# VALIDATION OF DEFLUORIDATION METHOD WITH "ACACIA ARABICA" PLANT BYPRODUCT THROUGH 2$^n$ FACTORIAL EXPERIMENTATION-A STATISTICAL APPROACH

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**ABSTRACT:** Adsorption is one of the most efficient physicochemical processes known to remove fluoride from drinking water. Activated carbon adsorption is conventionally the most used material for this purpose. The aim of this study was to know the variables that influence the adsorption process of fluoride ion from aqueous media, so as to optimize the operating conditions. Factorial experimentation within a certain domain was used to determine the influence level of several parameters, such as initial pH of the solution, particle size, adsorbent's concentration agitation time and their interactions. A statistical analysis of the results showed that within the selected domain all the parameters have influence at a significance level of 1% excepting initial pH that only has influence at a significance level of 5 %. Some of the possible interactions between these parameters also have significant influence on the adsorption process especially first order ones, including significance levels of 5 and 1%. This means then that optimization of operating conditions water treatment using the studied adsorption technique will not imply additional costs. This emphasizes the importance of Acacia arabica fruit carbon as an alternative to activated carbon.
**Key words**: Acacia arabica fruits, Activated carbon, factorial design, statistical analysis

## INTRODUCTION

Fluoride is a health affecting substance. The physiological effects of fluoride ingestion on human health have been studied extensively. The acceptable fluoride concentration in drinking water is generally in the range of 0.5 to 1.5 mg/l (APHA 2002). Concentration higher than that affects the metabolism of elements such as Ca, P in human body and lead to dental and skeletal fluorosis. Fluoride is present in the soil and rock formation in the form of fluorapatite, fluorspar, amphiboles and micas weathering rockalkali contribute fluoride natural waters (Brewer, 1996; Elrashidi and Lindsay, 1986; Ward et al., 1964; Bishnoi and Arora, 2007; Shailaja and Johnson, 2007). The fluoride present in these minerals is substituted by (OH-) ion under redox conditions resulting in the release of fluoride ions to the circulating waters.

India is among 23 nations in the world, where fluoride contaminated ground water is creating health problems. Sixty two million people including 6.0 million children in the country in 18 states are affected with dental, skeletal or non skeletal fluorosis (Chinoy, 1991; Susheela, 1993, Mehrothra 1999). In rural India, ground water (which contains high fluoride) remains the dominant source of drinking water.

Research has been carried out trying to find alternative materials that despite of being less efficient imply much lower costs.

Recently, considerable attention has been devoted to develop better and suitable adsorbents for defluoridation purpose but adsorption process is the cheapest, simplest, easily available and accessible process for Defluoridation in developing country like India (Kumar et al., 2007).

Materials like coconut shell carbon (Arulanantham et al., 1992), activated carbon (Muthukumaran et al., 1995; Mariappan et al., 2002; Sivabalan et al., 2002), activated alumina (Kumar, 1995; Li et al., 2001), bone char (Killedar and Bhargava, 1993) and ion exchange resins (Shrivastava and Deshmukh, 1994) have been used as adsorbents. Activated carbon prepared from various raw materials exhibits good capacity for removal of fluoride from drinking water. No reports on use of Acacia arabica fruits byproduct activated carbon appeared for defluoridation

It was advantageous to have theoretical information, as broad as possible, about the effects that variations in the operating conditions would have on the adsorption extension, though, in some cases, if a not too expensive process is aimed at, certain operating conditions may be forbidden from an economical point of view. With this knowledge it would be possible to have several options dealing with the conditions to be used according to the purpose aimed at. Taking in due consideration the above mentioned criteria, the following variables were selected: Granulometry (particle size), agitation time, pH and adsorbent concentration.

## EXPERIMENTAL

***Adsorbent material***: Acacia arabica belongs to mimosaceae family in the plat kingdom fruits are collected in bulky and sun dried.

***Solutions preparation:*** All the chemicals used are of analytical reagent grade. The reagents prepared are

***Standard fluoride solution***: 221.0 mg of anhydrous sodium fluoride (98% pure, LR quality, supplied by Ran boxy Laboratories Ltd.,) has been weighed accurately and is transferred into 1000 ml volumetric flask. The substance is dissolved in double distilled (fluoride free) water and then the solution is diluted to 1 litre. The resultant solution contains 100 mg/l of fluoride. This solution is said to be stock fluoride solution. Further concentration are diluted from the stock solution

***SPADNS solution*:** SPADNS is the abbreviation of sodium 2-parasulfophenylazo – 1,8 – dihydroxy – 3, 6 – naphthalene disulfonate, also called 4, 5 – dihydroxy – 3 – (parasulfophenylazo) -2, 7 – naphthalene disulphonic acid trisodium salt. 958 mg of SPADNS is dissolved in distilled water and is diluted to 500 ml. This solution is stable for at least 1 year if protected from direct sunlight.

***Zirconyl-acid reagent***: 133 mg of zirconyl chloride octahydrate $ZrOcl_2.8H_2O$ is dissolved in about 25 ml distilled water. 350 ml of conc. HCl is added to it and is diluted to 500 ml with distilled water.

***Acid zirconyl – SPADNS reagent***: Equal volumes of SPADNS solution and zirconyl-acid reagent are mixed. The combined reagent is stable for at least 2 years.

***Reference solution***: 10 ml. SPADNS solution is added to 100 ml distilled water. 7 ml conc. HCl is diluted to 10 ml and this is added to the diluted SPADNS solution. The resulting solution, used for setting the instrument reference point (Zero), is stable for at least 1 year. Alternatively a prepared standard of 0 mg F/L is used as a reference.

***Apparatus***: U V – Visible Spectrophotometer (Chemeto, model no: UV – 2600); Elico – pH Meter

***Process for activated carbon development:*** The waste materials were carbonized in the electrical conventional heating reactor by two stages carbonization process known as low temperature carbonization and high temperature carbonization in the range of 250-600 $^{O}C$ and 600-800 $^{O}C$ respectively. The materials were placed in closed stainless steel vessels by maintaining inert conditions and pyrolysis was carried out at 400 $^{O}C$ for 30 minutes followed by next stage to develop the pore size structure so that an accessible internal surface could be created.

The carbonized product was treated with 1N $HNO_3$ for the removal of unwanted materials. The acid washed product was thoroughly washed with hot distilled water to remove acidity and chlorides. Indigenously prepared carbon thus produced was thermally activated at 110 $^{O}C$ for 1 hr in an air oven. The product was finally dried and sieved to get particular particle size□□.

***Defluoridation:*** Adsorption experiments were earned out by shaking three different doses of adsorbent with 100 ml of Fluoride ion solutions of various concentrations, different pH and different concentrations by one another parameter may be constant in a 2L Remi made shaker at 200 rpm for a predetermined time. After agitation, the adsorbate and the adsorbent were separated by centrifugation and the uptake of Fluoride ions estimated spcctrophotometrically using the SPADNS reagent (APHA, 2002). The amount adsorbed at equilibrium, $q_c$ (mg/g), was computed as follows:

$$q_e = \frac{(C_0 - C_e)V}{W}$$

Where $C_0$ and $C_c$ are the initial and equilibrium solution concentrations (mg/1), V is the volume of the solution and W is the weight of precursor employed (g).

***2$^n$-Factorial experimentation***

One of the purposes of the factorial experimentation is to determine the effects of each factor and their interactions within the range of tested values. Tests must be carried out so as to get enough information in order to decide how many consider a more complex model (involving more factors and interactions) to adequately describe the phenomenon under study. For this it is necessary to use statistical techniques. In order to emphasize the variance of the answer it is necessary to do experimentation in disseminated points in the problem's domain, so that its most informative description may be possible. The aim of the following tests was to determine the influence level of the four mentioned factors [Granulometry (G), pH of adsorbate (pH), Time (T), and adsorbent concentration (D)], as well as that of their interactions, in order to optimize the operating conditions so as to obtain a higher adsorption capacity of fluoride ion.

A series of experiments was planned according to a $2^n$ centered factorial design and the results were analyzed by means of a variance study (Miller J. C. et al,1993. Barker T. B., 1994). Doing so, it was possible to search simultaneously the effects of the n variables. If four variables are being considered, using a $2^n$ factorial plan, $2^4$ experiments will be needed to measure the effect of all variables and their combinations when each variable is tested at a high and a low level. For each experimentation factor there were a test and it's duplicate. Experiments in a central point where the variables levels were the mean of the high and low levels were also carried out.

With this, it was aimed to detect any lack of linearity in the experimental answer between the two extreme levels. Naturally, the choice of the high and low levels for each variable will depend on the domain to be explored. As it was intended to study the potential use of gallinaceous feathers as a cheaper alternative for traditional adsorbents, the designed process should avoid everything that could turn it expensive.

**RESULTS AND DISCUSSION**

Design was done for $2^4$ experiments. For each experimentation factor there were a test and its replica, therefore the total number of tests was thirty-two. Another four tests were carried out in order to verify if there was linear response between the two levels. Table 2 includes the matrix of factorial design, the answers obtained and their statistical analysis. In this table the variables granulometry, pH of adsorbate, time, and adsorbent concentration are symbolically represented by G, pH, T and D, respectively, and high and low levels are represented by +1 and –1, respectively. Table 1 shows the chosen values of the variables in the factorial experimentation.

Table 1: Explored domain – Selected values of the variables investigated in the factorial Experimentation

| Variables | High level | Medium level | Low level |
|---|---|---|---|
| Granulometry (in μ) | 150 | 90 | 45 |
| pH | 9 | 7 | 5 |
| Time (min) | 120 | 60 | 40 |
| Dose (g) | 4 | 3 | 2 |

## Factorial experimentation

The results of the factorial experimentation can be seen in Table 2. Emphasis was given to the variable temperature as it revealed to have high influence on the process and also because it would be possible without extra expenses to take advantage of this fact in industrial practice.

### Statistical analysis

The statistical analysis of the results can be seen in Table 2. In order to verify the significance level of the influence of the several variables and their interactions on the adsorbed amount it was necessary to use Fisher's test [Miller J. C. 1993. Cegarra J., 1981), the values of F for the significance levels of 0.01 and 0.05 for the degrees of freedom of the variables and their interactions (Cooper P.,1995) and for experimental error (Barker T. 1994) were seen in Fisher's tables.

The first, second and third order interactions have no significance, as the ratio $F=Vi/V\varepsilon$ is smaller than $< F_{1,16} = 4.49$ what means that the significance level is higher than 5 %. The most influent variable on the adsorption process was undoubtedly the pH and agitation time as its statistical F is much higher than the one for the other variables.

The adsorbent concentration is still very influent being followed by granulometry only has influence for the significance level of > 5 %. Concerning first order interactions, T-pH and T-D interactions are the most conditioning one. Dealing with second order interactions only pH–T–D interaction has significant influence on the process. If a mathematical model describing the process were aimed at, it would be necessary to carry out additional tests for a third level of the factors. However, as the research purpose was the determination of the influence level of the parameters on the adsorption process, those tests were considered unnecessary.

## CONCLUSIONS

The study carried out allowed to conclude that, for the selected domain, the chosen variables – Agitation time ( T ), "Granulometry" ( G ) and adsorbent's concentration ( A ) have very significant influence on the process, with increasing importance as follows: G<T<A. Dealing with pH it was verified that its influence on the process corresponds to the significance level of 5 %. Concerning the variables interactions, it was observed that some of them also condition the adsorption process, mainly the first order ones, both for the significance levels of 5 and 1%. The fact that the adsorbent's concentration has a very significant influence on the process is very important as it allows industrial effluents treatments to be done with low adsorbent's concentration. Because the influence of "Granulometry" on the adsorption capacity becomes rather smaller when agitation time increases, there will be no need to grind the adsorbent.

As this adsorbent is a quite abundant plant waste material, whose price can be considered rather negligible when compared with that of activated carbon, this means that acacia arabica fruit carbon is in a fair way to be used in industrial adsorption processes.

**Table 2: Matrix of design of the factorial experimentation, obtained answers and their statistical analysis**

| Test | $q_e$ | G | pH | T | D | G -pH | G –T | G -D | pH -T | pH -D | T - D | G-pH-T | G-pH-D | G-T-D | pH-T-D | G-pH-T-D |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.772 | -1 | -1 | -1 | -1 | 1 | 1 | 1 | 1 | 1 | 1 | -1 | -1 | -1 | -1 | 1 |
| 1* | 1.773 | -1 | -1 | -1 | -1 | 1 | 1 | 1 | 1 | 1 | 1 | -1 | -1 | -1 | -1 | 1 |
| 2 | 0.896 | -1 | -1 | -1 | 1 | 1 | 1 | -1 | 1 | -1 | -1 | -1 | 1 | 1 | 1 | -1 |
| 2* | 0.904 | -1 | -1 | -1 | 1 | 1 | 1 | -1 | 1 | -1 | -1 | -1 | 1 | 1 | 1 | -1 |
| 3 | 1.84 | -1 | -1 | 1 | -1 | 1 | -1 | 1 | -1 | 1 | -1 | 1 | -1 | 1 | 1 | -1 |
| 3* | 1.86 | -1 | -1 | 1 | -1 | 1 | -1 | 1 | -1 | 1 | -1 | 1 | -1 | 1 | 1 | -1 |
| 4 | 0.94 | -1 | -1 | 1 | 1 | 1 | -1 | -1 | -1 | -1 | 1 | 1 | 1 | -1 | -1 | 1 |
| 4* | 0.942 | -1 | -1 | 1 | 1 | 1 | -1 | -1 | -1 | -1 | 1 | 1 | 1 | -1 | -1 | 1 |
| 5 | 1.91 | -1 | 1 | -1 | -1 | -1 | 1 | 1 | -1 | -1 | 1 | 1 | 1 | -1 | 1 | -1 |
| 5* | 1.908 | -1 | 1 | -1 | -1 | -1 | 1 | 1 | -1 | -1 | 1 | 1 | 1 | -1 | 1 | -1 |
| 6 | 0.99 | -1 | 1 | -1 | 1 | -1 | 1 | -1 | -1 | 1 | -1 | 1 | -1 | 1 | -1 | 1 |
| 6* | 0.98 | -1 | 1 | -1 | 1 | -1 | 1 | -1 | -1 | 1 | -1 | 1 | -1 | 1 | -1 | 1 |
| 7 | 2.04 | -1 | 1 | 1 | -1 | -1 | -1 | 1 | 1 | -1 | -1 | 1 | 1 | 1 | -1 | 1 |
| 7* | 2.06 | -1 | 1 | 1 | -1 | -1 | -1 | 1 | 1 | -1 | -1 | -1 | 1 | 1 | -1 | 1 |
| 8 | 1.04 | -1 | 1 | 1 | 1 | -1 | -1 | -1 | 1 | 1 | 1 | -1 | -1 | -1 | 1 | -1 |
| 8* | 1.05 | -1 | 1 | 1 | 1 | -1 | -1 | -1 | 1 | 1 | 1 | -1 | -1 | -1 | 1 | -1 |
| 9 | 1.702 | 1 | -1 | -1 | -1 | -1 | -1 | -1 | 1 | 1 | 1 | -1 | 1 | 1 | -1 | -1 |
| 9* | 1.703 | 1 | -1 | -1 | -1 | -1 | -1 | -1 | 1 | 1 | 1 | 1 | 1 | 1 | -1 | -1 |
| 10 | 0.864 | 1 | -1 | -1 | 1 | -1 | -1 | 1 | 1 | -1 | -1 | 1 | -1 | -1 | 1 | 1 |
| 10* | 0.863 | 1 | -1 | -1 | 1 | -1 | -1 | 1 | 1 | -1 | -1 | 1 | -1 | -1 | 1 | 1 |
| 11 | 1.739 | 1 | -1 | 1 | -1 | -1 | 1 | -1 | -1 | 1 | -1 | 1 | 1 | -1 | 1 | 1 |
| 11* | 1.74 | 1 | -1 | 1 | -1 | -1 | 1 | -1 | -1 | 1 | -1 | -1 | 1 | -1 | 1 | 1 |
| 12 | 0.877 | 1 | -1 | 1 | 1 | -1 | 1 | 1 | -1 | -1 | 1 | -1 | -1 | 1 | -1 | -1 |
| 12* | 0.879 | 1 | -1 | 1 | 1 | -1 | 1 | 1 | -1 | -1 | 1 | -1 | -1 | 1 | -1 | -1 |
| 13 | 1.762 | 1 | 1 | -1 | -1 | 1 | -1 | -1 | -1 | -1 | 1 | -1 | -1 | 1 | 1 | 1 |
| 13* | 1.764 | 1 | 1 | -1 | -1 | 1 | -1 | -1 | -1 | -1 | 1 | -1 | -1 | 1 | 1 | 1 |
| 14 | 0.892 | 1 | 1 | -1 | 1 | 1 | -1 | 1 | -1 | 1 | -1 | -1 | 1 | -1 | -1 | -1 |
| 14* | 0.884 | 1 | 1 | -1 | 1 | 1 | -1 | 1 | -1 | 1 | -1 | -1 | 1 | -1 | -1 | -1 |
| 15 | 1.7 | 1 | 1 | 1 | -1 | 1 | 1 | -1 | 1 | -1 | -1 | 1 | -1 | -1 | -1 | -1 |
| 15* | 1.9 | 1 | 1 | 1 | -1 | 1 | 1 | -1 | 1 | -1 | -1 | 1 | -1 | -1 | -1 | -1 |
| 16 | 0.91 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 16* | 0.93 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Average | 44.014 | | | | | | | | | | | | | | | |
| Effects and interactions | | 0.0167 | 0.0756 | 0.0698 | 0.0648 | 0.0606 | 0.02 | 0.0876 | 0.0184 | 0.0629 | 0.0225 | 0.0155 | 0.0164 | 0.0675 | 0.0159 | 110.413 |
| Variance of the results (Vi) | | 0.016 | 0.075 | 0.069 | 0.02 | 0.018 | 0.0155 | 0.0648 | 0.0876 | 0.0648 | 0.0876 | 0.0629 | 0.0164 | 0.0225 | 0.0675 | 0.0159 |
| Variance of the experimental error (V□) | | 3.8 | | | | | | | | | | | | | | |
| Statistical F (Vi/V□) | | 0.004 | 0.020 | 0.018 | 0.005 | 0.005 | 0.004 | 0.017 | 0.023 | 0.017 | 0.023 | 0.017 | 0.004 | 0.006 | 0.018 | 0.004 |

1*,1…etc indicates duplicate values

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