

Optimization of Fluoride Adsorption from Aqueous Solution by Bael Fruit Shell and *Pongamia pinnata* Using Taguchi Method

Kalpana Singh^{1*}, Dilip H. Lataye², Kailas L. Wasewar¹

¹ Department of Chemical Engineering, Visvesvaraya National Institute of Technology, Nagpur-440010, Maharashtra, INDIA. E-mail: kalpanatrue@gmail.com.

² Department of Civil Engineering, Visvesvaraya National Institute of Technology, Nagpur- 440010, Maharashtra, INDIA. E-mail: diliplataye@rediffmail.com.

¹ Department of Environmental Science, Women's College Samastipur, Bihar, 848101.

ABSTRACT

Taguchi method is a powerful design in experimental studies. This method uses the minimum number of test factors affecting the overall process which will save cost and time. Taguchi method was used to optimize the adsorption of fluoride from aqueous solutions by adsorbents prepared from Bael Fruit Shell and Pongamia Pinnata. The carbons from Bael Fruit Shell (CBS) and bark of Pongamia Pinnata (PP) have been used as adsorbent to remove fluoride from water. The experiments were designed according to Taguchi's (L_9) orthogonal array to optimize experimental runs. The Batch studies were carried out using Ion electrode (HI-3222 pH/ORP/ISE meter, Hanna instruments, India) with four process parameters viz. Dose (m), Initial concentration of fluoride (C_0), Temperature (T), Contact time (t). Analysis of variance was applied to determine the significant parameters that effect adsorption. The results indicated that the % of fluoride removal was influenced primarily by adsorbent dose (70.25%) followed by initial concentration (22.09%) in case of CBS while in case of PP initial concentration (45.83%) is most significant factor followed by the adsorbent dose (34.29 %) for the removal of fluoride. In both case Temperature (T) and Contact time (t) have little effect on fluoride removal. This study focuses on understanding of adsorption process and developing a cost effective technology for treatment of fluoride in water.

Keywords: Fluoride ions, Adsorption, Taguchi method, Parameters, ANOVA

INTRODUCTION

Water is essential for all physiological activities associated with humans, animals, and the plant kingdom. However, the nature and the quality of surface and ground water are widely variable and are determined by the local geological history, including the rocks and hidden ore deposits surrounding the sites for the collection of the water, and other factors, such as the movement of elemental particles and pollutants by lentic, lotic waters and underground aquifers¹.

Fluoride mineral is essential as well as fatal for the dental and skeletal growth of human. It inhibits dental carries at low doses, and accelerates dental and skeletal fluorosis at high doses². Depending upon the body weight, a minimum quantity of fluoride intake is essential for the formation of caries resisting dental enamel and for the normal process of mineralization

in hard tissues. The element is metabolized from both electrovalent and covalent compounds. Low fluoride concentrations stabilize the skeletal system by increasing the size of the apatite crystals and reducing their solubility. About 95% of the fluoride in the body deposited in hard tissues, and it continues to be deposited in calcified structures even after other bone constituents (Ca, P, Mg, CO_3^{2-} and citrate) have reached a steady state. Drinking of water from the groundwater sources is the main route of fluoride intake in rural areas of underdeveloped countries like India. The World Health Organization (WHO, 2006) set up the limits of maximum allowed concentration (MAC) of fluoride (mg/L) in drinking water is 1.0 for the tropical countries and 1.5 for the cooler climatic countries³. Latest guidelines from the Bureau of Indian Standards (BIS) suggest that the fluoride limit in ground water used for drinking and cooking purposes

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should not be greater than 1 mg/L^4 . Thus, the drinking of groundwater that contains fluoride above the MAC level (1.5 mg/L) is a serious concern to the public health. In India, it is one of the biggest natural calamities. Depending on the geological formation, fluorite (CaF_2) and fluoroapatite [$3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$] minerals are hosted in the vein of all most all rocks in sub-surface soil. Surface water rich with bicarbonate when percolated through mineral beds undergoes water–mineral interaction, and releases fluoride due to some chemical reactions⁵ under the appropriate geophysical conditions. The fluoride being released mobilizes to the ground water unless any other natural phenomena play any significant role for arresting fluoride from the water that percolates.

The fluoride content in ground water tends to increase due to heavy withdrawal of water for agriculture purpose, poor recharging, low rainfalls and pollution from industrial effluents. India has declared fluorosis as an epidemic and has banned the use of water for drinking and cooking if the fluoride content is more than 1.5 mg/L . A study by United Nations International Children's Emergency Fund (UNICEF) shows that fluorosis is endemic in at least 27 countries across the globe. These countries are Algeria, Argentina, Australia, Bangladesh, China, Egypt, Ethiopia, India, Iran, Iraq, Japan, Jordan, Kenya, Libya, Mexico, Morocco, New Zealand, Palestine, Pakistan, Senegal, Sri Lanka, Syria, Tanzania, Thailand, Turkey, Uganda, and United Arab Emirates^{6,7}. In India, Fluorosis was first detected in Nellore district of Andhra Pradesh in 1937⁸. "According to the CGWB Annual Ground Water Quality Report 2025, 8.05% of the groundwater samples analysed across India exceeded the BIS permissible limit of 1.5 mg/L for fluoride, indicating that fluoride contamination remains a significant groundwater-quality concern in several regions of the country⁹." Several methods have been applied to remove excessive fluoride from aqueous solution, such as adsorption^{10,11} precipitation¹² ion-exchange¹³, electrodialysis¹⁴ and reverse osmosis¹⁵. Among these methods, adsorption is still one of the most extensively used methods, because of its simplicity and the availability of a wide range of adsorbents. Various materials such as activated alumina¹⁰, clay¹⁶, soil¹⁷, bone char¹⁸, zeolites¹⁹ granular ferric hydroxide²⁰ and biosorbent²¹ have been successfully tested for defluoridation of drinking water. De et. al. used de-oiled

Pongamia Pinnata seed cake, a waste which is generated after oil extraction and converted it into engineered biochar (EBC)²². This EBC was used for the removal of fluoride from ground water. Pongamia Pinnata has been extensively investigated for other contaminants than fluoride for examples iron oxide impregnated pongamia pinnata biochar has been studied for arsenic removal from water by Indurkar et.al.²³

Taguchi design approach helps in finding the effect of the factors on characteristic properties and the optimal condition of the factors. This is one of the better and simple ways to optimize design for performance, cost and quality. The advantage of the Taguchi optimization design over the conventional optimization is the experimental conditions are determined with least variability where as in conventional optimization it is determined on the basis of measured values of the characteristic's properties. The Signal/noise ratio is used to measure the quality characteristics deviating from the desired value in Taguchi method. The experimental conditions having the maximum S/N ratio are considered as the optimal conditions and the variability characteristics are inversely proportional to the S/N ratio. The steps for implementing Taguchi experimental design: a) Select the output variable to be optimized, b) identify factors (input variables) affecting output variable and choose levels to be tested, c) select orthogonal array, d) assign factors and interactions to the columns of the array e) perform experiments f) carry out a statistical analysis and the signal-to-noise ratio and determine the optimal conditions to adjust factor levels and g) perform confirmatory experiments²⁴.

Kim et al. optimized the experimental conditions based on Taguchi design for the formation of nano-sized silver particles by chemical reduction method²⁵. Mohammadi et al. separated copper ions by electrodialysis²⁶ Madaeni and Koochehi optimized the conditions for wastewater treatment using spiral- wound reverse osmosis element²⁷. Kaminari et al. used an electrochemical reactor for recovering heavy metals from acidified aqueous solutions for different process parameters as metallic ion concentration, current density and bed expansion²⁸. Plessis and Villiers applied Taguchi's method in evaluation of mechanical flotation in waste activated sludge thickening²⁹. Moghaddama et al. used Taguchi's design methodology to determine the optimum purification conditions

for minimizing the lead, cadmium, nickel and cobalt contents in the leaching solutions obtained from ammoniacal ammonium carbonate leaching of non-sulphide zinc ores³⁰. Srivastav et al applied this methodology for multi-component adsorption of metal ions onto bagasse fly ash (BFA)³¹. Srivastav et al., used this methodology for adsorption of metal ions onto rice husk ash³². Lataye et al. used optimization process for multicomponent sorptive removal of toxics pyridine, 2-Picoline and 4-Picoline from aqueous solution by Bagasse fly ash³³. This method was applied to optimize the treatment conditions of polyester-resin effluent by means of Advanced Oxidative Processes (AOPs) using chemical oxygen demand (COD) as response parameter by Siliva et al³⁴. The influence of each independent parameter including respective interactions was evaluated by Taguchi Method, which allowed determining the most statistically significant variables and conditions to best fit the process.

Gottipati and Mishra studied adsorption of activated carbon prepared from bael fruit (*Aegle marmelos*) shell (BFS) for the removal of hexavalent chromium in aqueous solution³⁵. They found 92.81% removal at pH 6.39 at dose of 2.18 g/L. Anandkumar and Mandal also studied the Cr (VI) removal from aqueous phase by using activated bael shell. Maximum removal was found at pH 2 and maximum adsorption capacity was 17.27 mg/g. However *Pongamia Pinnata* as adsorbent has not been found in literature. This is the first study of *pongamia pinnata* as adsorbent for fluoride removal³⁶.

MATERIAL AND METHODS

Carbon from Bael Fruit Shell (CBS) was obtained from Local Park, Kitchen garden of sadar area of Nagpur, India. It was crushed to reduce the size, washed several times with distilled water, dried, heated in muffle furnace for about 2 hours at 450 °C, washed, oven dried at 100 °C and stored for use. *Pongamia Pinnata* locally known as *Karanja* (PP) was obtained from VNIT campus and sadar area of Nagpur. It was cut into small pieces washed several times with double distilled water, Sun dried for 3-4 days, oven dried for 3-4 hours at 100 °C, stored in vacuum dessicators.

The physico-chemical characteristics of CBS and PP were determined using standard methods mention in APHA³⁷. Proximate analysis was carried out using

standard procedure³⁸ (IS: 9235-1979, 2003). Scanning electron microscopy (SEM) micrographs of samples were obtained using a field emission scanning electron microscope (JSM-7600F, Jeol). The zero surface charge characteristics of the CBS and PP were determined by using solid addition method³⁹. Particle size analysis of the adsorbent was carried out as per IS 2720 (part-4), 1985 using standard sieves⁴⁰. Surface area was analysed (using Brunauer Emmett and Teller method) by using Micromeritics USA, ASAP 2020, surface area and porosity analyser.

All the chemicals used in present study were of analytical reagent grade and were procured from the Global Marketing, Nagpur, India. Fluoride buffer was prepared by placing approximately 500 ml DDW in a liter beaker and 57 ml glacial acetic acid, 58 g NaCl, 4.0 g 1, 2 Cyclohexylenediaminetetraacetic acid (CDTA) was added. Beaker was placed in cool water bath and 6 N NaOH was slowly added until pH was in between 5.3 and 5.5. This mixture was transferred to 1 liter volumetric flask and distilled water was added to the mark. For measuring unknown concentration of fluoride equal volume of sample and buffer was taken in beaker. Electrodes (HI-3222 pH/ORP/ISE meter, Hanna Instruments, India) were immersed in it while stirring on a magnetic stirrer and direct reading of fluoride was taken³⁷.

3. Taguchi's Design of Experimental Methodology

Taguchi's parameter design method is a powerful tool for optimizing the performance characteristic of a product/process^{41,42}. The aim of a parameter design experiment is to identify and design the settings of the process parameters that optimize the chosen quality characteristic and are least sensitive to noise (uncontrollable) factors. In the present study, the goal is to evaluate the effects of process parameters on the performance measure and the optimum combination of control factors that would maximize the adsorption capacity, of CBS and PP for fluoride removal. Selection of control factors and their levels are made on the basis of some preliminary trial experiments conducted in the laboratory and also from literature review on the subject. Four control factors such as Dose (m), Initial concentration of fluoride (C_o), Temperature (T), Contact time (t) have been selected for present study. Each of the four control factors is treated at three levels in case of CBS and PP as shown in Table 1

Table 1: Process Parameters for Fluoride Removal by Using CBS and PP

Factors	Parameters	CBS				PP		
		Level 1	Level 2	Level 3		Level 1	Level 2	Level 3
A	Dose, m (g/100ml)	0.2	0.4	0.6		0.1	0.2	0.3
B	Initial concentration of fluoride, C_o (mg/L)	4	6	8		2	4	6
C	Temperature, T (K)	293	303	313		293	303	313
D	Contact time, t (min.)	30	60	90		30	60	90

The choice of three levels has been made because the effect of these factors on the performance characteristic may vary nonlinearly.

3.1. Design of Experiment

The experiments were designed based on the orthogonal array technique. An orthogonal array is a fractional factorial design with pair wise balancing property. Using orthogonal array design the effects of multiple process variables on the performance characteristic can be estimated simultaneously while minimizing the number of test runs. An L_9 (3^4) standard orthogonal array as shown in Table 3 was employed for the present investigation. This array is most suitable to provide the minimum degrees of freedom as 9 [$= 1 + 4 \times (3-1)$] required for the experimental exploration.

The next step is to design the matrix experiment and define the data analysis procedure. Before selecting a particular OA for an experiment two items must be established first⁴³ (Ross, 1988).

- (i) The number of parameters
- (ii) The number of levels for the parameters of interest.

The OA selected must satisfy the total degrees of freedom of the OA $\geq$ total degree of freedom required for the experiment.

It is decided to study each selected parameter at three levels, because non-linear behaviour (if any) of the parameters of a process can only be determined if more than two levels are used⁴⁴. With four parameters each at three levels the, the total DOF required is 8 [$= 4 \times (3-1)$], since a three level parameter has 2 DOF (No. of level-1). Hence, an L_9 (3^4) OA (a standard 3-level OA) has been selected for these phases of work.

Table 2 represents the layout of the experimental design, which has been obtained by assigning the selected factors and their levels to appropriate columns of L_9 orthogonal array. This array has 9 rows and 4 columns and each row represents a trial condition while each column accommodates a specific process parameter. Moreover, the notation 3^4 implies that at most 4 factors, each at 3 levels can be investigated using this OA and their main effects can be estimated provided all other interactions are negligible which is assumed in the present case. The numbers in each column indicate the levels of specific factors (A, B, C and D). However, while conducting the experiments the test runs have been randomly made to avoid the unidentified noise sources, which are not considered but could have an adverse impact on the response characteristic

Table 2: Taguchi's Orthogonal Arrays L_9 (3^4) Design⁴⁴

Order of Expt.	Run	Factors			
		Dose	C_o	Temp.	Time
		A	B	C	D
6	1	2	3	1	2
5	2	2	2	3	1
7	3	3	1	3	2
2	4	1	2	2	2

Order of Expt.	Run	Factors			
		3	2	1	3
8	5	3	2	1	3
9	6	3	3	2	1
3	7	1	3	3	3
4	8	2	1	2	3
1	9	1	1	1	1

3.2. Batch Experimental Adsorption Studies (phase 2)

Batch adsorption experiments were performed for fluoride removal by using the selected 9 experimental trials, in combination with four parameters at three levels as shown in Table 2. For each experimental run 100 ml of aqueous solution, having different fluoride concentration was taken in 250 ml stoppered conical flask containing specific dosages of all three adsorbents. These flasks were agitated at constant shaking speed of 150 ± 5 rpm in temperature controlled orbital shaker (REMI Instruments, Mumbai, India) at required temperatures. The samples were withdrawn at appropriate time interval filtered and analysed for the residual fluoride by using Ion electrode (HI-3222 pH/ORP/ISE meter, Hanna instruments, India).

In Taguchi technique, the variation of the response is also examined using an appropriately chosen S/N ratio. Broadly speaking, the S/N ratio is the ratio of the mean (signal) to the standard deviation (noise). These S/N ratios, derived from the quadratic loss function, are expressed on a decibel (dB) scale. The formula used to compute the S/N ratio depends on the objective function. Generally, three standard S/N equations are widely used to classify the objective function as: 'larger the better', 'smaller the better', or 'nominal the best'. However, regardless of the type of performance characteristic, a larger S/N ratio is always desirable. The equation for calculating S/N ratios for HB type characteristics is given as follows:

$$(S / N)_{HB} = -10 \log \left(\frac{1}{R} \sum_{i=1}^R \frac{1}{y_i^2} \right)$$

(1)

Where Y_i is the value of characteristic in an observation i . R is the number of observations or number of repetitions in a trial

3.3. Analysis of Experimental Data and Prediction of Performance (phase 3).

The obtained experimental data was processed with "higher is better" (HB) quality characteristics to determine the optimum conditions for the adsorption, to identify the influence of individual factors on adsorption and to estimate the performance (q_{tot}) under the optimum condition.

From among the methods suggested by Taguchi for analyzing the data, following methods have been used in the present work:

- Plot of the average response curves
- ANOVA (Analysis of Variance) for raw data

The plot of the average response at each level of a parameter indicates the trend. It is a pictorial representation of the effect of parameters on the response. The change in the response characteristic with the change in levels of a parameter can easily be visualized from these curves.

For parameter A (Table 3), the level totals of the response raw data at A_1 , A_2 and A_3 are calculated by adding the responses corresponding to the levels L_1 , L_2 and L_3 are respectively. For example

$A(1)$ = Level total due to parameter A at level L_1

$$A(1) = (y_{11} + y_{22} + y_{13}) + (y_{21} + y_{22} + y_{23}) + \dots + (y_{41} + y_{42} + y_{43}) \quad (2)$$

Where y_{ij} = response of trial i and repetition j

i.e. y_{11} = response of trial 1 and repetition 1.

Similarly, other level total $A(2)$, $A(3)$ are calculated. Similarly for other parameters level total are calculated.

3.3.1 Main effects due to parameters and interactions⁴⁶

Main effects due to parameter A when level changes from L_1 to L_2 and L_2 to L_3 and L_3-L_1 are⁴⁵.

Main effect of parameter A when A changes from level 1 to level 2 ($L_1 \rightarrow L_2$) = Distance in average values of the response between level 2 and Level 1 of parameter A = $\bar{A}(2) - \bar{A}(1)$ (3)

Main effect of parameter A when A changes from level 2 to level 3 ($L_2 \rightarrow L_3$) = Distance in average values of the response between level 3 and Level 2 of parameter A = $\bar{A}(3) - \bar{A}(2)$ (4)

3.3.2 Calculation of variance⁴⁵ (ANOVA)

ANOVA calculation follows the following procedure:

Step 1. Total of all results (T_T)

$$T_T = \sum_{i=1}^n \sum_{j=1}^R y_{ij}$$

(5)

n = Total numbers of trials = 27

R = Total number of repetitions = 3

Step 2. Correction factor (C.F.)

$$\frac{T_1^2}{N}$$

C.F. = (6)

Where, N = Total number of experiments = Rx n = 9x3 = 27

Step 3. Total sum of squares (SS_T)

= (Sum of Sq of All Results - C.F.)

$$\sum_{i=1}^n \sum_{j=1}^R y_{ij}^2$$

$SS_T = C.F$ (7)

Step 4. Sum of squares due to a parameter (SS)

$$SS_A = \left(\frac{A(1)^2}{N_{A1}} + \frac{A(2)^2}{N_{A2}} + \frac{A(3)^2}{N_{A3}} \right) - C.F$$

(8)

Where N_{A1} , N_{A2} , N_{A3} are number of trials with parameter A at level 1, 2 and 3 respectively. The sum of squares SS_B , SS_C , SS_D etc. are also calculated in similar manner.

Step 5. Error sum of squares (SS_e)

$$SS_e = SS_T - (SS_A + SS_B + SS_C + SS_D + SS_E + SS_F + SS_G + SS_H) \quad (9)$$

Where 'e' stands for error term.

Step 6. Total and parameter degrees of freedom (DOF)

$$f_T = \text{Total DOF} = \text{Total number of results} - 1 \quad (10)$$

$$= (\text{Total number of trials} \times \text{no. of repetition}) - 1 = 9 \times 3 - 1 = 26$$

f_A = DOF of parameter A

$$= (\text{Number of levels of parameter A} - 1) = 3 - 1 = 2 \text{ similarly, } f_B = 2, f_C = 2, f_D = 2, f_E = 2, f_F = 2.$$

Step 7. Mean square of Variance (V_m)

$$V_A = \text{variance due to parameter A} = SS_A / f_A \quad (11)$$

$$V_B = SS_B / f_B, V_C = SS_C / f_C \text{ etc.}$$

$$V_e = \text{Variance due to error} = SS_e / f_e$$

Step 8. Percentage contribution (P)

P_A = % contribution of parameter A towards mean of the response

$$\frac{SS_A}{SS_T} \times 100$$

= (12)

Similarly P_B , P_C etc is calculated.

Step 9. F- ratios

$$F_A = \frac{V_A}{V_e}$$

$$F_B = \frac{V_B}{V_e}$$

„ (13)

Where, F_A , F_B , F_C , etc. are F-series due to parameters A, B, C, etc respectively.

Step 10. Pooling

If the calculated F-ratio (Step 9) for a parameter is less than F-ratio tabulated at a stated confidence level (95% confidence level) then the effect of the parameter is insignificant and the parameter is pooled⁴³. If a parameter is pooled, the sum of square due to the parameter is added to the error sum of squares and the other ANOVA terms are modified. If parameter A is pooled,

$$SS_e (\text{pooled}) = SS_e + SS_A \quad (14)$$

$$f_e (\text{pooled}) = f_e + f_A \quad (15)$$

$$V_e (\text{pooled}) = SS_e (\text{pooled}) / f_e (\text{pooled}) \quad (16)$$

Step 11. Pure sum of squares (SS')

If parameter A is significant

$$SS_A = SS_A - (V_e \times f_A) \quad (17)$$

Similarly, for other significant parameters pure sum of squares can be calculated. The subtracted amount of sum of squares must be added to the error sum of squares in order that the total sum of squares is unchanged.

$$SS_e = SS_e + (V_e \times f_A) \quad (18)$$

Step 12. Modified percentage contributions

After pooling of the insignificant parameters, the percentage contribution of significant parameters is calculated. If parameter A is significant, the percent contribution is calculated as:

$$P_A = \frac{SS_A'}{SS_T} \times 100$$

(19)

Similarly,

$$P_B = \frac{SS_B'}{SS_T} \times 100$$

$P_B = (20)$

$$P_c = \frac{SS_c'}{SS_T} \times 100$$

$P_C = (21)$

P_e = Percentage contribution of error term

$$P_e = \frac{SS_e'}{SS_T} \times 100$$

(22)

P_T = Total percentage contribution

$$= P_A + P_B + P_C + P_D \quad (23)$$

Where P_A, P_B, P_C, P_D etc. are percent contributions due to parameters A, B, C, D.

3.3.3 Prediction of the Mean

After determination of the optimum condition, the mean of the response (μ) at the optimum condition is predicted. This mean is estimated only from significant parameters. The ANOVA identifies the significant parameters.

3.3.4 Determination of Confidence Interval

The confidence interval is a maximum and minimum value between which the true average should fall at some stated percentage of confidence. The following two types of confidence intervals are suggested by Taguchi⁴³:

- Confidence interval for the population (CI_{pop})- Around the estimated average of a treatment condition predicted from the experiment.
- Confidence interval of sample group (CI_{CE})- Around the estimated average of a treatment condition used in a confirmation experiment to verify predictions.

3.4 Confirmation Experiment

The confirmation experiment is the final step in verifying the conclusions drawn from previous round of experimentation. The optimum conditions are set for the significant parameters (the insignificant parameters are set at economic levels), and a selected number of tests are conducted under constant specified conditions. The average of the results of the confirmation experiments is compared with the anticipated average, based on the parameters and level tested.

RESULTS AND DISCUSSION**4.1 Physico – Chemical Characterization of Adsorbents**

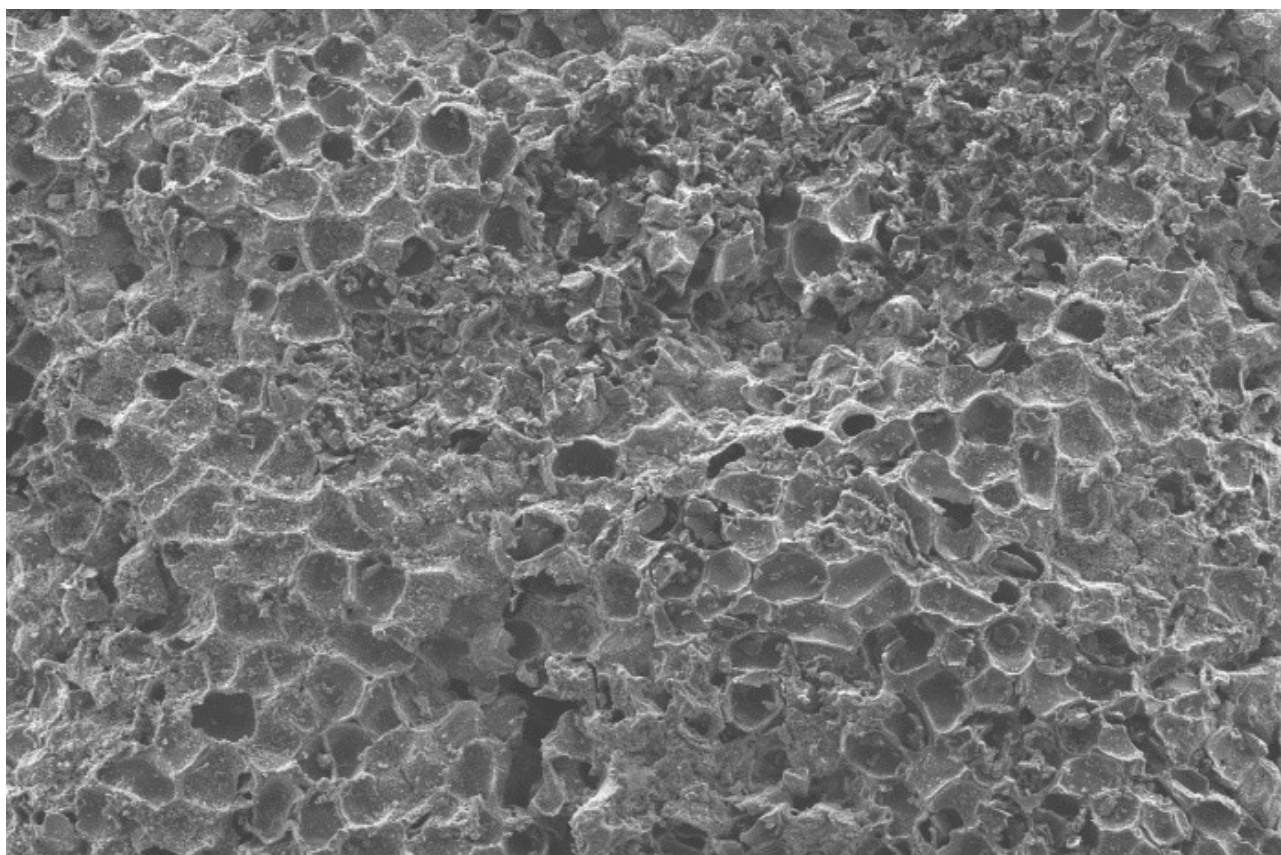
The physico-chemical properties viz. moisture content, ash content, volatile matter, fixed carbon and specific volume of CBS and PP have been analysed. Physical characteristics of adsorbents are presented in Table 3. It is observed that the amount of ash is very high in case of CBS as compared to PP. The amount of carbon content is also highest in case of CBS. Due to low carbon content, PP might have low porosity and there by low surface area than CBS.

Table 3: Physical Characteristics of Adsorbents

Adsorbents	Moisture content (%)	Ash content (%)	Volatile matter (%)	Fixed Carbon (%)	Size (mm)	surface area (m ² /g)
CBS	2.88	55.07	33.01	9.04	0.836	2
PP	8.40	10	76.6	5	2-3	-

The morphologies of blank and fluoride loaded adsorbents were examined by scanning electron microscopy (SEM) analysis. These figures reveal the surface texture and porosity of the blank and loaded adsorbents. Fig. 1 (a) and Fig.1 (b) show the SEM of blank and fluoride loaded CBS at 100X magnification respectively. Well developed hexagonal pores are visible before adsorption while slightly hazy pores are visible after adsorption. Fig. 2 (a) and Fig. 2 (b) show

the SEM of blank and fluoride loaded PP at 100X magnification respectively. From the figure it can be seen that very small pores with fibrous structure are visible in case of blank PP while in case of loaded PP such pores are not clear. It can be concluded from these figures that the surface texture of the blank adsorbents changes after adsorption of fluoride. From the SEM analysis only the morphological changes in structure can be observed.

**Figure 1: (A) SEM of Blank CBS at 100X Magnification**

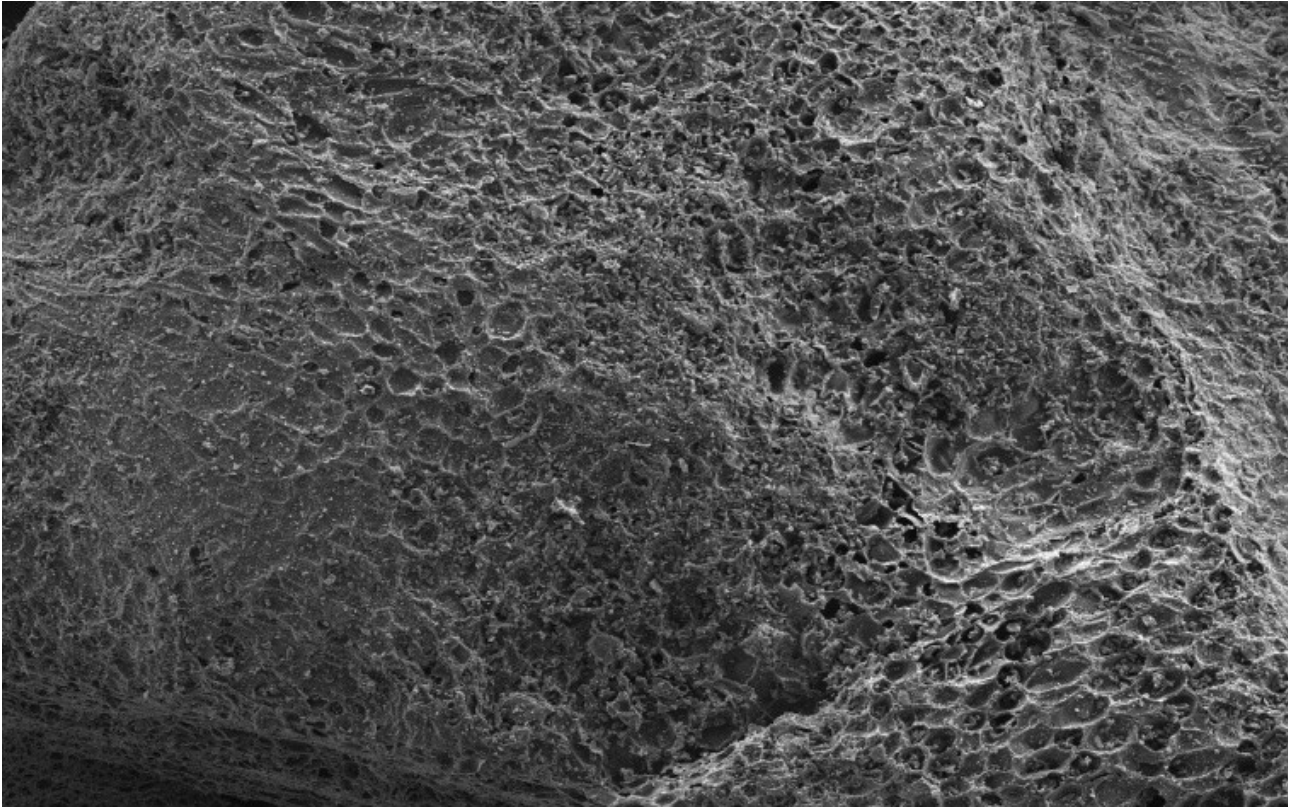


Figure 1: (B) SEM of Fluoride Loaded CBS at 100X Magnification

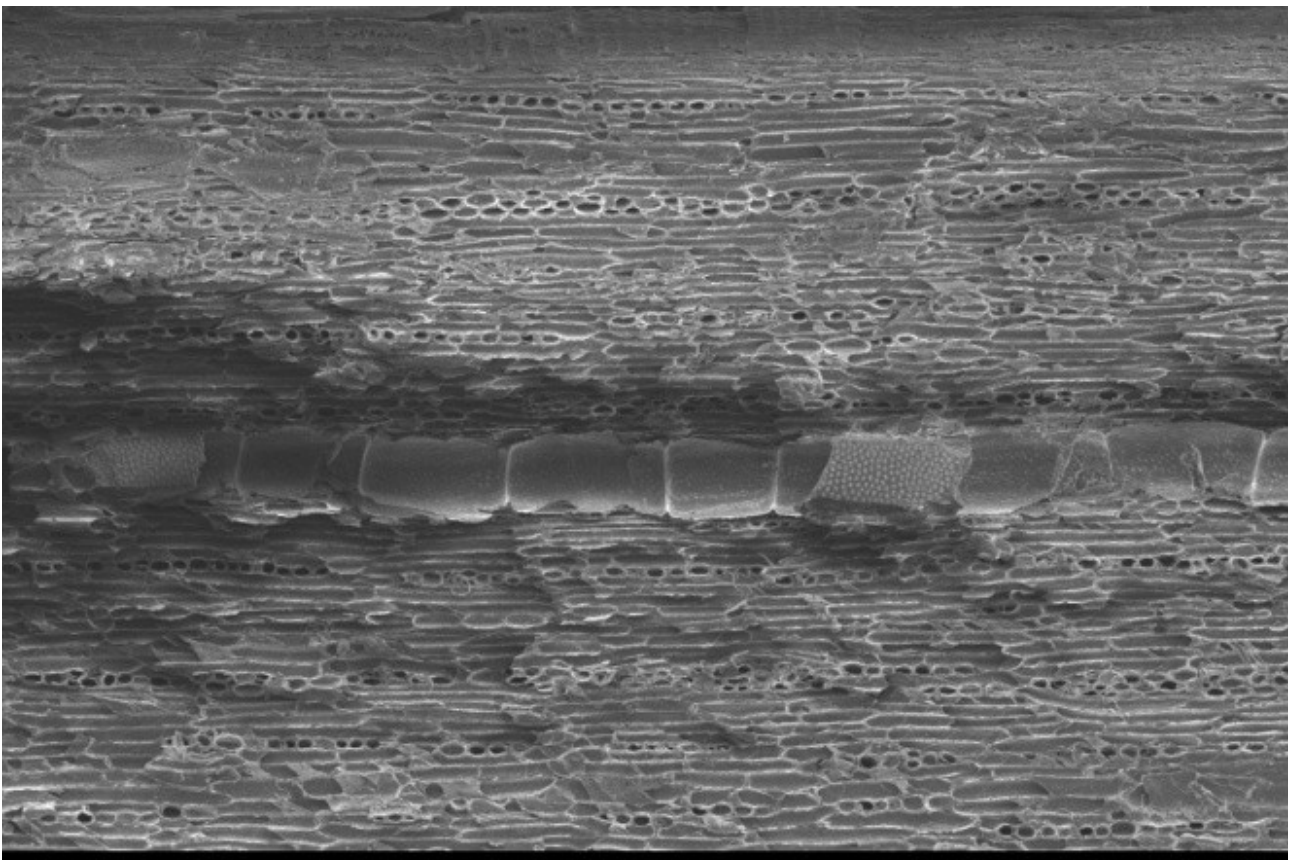


Figure 2: (A) SEM of Blank PP at 100X Magnification

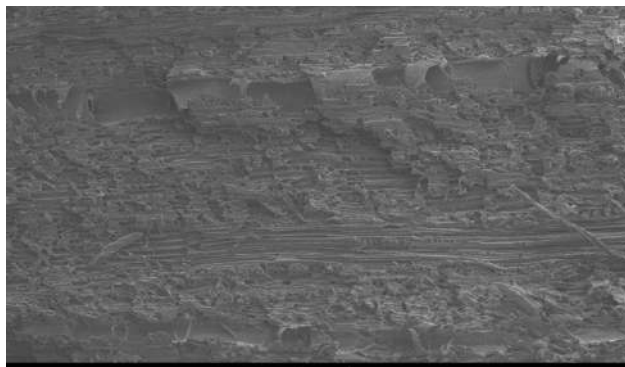


Figure 2: (B) SEM of Fluoride Loaded PP at 100X Magnification

FTIR spectra is a useful tool to identify functional groups in a molecule, as each specific chemical bond often has a unique energy absorption band, and can obtain structural and bond information. The FTIR spectra of CBS and PP were used to determine the vibrational frequency changes in the functional groups in the adsorbent. The spectra of adsorbent were measured within the range of 500-4000 cm^{-1} wave number. Spectra were plotted using same scale on the transmittance axis for all the adsorbent before and after adsorption. The FTIR spectra of the adsorbents display a number of adsorption peaks, indicating the complex nature of the studied adsorbents.

Structurally agricultural material consists of lignin, cellulose, hemi-cellulose and some protein which make them effective biosorbents. SB contained 35% cellulose, 25% hemi-cellulose and 22% lignin⁴⁶ Fig. 3 shows the FTIR spectra of blank and loaded CBS. From figure small bending frequency around 763, 823, 877 which shifted to slightly higher frequencies can be seen. Peaks around 2368 corresponds to amino group, that exists as $(-\text{NH}_2^+$ and $\text{NH}^+)$ which shows slight shift to 2350. A peak around 2860 is due to –

CH stretching⁴⁷ which also shows shift in frequency to 2866. Band around 2918 is due to stretching vibration of C-H group. Peaks around 1590 are identification of COO, C=O group³⁶.

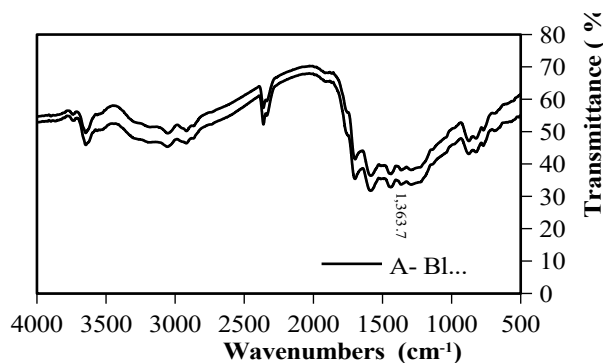


Figure 3: FTIR of Blank and Fluoride Loaded CBS

Fig.4 shows the FTIR of blank and fluoride loaded PP. From Figure it can be seen that small peaks are present at 609.5, 769.6, and 891.1. Peaks at 1047.3 confirmed the presence of C-O bond and lignin structure can be confirmed by this peak⁴⁸, peaks around 1251.8 is due to $-\text{CH}_2$ deformation. Peaks around 1726 corresponds to the C=C bond. Peaks around 2364.7 (which shifts to 2360.87) can be due to N-H stretching vibrations or to C=O stretching vibration, probably due to ketones, thus suggesting the possibility of oxygen or nitrogen that might be involved in adsorption. Peaks around 2893.2 (which shift to 2887) assigned to the C-H bonds of aliphatic acids⁴⁹. Band at 3400 cm^{-1} is typical from cellulose which shifts to 3414; very small peak at 3240 is related to hemi-cellulose. Small peaks between 1508 and 1749 are due to the carboxylic group, present in lignin and hemi-cellulose⁵⁰. The adsorption peak around 3408.2 indicates the existence of free and intermolecular bonded hydroxyl groups.

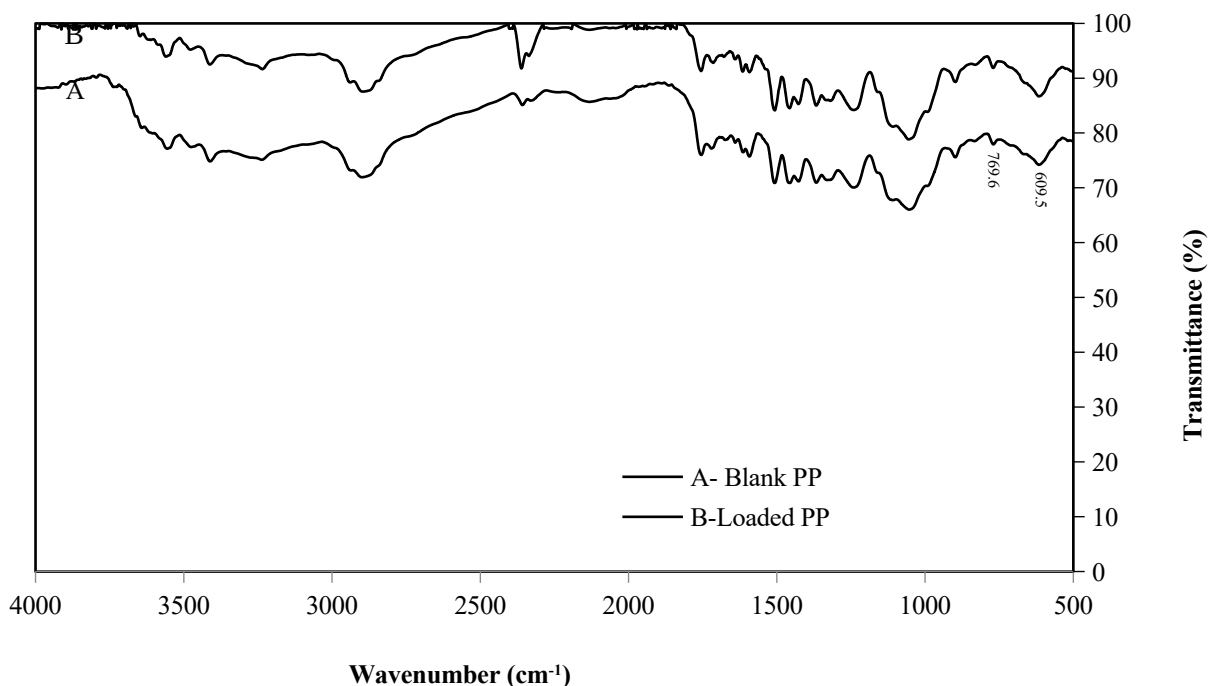


Figure 4: FTIR of Blank and Fluoride Loaded PP

“Point of zero charge” for a given adsorbent surface is the pH at which that surface has a net neutral charge. The significance of this kind of plot is that a given adsorbent surface will have positive charge at solution pH less than the pH_{pzc} and thus be a surface on which anions may adsorb. On the other hand, that

adsorbent surface will have negative charge at solution pH greater than the pH_{pzc} and thus be a surface on which cation may adsorb^{51,33} Fig . 5 shows the pH_{pzc} of CBS and PP. pH_{pzc} for CBS and PP are found to be 6.3 and 6.6 with 0.1M KNO_3 respectively. Similar results were noticed at 0.01 M concentration of KNO_3 .

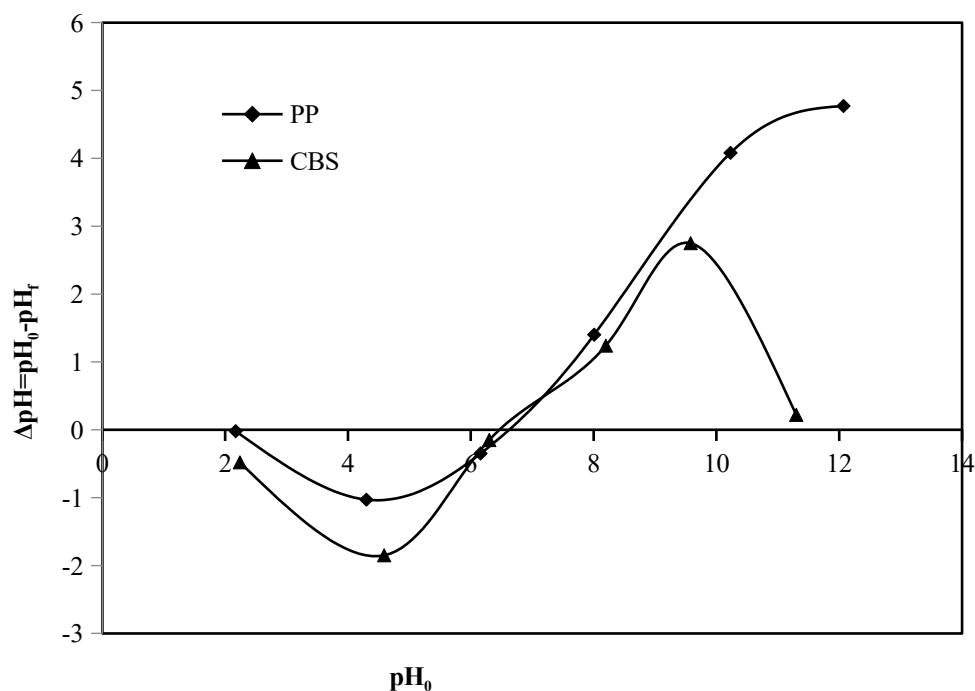
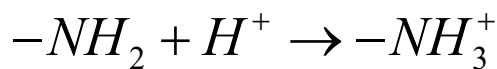


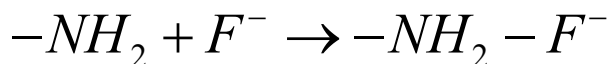
Figure 5: Point of Zero Charge pH_{pzc} of CBS and PP

In pH range 5.5-6, the specific adsorption is due to the electrostatic interaction between the positively charged surface ($\text{pH} < \text{pH}_{\text{pzc}}$) and fluoride ion for CBS

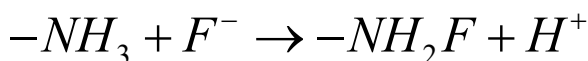
The probable mechanism can be:



(24)



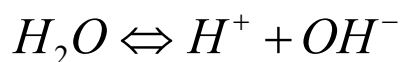
(25)



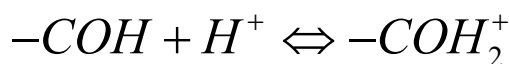
(26)

Where $-\text{NH}_2$ represents the surface amine group.

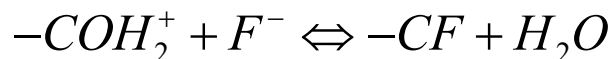
The probable mechanism in case of PP for pH range 5.4-6 and at $\text{pH} < \text{pH}_{\text{pzc}}$ can be:



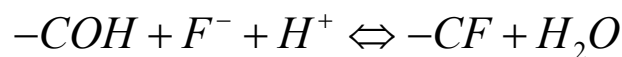
(27)



(28)



(29)



(30)

Where $-\text{COH}$ represents the surface hydroxyl group.

4.2 Batch Adsorption Study using Taguchi's Design of Experimental Methodology

Taguchi method is used to achieve two main objectives through the design of the experiments.

1. To determine the optimum process parameters values conditions for CBS and PP for the removal of fluoride.
2. To estimate the percentage contribution of each process parameter in batch adsorption system.

Various parameters and their levels which affect the removal of fluoride from aqueous solution onto CBS and PP are presented in Table 4.

Table 4: Significant Optimization Parameters and Their Levels for Adsorption of Fluoride onto CBS and PP

Factors	Parameters	CBS				PP		
		Level 1	Level 2	Level 3		Level 1	Level 2	Level3
A	Dose, m (g/100ml)	0.2	0.4	0.6		0.1	0.2	0.3
B	Initial concentration of fluoride, C_o (mg/L)	4	6	8		2	4	6
C	Temperature, T (K)	293	303	313		293	303	313
D	Contact time, t (min.)	30	60	90		30	60	90

Factors and ranges were selected based on the earlier batch experiments for both CBS and PP. Based on the experiments, four process parameter those having significant influence on the fluoride adsorption viz. Dose (m), initial concentration of fluoride (C_o), temperature (T), contact time (t) were selected for the present study. Experiments were conducted for fluoride ion adsorption onto CBS and PP according to test

conditions specified by L_9 OA (Table 5 - Table 6). Each experiment was repeated three times for each trial condition. The average or mean values of q_{tot} and S/N ratio for each parameter at levels 1, 2, and 3 are calculated for each of CBS and PP as shown in Table 7 - Table 8 respectively. It is observed that fluoride adsorption is strongly dependent on the parametric conditions.

Table 5: Taguchi L₉ (3⁴) Orthogonal Array with Experimental Q_{tot} Values and S/N Ratio Data for Adsorption of Fluoride by CBS

Run No.	Factors				q _{tot} (mg/g)			S/N Ratio
	Dose	C ₀	Temp	Time	R ₁	R ₂	R ₃	
	A	B	C	D				
1	2	3	1	2	0.20	0.24	0.28	-11.75
2	2	2	3	1	0.51	0.35	0.08	-17.14
3	3	1	3	2	0.40	0.42	0.39	-7.92
4	1	2	2	2	0.72	0.68	0.78	-2.86
5	3	2	1	3	0.02	0.02	0.02	-34.66
6	3	3	2	1	0.05	0.15	0.13	-22.74
7	1	3	3	3	0.72	0.46	0.83	-4.32
8	2	1	2	3	0.53	0.55	0.56	-5.28
9	1	1	1	1	1.06	1.06	1.05	0.46

Table 6: Taguchi L₉ (3⁴) Orthogonal Array with EXPERIMENTAL q_{tot} Values and S/N Ratio Data for Adsorption of Fluoride by PP

Run No.	Factors				q _{tot} (mg/g)			S/N Ratio
	Dose	C ₀	Temp	Time	R ₁	R ₂	R ₃	
	A	B	C	D				
1	2	3	1	2	0.05	0.02	0.10	-30.38
2	2	2	3	1	1.13	1.06	0.11	-14.21
3	3	1	3	2	0.16	0.14	0.14	-16.57
4	1	2	2	2	2.09	2.06	2.08	6.35
5	3	2	1	3	0.70	0.73	0.71	-2.95
6	3	3	2	1	0.02	0.00	0.11	-44.07
7	1	3	3	3	1.16	0.60	0.87	-2.09
8	2	1	2	3	0.17	0.21	0.22	-14.14
9	1	1	1	1	0.38	0.37	0.34	-8.80

4.3 Effect of Process Parameters

Various parameters (C_0 , T , m and t) significantly affect the q_{tot} values. In case of CBS it can be seen from Table 7 that parameter A (m), parameter B (C_0) and parameter D (t) have highest influence at level 1 while parameter C (T) has the highest influence at level 3. The difference between level 2 and level 1 ($L_2 - L_1$) of each factor indicates the relative influence of the effect. The larger is the difference between two levels

the stronger will be the effect. Table 7 shows that parameter C (T) has stronger influence on q_{tot} than that of the other parameters. In case of PP it can be seen from Table 10 that parameter A (m) has highest influence at level 1 while parameter B (C_0), parameter C (T) and parameter D (t) have the highest influence at level 2. Table 8 shows that C_0 (parameter B) has stronger influence on q_{tot} than that of the other parameters. Tables 9 and Table 10 show the ANOVA of fluoride ion adsorption on CBS and PP respectively.

Table 7: Average and Effects of q_{tot} Values for CBS: Raw and S/N Data

Parameter	Raw data, average value			Main Effects (Raw data)		S/N Data, Average value			Main effects	
	L ₁	L ₂	L ₃	L ₂ -L ₁	L ₃ -L ₂	L ₁	L ₂	L ₃	L ₂ -L ₁	L ₃ -L ₂
A	0.82	0.37	0.18	-0.44	-0.20	-2.39	-11.39	-21.78	-9.00	-10.38
B	0.67	0.35	0.35	-0.31	-0.01	-4.24	-18.22	-12.94	13.98	5.29
C	0.44	0.46	0.47	0.02	0.01	-15.32	-10.29	-9.79	5.02	0.50
D	0.49	0.46	0.41	-0.03	-0.05	-13.14	-7.51	-14.75	5.63	-7.24

Table 8: Average and Effects of q_{tot} Values for PP: Raw and S/N Data

Parameter	Raw data, average value			Main Effects (Raw data)		S/N Data, Average value			Main effects	
	L ₁	L ₂	L ₃	L ₂ -L ₁	L ₃ -L ₂	L ₁	L ₂	L ₃	L ₂ -L ₁	L ₃ -L ₂
A	1.11	0.34	0.30	-0.76	-0.04	1.42	-19.58	-21.19	-20.99	-1.62
B	0.24	1.19	0.33	0.95	-0.86	-13.17	-3.60	-25.51	9.57	-21.91
C	0.38	0.77	0.60	0.40	-0.19	-14.04	-17.29	-10.96	-3.25	6.33
D	0.39	0.76	0.60	0.37	-0.16	-22.36	-13.53	-6.40	8.83	7.14

Table 9: ANOVA of Fluoride Ion Adsorption on CBS

Factors	Total variance of each factor	DOF	Variance	Variance ratio	Pure sum of square	Percent Contribution
A	1.93	2.00	0.97	97.30	1.91	70.25
B	0.61	2.00	0.30	30.60	0.59	22.09
C	0.00	2.00	0.00	0.08	-0.02	0.06
D	0.03	2.00	0.02	1.53	0.01	1.10
Error	0.18	18.00	0.01	1.00	0.10	6.50
Totals	2.75	26.00	1.29			100.00

Table 10: ANOVA of Fluoride Ion Adsorption on PP

Factors	Total variance of each factor	DOF	Variance	Variance ratio	Pure sum of square	Percent Contribution
A	3.69	2.00	1.85	40.82	3.60	34.29
B	4.93	2.00	2.47	54.56	4.84	45.83
C	0.71	2.00	0.36	7.86	0.62	6.61
D	0.61	2.00	0.31	6.79	0.52	5.70
Error	0.81	18.00	0.05	1.00	0.45	7.56
Totals	10.77	26.00	5.02			100.00

Fig 6. Shows the response curve for the fluoride adsorption parameters by CBS on the average values of q_{tot} . In case of m (parameter A) i.e. the adsorbent dose, an increase in m from level 1 to level 3 led to decrease in the value of q_{tot} , showed that the adsorption capacity of adsorbent decreases with increase in m . An increase in initial concentration C_o from level 1 to 2 increases the amount of q_{tot} and increase in level 2 to

3 shows more or less same q_{tot} values. An increase value of parameter C (temperature, T) from level 1 to 2 shows increase in q_{tot} and increase in level 2 to 3 also shows an increase in the q_{tot} value. An increase in the level of contact time (t) (parameter D) from 1 to 2, results in an increase in the q_{tot} value. However, the q_{tot} value remains the same with subsequent increase from level 2 to level 3.

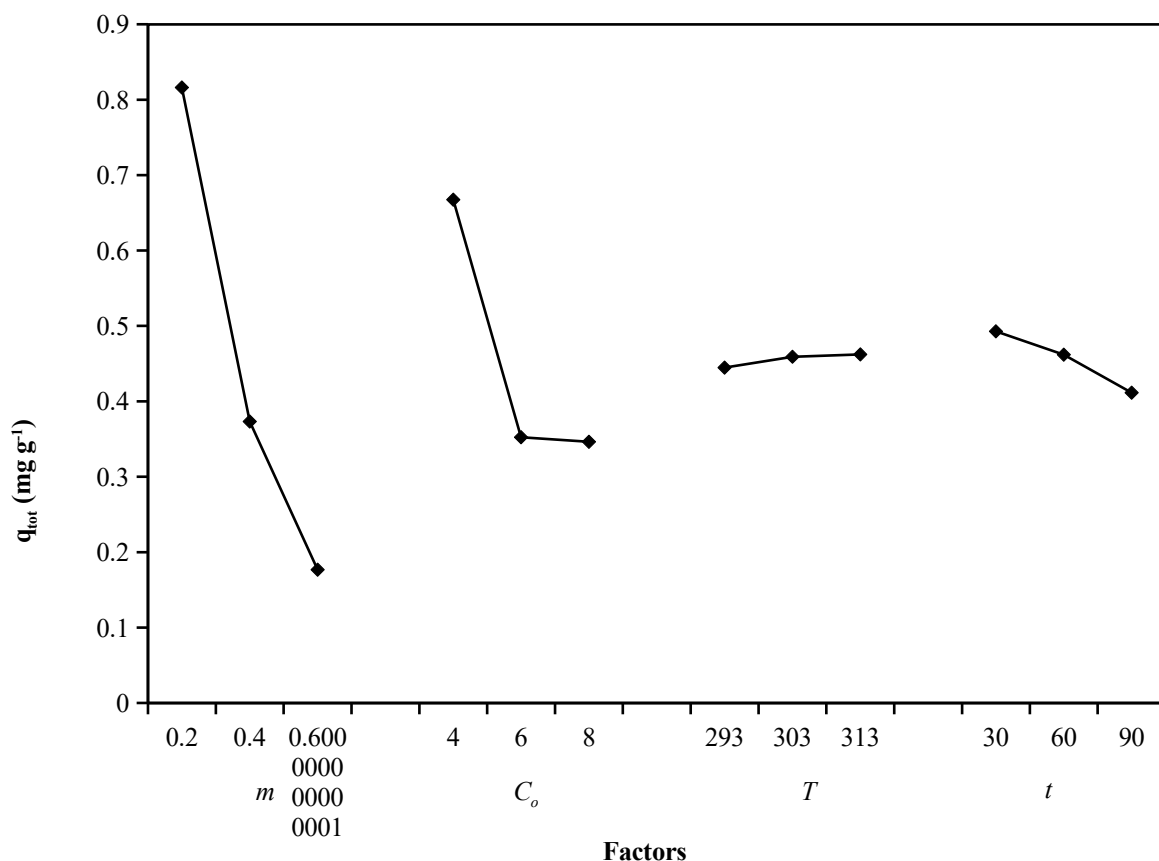


Figure 6: Effect of Process Parameters on q_{tot} for Adsorption

OF FLUORIDE ON CBS

The Fig. 7 Shows the response curve for the fluoride adsorption parameters by PP on the average values of q_{tot} . In case of m (parameter A) i.e. the adsorbent dose, an increase in m from level 1 to level 3 led to decrease in the value of q_{tot} , showed that the adsorption capacity of adsorbent decreases with increase in m , this may be due to increase in adsorbate to adsorbent ratio with increase in m . An increase in initial concentration C_o from level 1 to 2 increases the amount of q_{tot} and increase in level 2 to 3 shows decrease in q_{tot} values. Initially the q_{tot} increased with increase in C_o as the resistance to uptake of fluoride from the solution decreases with the increase in fluoride concentration⁵². The q_{tot} should increase with increasing initial concentration due to the increasing driving force but after level two in the present study it decreases which may be due to the combined effect of the other parameters viz. adsorbent dose, temperature and time of agitation. An increase values of parameter C (temperature, T) from level 1 to 2 shows increase in q_{tot} and increase in level 2 to 3 shows more or less same value because sorption is an exothermic process, it would be expected that an increase in T would result

in decrease in the q_{tot} value. However, if the diffusion process controls the adsorption process, the q_{tot} value will increase with increase in temperature, because of the endothermicity of the diffusion process. An increase in T results in increased mobility of the fluoride ions and a decrease in the retarding forces acting on the diffusing ions. These results in the enhancement in the sorptive capacity of the adsorbents. However, the diffusion of the fluoride ions into the pores of the adsorbent is not only rate- controlling step and the diffusion resistance can be ignored with adequate contact time^{32,33,53,54}. Therefore, the increase in sorptive uptake of fluoride with increase in temperature may be attributed to chemisorption. An increase in the level of contact time (t) (parameter D) from 1 to 2, results in an increase in the q_{tot} value. However, the q_{tot} value decreases with subsequent increase from level 2 to level 3. Also, the adsorption of fluoride ions increases as t increases until equilibrium is attained between the solute molecules in the liquid and the solid phases. During initial stage of adsorption, all adsorbent sites are vacant and the solute concentration gradient was high. Afterwards, the fluoride uptake rate by the adsorbent decreases significantly, due to decrease in adsorption sites⁵⁵.

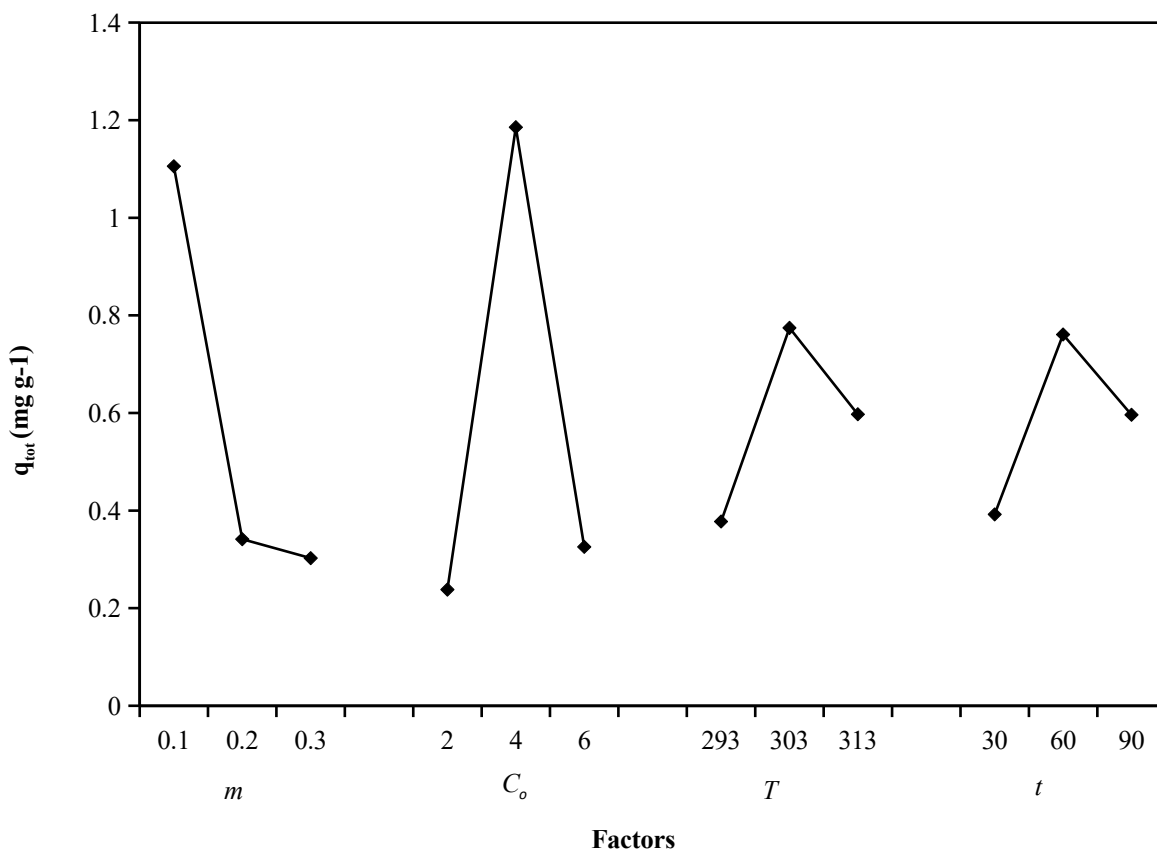


Figure 7: Effect of Process Parameters on Q_{tot} for Adsorption

OF FLUORIDE ON PP

By studying the main effects of each of the factors, the general trends of the influence of the factors on the adsorptive removal of fluoride process can be characterized. The characteristics can be controlled such that lower or higher values in a particular influencing factor produce the preferred result. Thus, the levels of factors necessary to produce the best results can be predicted. The percentage contribution of each parameter, for q_{tot} as the desired response characteristic for CBS is shown in Fig. 8. It shows that parameter A (m) is the most significant factor with 70.25% contribution followed by parameter B (C_0) with contribution of 22.09% for the removal of fluoride. The percentage contribution of each parameter, for q_{tot} as the desired response characteristic for PP is shown in Fig. 9. It

shows that parameter B (C_0) is the most significant factor with 45.83% contribution followed by parameter A (m) with contribution of 34.29% for the removal of fluoride

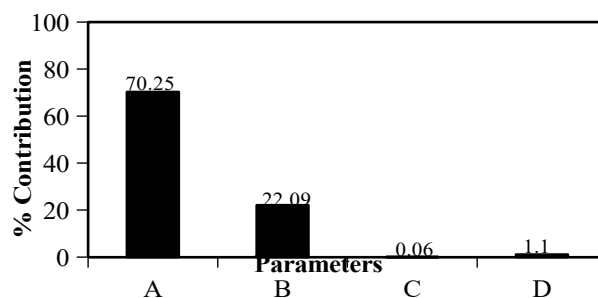


Figure 8: The Percentage Contribution of Each Parameter, for q_{tot} (CBS) (a: Dose of CBS; B: Initial Concentration; C: Temperature; D: Contact Time)

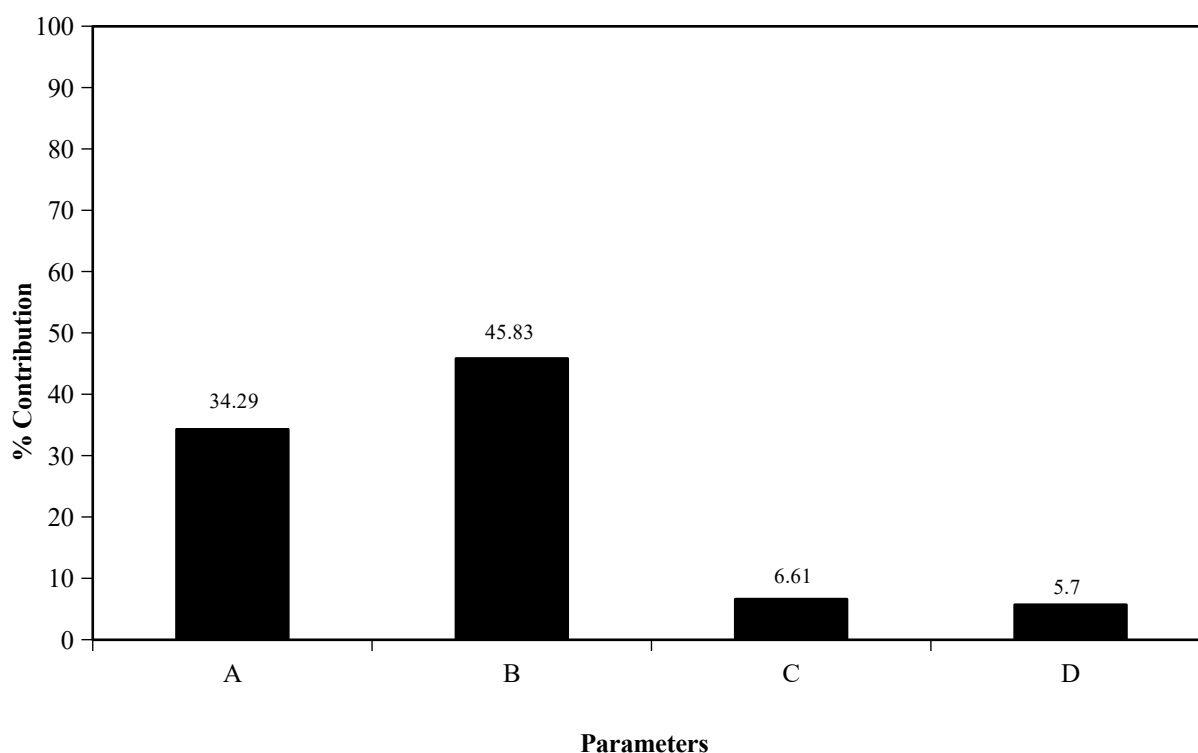


Figure 9: The Percentage Contribution of Each Parameter, for q_{tot} (PP) a: Dose of PP; B: Initial Concentration; C: Temperature; D: Contact Time)

4.4 Selection of Optimal Levels and Estimation of Optimum Response Characteristics

Because q_{tot} is a higher is better (HB) type quality characteristic, the greater q_{tot} value is considered optimal. Table 13 summarizes the optimal level of various parameters obtained after examining the response curve (Fig. 8- Fig. 9). Table 13 indicates that in case CBS the first level of parameter A (m), B (C_0), D (t) and third level of Parameter C have higher values of q_{tot} and S/N ratio while in case of PP the first level of parameter A (m) the second level of parameter B (C_0), C (T) and D (t) have higher values of q_{tot} and S/N ratio.

4.5 Confirmation Experiments.

The confirmation experiments have been conducted for the adsorption of fluoride onto CBS and PP at selected optimal levels of the process parameters. The average values of the characteristic are obtained and compared with the predicted values. The results are given in Table 13. The values of q_{tot} obtained through the confirmation experiments are within 95% of CI_{CE} . These optimal values are valid within the specified range of process parameters.

CONCLUSIONS:

- The Taguchi orthogonal array design of experimental methodology was determined to be very economical in experimental sorption of fluoride onto CBS and PP. This approach facilitated understanding of the interaction of a large number of variables spanned by factors and their setting with small number of experiments. Factors such as initial fluoride concentration, adsorbent dose, temperature, contact time at three levels with OA L_9 (3^3) could be optimized with 9 sets of experiments only.
- The Taguchi and ANOVA methods were applied to investigate the effects of dose, initial fluoride ion concentration, temperature and contact time of both the CBS and PP on the fluoride removal from aqueous solution.
- Dose is the most significant factor with 70.25% contribution followed by initial concentration with contribution of 22.09% for the removal of fluoride by using CBS as adsorbent for fluoride removal.
- Initial concentration is the most significant factor with 45.83% contribution followed by adsorbent

dose with contribution of 34.29% for the removal of fluoride by using PP as an adsorbent.

- Temperature and contact time have a very little effect on fluoride removal in both cases.
- The optimum test condition, at which lowest rate is obtained has been determined to $A_1B_1C_3D_1$ levels for CBS and $A_1B_2C_2D_2$ levels for PP.
- From Batch Study it was found that CBS was able to reduce fluoride upto 52% at optimum dose of 2g/l, pH=6, Co=4 mg/L, time=60 minute at 373 K, PP was able to reduce 48.8 % of fluoride in the field sample at optimum dose 1g/L, pH 5.4, initial concentration 4mg/l, time=60 minute temperature= 303
- Finally it was observed that CBS and PP can be used as an alternative low cost adsorbent for Fluoride removal.

Notations

q_{tot} = Equilibrium adsorption uptake (mg/g)

C_o = Initial fluoride concentration (mg/l)

C_e = Equilibrium fluoride ion concentration (mg/l)

m = Adsorbent dose (g/l)

V = Volume in litre

$L(y)$ = Loss function

K = Proportionality constant

m_T = Target value

y = Experimental value obtained in each trial

R = Sample size

μ = Mean of the response

$\overline{T}$

= Overall mean of the response

$\overline{A_2}$

= Average values of response at the second level of parameter A

$\overline{B_2}$

= Average values of response at the second level of parameter B

CI_{POP} = Confidence interval for the population

CI_{CE} = Confidence interval of sample group

V_e = Error of variance

N = Total number of results

T = Grand total of results

f_e = Degree of freedom of error.

REFERENCES

1. Davis, S.N. and Deweist, R.J.M. (1966) *Hydrogeology*; John Wiley and Sons New York, NY, USA., 463 PP
2. A. K Susheela, Fluorosis management programme in India. *Curr. Sci.* 77; 1999,1250–1256.
3. WHO (2006) *Guidelines for Drinking Water Quality*, First Addendum to Third edition, vol. 1, WHO, Geneva, 375.
4. BIS, hppcb.gov.in/eiasorang/spec.pdf, Indian standard specification for drinking water IS: 10500.
5. V.K. Saxena, and S Ahmed,. Dissolution of fluoride in groundwater. *Environ. Geol.*, 40, 2001,1084–1087.
6. J. Qian, A. K. Susheela, A. Mudgal, A. G. Keast, G., Fluoride in Water: *An Overview*, UNICEF Publication on Water, Environment Sanitation and Hygiene,1999 11–13.
7. J. Fitzegerald, D., Cunliff, S. Rainbow, S. Dodds, S. Hostetler, G.Jacobson, (1999) Groundwater Quality and Environmental Health Implications; Anangu Pitjantjara Lands, South Australia, *A Report from Bureau of Rural Science 1999*, 1–30.
8. J.O. Hem, Study and Interpretation of Chemical Characteristics of Natural Water. U.S. *Geological Survey Water Supply*, 1959,1473
9. Central Ground Water Board (CGWB), *Annual Ground Water Quality Report 2025*, Ministry of Jal Shakti, Government of India.
10. S. Ghorai, K.K Pant, Investigations on the column performance of fluoride adsorption by activated alumina in a fixed-bed. *Chem. Eng. J.*, 98, 2004,165–173.
11. A.A.M Daifullah, S.M. Yakout, S.A Elreefy, Adsorption of fluoride in aqueous solutions using KMnO4-modified activated carbon derived from steam pyrolysis of rice straw. *J. Hazard. Mater.*, 147, 2007, 633–643.

12. S. Saha, Treatment of aqueous effluent for fluoride removal. *Water Res.*, 27, 1993, 1347–1350.
13. K. Vaaramaa, J. Lehto, Removal of metals and anions from drinking water by ion exchange. *Desalination*, 155, 2003, 157–170.
14. Z. Amor, B. Bariou, N. Mameri, M. Taky, S. Nicolas, A. Elmidaoui, Fluoride removal from brackish water by electrodialysis, *Desalination*, 133, 2001, 215–223.
15. P.I Ndiaye, P., Moulin, L., Dominguez, J.C. Millet, F. Charbit, (2005) Removal of fluoride from electronic industrial effluent by RO membrane separation. *Desalination*, 173, 2005, 25–32.
16. G. Moges, F. Zewge, M. Socher, Preliminary investigations on the defluoridation of water using fired clay chips, *J. Afr. Earth Sci.*, 21, 1996, 479–482.
17. Y. Wang, E. J Reardon, Activation and regeneration of a soil sorbent for defluoridation of drinking water, *Appl. Geochem.*, 16, 2001, 531–539.
18. D.S. Bhargava, D. J. Killedar, Fluoride adsorption on fishbone charcoal through a moving media adsorber. *Water Res.*, 26, 1992, 781–788.
19. M.S. Onyango, Y. Kojima, A. Kumar, D Kuchar, M. Kubota, H Matsuda, (2006) Uptake of fluoride by Al³⁺-pretreated low-silica synthetic zeolites: adsorption equilibrium and rate studies. *Sep. Sci. Technol.* 41, 2006, 683–704.
20. E. Kumar, A., Bhatnagar, M.J.W. Jung, S. Lee, S.J. Kim, G. Lee, H. Song, J. Y. Choi, J. Yang, B.H. Jeon, Defluoridation from aqueous solutions by granular ferric hydroxide (GFH). *Water Res.*, 43, 2009, 490–498.
21. S.V Mohan, S.V. Ramanaiah, B. Rajkumar, P. N. Sarma, Removal of fluoride from aqueous phase by biosorption onto algal biosorbent *Spirogyra* sp.- sp.-IO2: sorption mechanism elucidation. *J. Hazard. Mater.*, 141, 2007, 465–474.
22. D. De, S. Santosha, V. Aniya, A. Sreeramoju, B. Satyavathi, Assessing the applicability of an agro-industrial waste to engineered bio char as a dynamic adsorbent for fluoride sorption. *Journal of environmental chemical engineering*, 6 (2), 2018, 2998-3009, doi: 10.1016/J.jece.2018.04.021
23. P.D Indurkar, A.R Gupta., S. Sharma Iron oxide impregnated pongamia pinnata microporous biochar composite as an effective bio-adsorbent for the remediation of arsenic ions from water. *Biomass conversion and biorefinery* 14 (16), 2023, 19705-19722.
24. E. Barrado, M.Vega., Grande, P. and J.L Del Valle, Optimization of a Purification Method for Metal-Containing Wastewater by Use of a Taguchi Experimental Design. *Water Resource*, 30: 1996, 2309-2314.
25. K. D. Kim, D.N. Han, and H. T Kim, Optimization of experimental conditions based on the Taguchi robust design for the formation of nano-sized silver particles by chemical reduction method, *Chem. Eng. J.*, 104, 2004, 55-61.
26. J. Moghaddama, R., Sarraf-Mamoor, M. Abdollahy, Y. Yamini, Purification of zinc ammoniacal leaching solution by cementation: determination of optimum process conditions with experimental design by Taguchi's method. *Sep. Purif. Technol.* 51, 2006, 157-164.
27. S. S. Madaeni, S. Koocheki, Application of Taguchi method in the optimization of wastewater treatment using spiral- wound reverse osmosis element. *Chem. Eng. J.*, 119, 2006, 37-44
28. N.M.S Kaminari, D.R. Schultz, M.J.J.S Ponte, H.A Ponte, C.E.B Marino, A.C Neto, Heavy metal recovery from industrial wastewater using Taguchi method. *Chem Eng. J.*, 126, 2007, 139-146.
29. B.J.D. Plessis, G.H. D Villiers, The application of the Taguchi method in the evaluation of mechanical flotation in waste activated sludge thickening. *Resour. Conserv. Recycl.*, 50, 2007, 202-210.
30. T. Mohammadi, A. Moheb, M. Sadrazadeh, A. Razmi, Separation of copper ions by electrodialysis using Taguchi experimental design. *Desalination*, 169, 2004, 21-31.
31. V.C. Srivastav, I.D. Mall, I. M. Iand Mishra., Multi component adsorption study of metal ions onto bagasse fly ash using Taguchi's design of experimental methodology, *Ind. Eng. Chem. Res.*, 46, 2007 5697-5706.
32. V.C Srivastav, I. D Mall, I. M Mishra, Optimization of parameters for adsorption of metal

- ions onto rice husk ash using Taguchi's experimental design methodology. *Chem. Eng. J.*, 140, 2008, 136-144.
33. D. H Lataye, I. M Mishra, I. D. Mall, Adsorption of 2-picoline onto bagasse fly ash from aqueous solution. *Chem. Engg. Journal*, 138, 2008, 35-46.
 34. M. B. Silva., L. M. Carneiro, J.P. A Silva., I.D.S Oliveira., H.J.I. Filho, C.R.O. Almeida An Application of the Taguchi Method (Robust Design) to Environmental Engineering: Evaluating Advanced Oxidative Processes in Polyester-Resin Wastewater Treatment, *American Journal of Analytical Chemistry*, 5, 2014, 828-837.
 35. R. Gottipati, S Mishra, Process optimization of adsorption of Cr (VI) on activated carbons prepared from plant precursors by a two-level full factorial design. *Chem. Engg. Journal*, 160, 2010, 99-107.
 36. J. Anandkumara, B. Mandal, Removal of Cr (VI) from aqueous solution using Bael fruit (Aegle marmelos correa) shell as an adsorbent. *J. Hazard. Mater.* 2009, 168: 633-640
 37. APHA, American Public Health Association, *Standard methods for Examination of Water and Waste Water*, 21st ed., 2005, Washington, DC.
 38. IS 9235-1979, (2003) Indian standard methods for physical analysis and determination of solid wastes (excluding industrial solid waste).
 39. L. S. Balistrieri, J. W Murray, The surface chemistry of goethite (α -FeOOH) in major ion seawater. *Am. J. Sci.*, 281 (6), 1981,788-806,
 40. IS 2720 (part-4), (1985) Methods for test for soil: Part 4. Grain size analysis (second revision), Bureau of Indian standards, Manak Bhawan, New Delhi, India.
 41. Lance, A. E. (1994). *Quality up, costs down: A primer on Shipley's Taguchi methods*. Shipley Company.
 42. Montgomery D.C. (1997) *Design and analysis of experiments*; John Wiley, New York .
 43. Ross, P. J. (1988). *Taguchi Techniques for Quality Engineering: Loss Function, Orthogonal Experiments, Parameter and Tolerance Design*. McGraw-Hill, New York.
 44. Byrne, D. M., Taguchi, S. (1987) *The Taguchi Approach to parameter Design*; Quality Progress: New York.
 45. Roy, R. K. (1990) A primer on the Taguchi Method, Society of Manufacturing Engineers; Dearborn, MI.
 46. C.A Rezende, M.A de Lima., P. Maziero, E.R. deAzevedo, W. Garcia., I. Polikarpov, Chemical and morphological characterization of sugarcane bagasse submitted to a delignification process for enhanced enzymatic digestibility. *Biotechnology for Biofuels*, 4, 54, 2011, <https://doi.org/10.1186/1754-6834-4-54>
 47. H. Li., Z. Li, U. Li, T. X., Xiao, T. X., Z. Peng, L. Deng, A novel technology for biosorption and recovery of hexavalent chromium in wastewater by bio-functional magnetic beads. *Bioresour. Technol.*, 99, 2008, 6271-6279.
 48. D. L Pavia, G. M. Lampman, G.S. Kriz.. (1996) *Introduction to spectroscopy*; 2nd edition, Saunders Golden Sunburst Series, New York.
 49. N. V Farinella., G. D Matos., E. L Lehmann, M. A. Z Arruda, Grape bagasse as an alternative natural adsorbent of cadmium and lead for effluent treatment. *J. Hazard. Mater.*, 154, 2008, 1007-1012.
 50. P. C Brandao, T. C. Souza, C. A. Ferreira, C. E Hori, Removal of petroleum hydrocarbon from aqueous solution using sugarcane bagasse as adsorbent. *J. Hazard. Mater.* 175, 2010, 1106-1112.
 51. D. H. Lataye, I. M Mishra, I. D. Mall, (2006) Removal of pyridine from aqueous solution by adsorption on bagasse fly ash. *Ind. Eng. Chem. Res.*, 45 (11), 2006, 3934-3943.
 52. U. R Lakshmi, V.C. Srivastav, I. D. Mall, D. H. Lataye., Rice husk ash as an effective adsorbent: Evaluation of adsorptive characteristics for Indigo Carmine dye. *J. Env. Mangm*, 85 (3) , 2008, 757-773.

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