At a temperature of 333 K , the rate constant is $0.2631 \text{ g mg}^{-1} \text{ min}^{-1}$ and the initial adsorption rate was $3.9 \text{ mg g}^{-1} \text{ min}^{-1}$. This phenomenon indicates that activated carbon from tea waste can be effectively used for fluoride adsorption in batch studies.

Thermodynamic parameters

From the experimental data following equation (7-9) it represents that the negative value of ΔG_0 increases with increasing in the temperature (upto 333 K) which indicated that the adsorption is thermodynamically feasible in nature and the positive values of ΔH_0 supports endothermic nature of the reaction due to consuming energy from the reaction system. The values of ΔH_0 and ΔS_0 are estimated from the slopes and intercept of the plot $\ln K_c$ vs. $(1/T)$ (Fig. not shown) and the values are listed in Table 2. It is observed that the negative value of ΔG_0 at all temperatures represents that the fluoride adsorption reaction is spontaneous in nature (Vimonses, *et al.*, 2009). In this case ΔG_0 decreases up to 333 K and after that it increases which implies that the adsorption reaction is feasible up to 333 K . As a consequence, the randomness in between fluoride ion and ACTW surface is increased. As the reaction is endothermic in nature, it is expected that the uptake capacity of fluoride ions by ACTW is increasing with temperature. But after 333 K , the reverse reaction occurs. Mathematically, entropy of the reaction is estimated from the experimentally obtained data that

is positive ($297.61 \text{ J mol}^{-1} \text{ K}^{-1}$). So it can be explained that as temperature is increased above 333 K , the desorption occur on the ACTW surface which results the concentration of fluoride in solution in increased in small amount in solution.

Table 2. Estimation of different thermodynamic parameter using batch adsorption study

| Serial No. | T, K | ΔG , kJ/mol | ΔH , kJ/mol | ΔS , $\text{J mol}^{-1} \text{ K}^{-1}$ |
|------------|------|---------------------|---------------------|---|
| 1 | 308 | -10.85 | 86.82 | 297.61 |
| 2 | 318 | -11.43 | | |
| 3 | 328 | -13.87 | | |
| 4 | 333 | -14.76 | | |
| 5 | 343 | -12.86 | | |

Response surface methodology for optimization of adsorption parameters

The determination of optimum conditions (Amini, *et al.*, 2008) for fluoride adsorption by ACTW depends on the three process variables, which are adsorbent dose, temperature and contact time. The experimental ranges along with the levels of variables are given in Table 2. The percent removal of fluoride is the output of the system.

Percent removal of fluoride is estimated with a standard RSM design (CCD) (Ghorbani, *et al.*, 2008) and 20 experiments are conducted which is described in Tables 2 and 3. The percent removal (%) of fluoride is determined by using the following equation (10):

Table 3. Experimental range and levels of independent variables

| Process parameters | | $-\alpha$ | -1 | 0 | $+1$ | $+\alpha$ | |
|--------------------|------------------|-----------|-------|-----|-------|-----------|-------|
| (1) | Adsorbent dose g | A | 0.33 | 0.5 | 0.75 | 1.0 | 1.17 |
| (2) | Contact time min | B | 3 | 20 | 45 | 70 | 87 |
| (3) | Temperature K | C | 299.4 | 308 | 320.5 | 333 | 341.5 |

$$R(\%) = \frac{C_i - C_0}{C_i} \times 100 \quad (10)$$

Where C_i is the initial fluoride concentration (mg L^{-1}) and C_0 is the final fluoride concentration in solution (mg L^{-1}).

Design expert version 7.1.6 (Stat Ease, USA) is utilized for regression and graphical analysis of the experimentally obtained data (Jain, *et al.*, 2011). The optimum values of the independent variables are achieved by solving the regression equation. The coefficient of correlation and the quadratic model equation (Senthilkumar, *et al.*, 2013) is used to predict the interaction effect of different factors within the specified range.

Estimation of response surface for maximum fluoride removal

The results of the 20 experiments as per CCD analysis

represented in Table 4. The maximum fluoride removal is obtained 99.59% at 70 min contact time, at 60°C and 1 g of adsorbent.

Table 4. Central composite design (CCD) used for optimizing three independent variables along with the obtained response

| Serial No. | A: Adsorbent dose(g) | B: contact time (min) | C: Temperature (K) | Removal of fluoride (%) |
|------------|----------------------|-----------------------|--------------------|-------------------------|
| 1 | 0.75 | 45 | 320.5 | 99.51 |
| 2 | 0.75 | 45 | 320.5 | 99.51 |
| 3 | 0.5 | 20 | 308 | 99.07 |
| 4 | 0.33 | 45 | 320.5 | 99.11 |
| 5 | 0.5 | 70 | 308 | 99.17 |
| 6 | 0.75 | 3 | 320.5 | 99.02 |
| 7 | 0.5 | 20 | 333 | 99.23 |
| 8 | 0.75 | 45 | 320.5 | 99.51 |
| 9 | 1.17 | 45 | 320.5 | 98.99 |
| 10 | 0.75 | 45 | 320.5 | 99.51 |
| 11 | 1 | 70 | 308 | 99.49 |
| 12 | 1 | 20 | 308 | 99.24 |
| 13 | 0.75 | 45 | 341.5 | 99.27 |
| 14 | 0.5 | 70 | 333 | 99.33 |
| 15 | 0.75 | 87 | 320.5 | 99.52 |
| 16 | 1 | 70 | 333 | 99.59 |
| 17 | 0.75 | 45 | 320.5 | 99.51 |
| 18 | 1 | 20 | 333 | 99.42 |
| 19 | 0.75 | 45 | 320.5 | 99.51 |
| 20 | 0.75 | 20 | 299.4 | 99.21 |

It is observed that A, B, C, BC, A², B², C² are significant model terms. There is only 0.02% chance that an F-value this large could occur due to noise.

In order to study the interaction among the different independent variables and their corresponding effect on the response, contour plots are drawn Fig. 8-11. Statistically contour plot is defined as graphical representation of a three-dimensional response surface as a function of two process variables without changing another variable. The response variable is represented as a function of independent variables defined in quadratic response surface model equation (12) as given below:

Removal % of fluoride

$$(R1) = +99.59 + 0.087 * A + 0.075 * B + 0.089 * AB - 0.021 * AC + 0.097 * BC - 0.009 * A^2 - 0.079 * B^2 - 0.15 * C^2 \quad (11)$$

$$\frac{\partial R1}{\partial A} = 0.087 + 0.089B - 0.021C - 0.018A \quad (12)$$

$$\frac{\partial R1}{\partial B} = 0.075 + 0.089A + 0.097C - 0.158B \quad (13)$$

$$\frac{\partial R1}{\partial C} = -0.021A + 0.097B - 0.3C \quad (14)$$

$$\frac{\partial^2 R}{\partial A^2} = -0.018; \quad \frac{\partial^2 R}{\partial B^2} = -0.158; \quad \frac{\partial^2 R}{\partial C^2} = -0.3$$

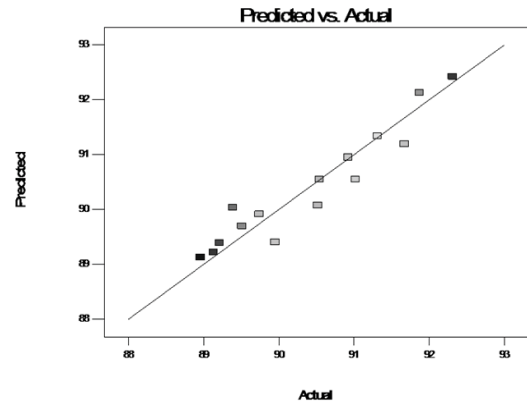


Fig. 8 The graph showing predicted removal % Vs actual removal % of fluoride by adsorption.

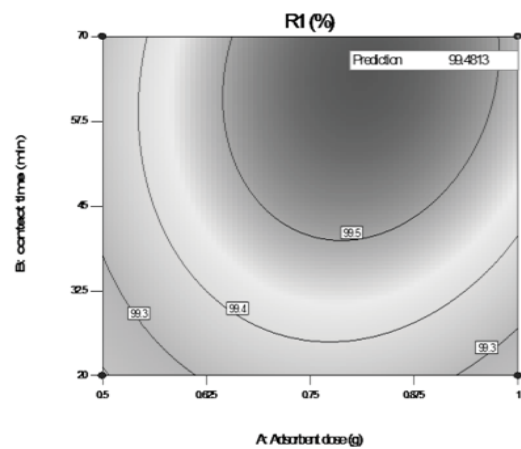


Fig. 9 RSM plot showing interaction effect of adsorbent dose and contact time.

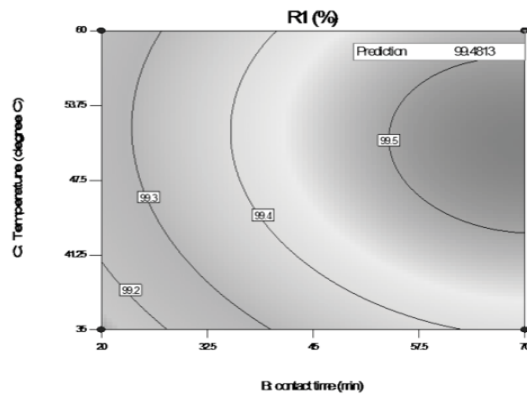


Fig. 10 RSM plot showing interaction effect of temperature and contact time.

Where A represents adsorbent dose (g), B denotes contact time (min), C indicates reaction temperature (K) and R1 is the % fluoride removal. For solving partial differential equation (12,13,14), the above mentioned equation are equated to zero. Under this condition A, B and C were estimated to be 1.02 g, 69.89 min and 332.76 K, respectively, and % defluoridation obtained to be 99.589%.

The validity of model is verified by the correlation coefficient between the experimental and model

predicted values of the response variable Fig. 8. A high R2 value indicates high correlation between the values of the predicted variable by experimental and model. Overall, the applicability of the model is used to predict the percentage removal of fluoride in solution within the limits of the experimental factors.

Interaction effect of process variables

Effect of variation in adsorbent dose and reaction time

The contour plot of Fig. 9 demonstrated the interaction effects of the independent variables (contact time and adsorbent dose) in the above response. According to the contour plot of Fig. 9, defluoridation efficiency is increased with increase in dose of adsorbent and time of reaction. This is followed by maximum removal efficiency of 99.59%, obtained at 70 min contact time and adsorbent dose of 1 g.

Effect of variation in temperature and contact time

The effect of different temperature and reaction time are required to remediate fluoride in solution using ACTW. It is illustrated in the contour plot as shown in Fig. 10. It is evident from Fig. 10 that both the independent process variables are very effective on the % fluoride adsorption process. From this contour plot, a maximal removal efficiency of 99.59% is obtained at 333 K and 1.0 g of ACTW while the other variable is set at the middle value. As the temperature increased from 300 K to 333 K, the fluoride uptake capacity increased at particular adsorbent dose which indicated that at higher temperature with higher contact time, the percentage of bound fluoride ions adsorbed increases (due to higher attraction force between fluoride ions and ACTW), as a result of which percentage efficiency of removal of fluoride ions increased.

Effect of variation in adsorbent dose and temperature

The combined effect of adsorbent dose and temperature for adsorption on fluoride removal is depicted in the contour plot of Fig. 11. It is observed that percentage of fluoride removal increased on increasing the temperature from 300 K to 333 K and also increases in the range of adsorbent dose from 0.33 g to 1.0 g. This suggests that higher values of fluoride removal may be obtained by increase in temperature and also with increase in adsorbent dose. Due to increment of adsorbent dose, the % removal of fluoride increased which supported the attractive forces between fluoride ion and adsorbent surface. Due to adsorbent dose increase, physical force of attraction between the fluoride ions and

ACTW increased due to increase in charge density of adsorbent surface. From this plot, a maximal removal efficiency of 99.59% is achieved at a 1.0 g adsorbent dose, at 333 K and 70 min of contact time.

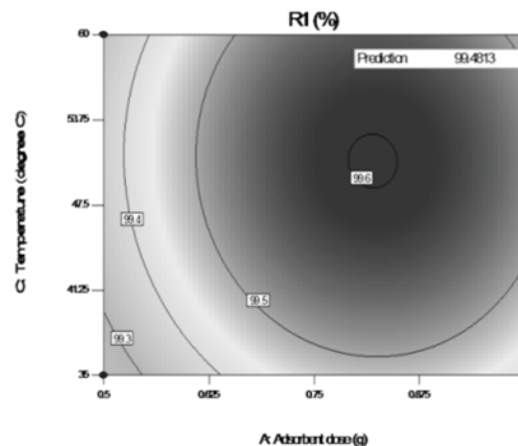


Fig. 11 RSM plot showing interaction effect of temperature and adsorbent dose.

Confirmational study

To support the optimized data given by numerical modeling confirmatory experiments are conducted with the parameters as suggested by the model (adsorbent dose 1.0 g; temperature 333 K; contact time 70 min). These are found to be optimum condition for maximum percent fluoride removal. The corresponding removal efficiency in optimum conditions is found 99.59% and experimentally it is observed as 99.61%. The difference between the removal efficiency in the two conditions being 0.02%.

CONCLUSION

The present study was conducted with the target of studying fluoride adsorption process onto ACTW and to investigate the influence of various process parameters on fluoride removal using response surface methodology. The adsorption studies (Prado, *et al.*, 2004) were performed as a function of temperature, contact time, adsorbent dose. The fluoride removal efficiency was significantly affected by reaction temperature, contact time, adsorbent dose. The level of the three variables such as temperature 333 K, contact time 70 min, adsorbent dose 1.0 g were found to be optimum for maximum fluoride removal. The corresponding removal efficiency in optimum conditions was found to be 99.59%. As TW is very cheap and easily available and ACTW is synthesized chemically, so it may serve as an effective adsorbent for removal of fluoride ion from solution.

ACKNOWLEDGEMENTS

The authors would like to acknowledge all members

of Department of Chemical Engineering, Jadavpur University and West Bengal Pollution Control Board for their undue cooperation and support throughout this study.

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