

An Analysis of Defluoridation Process of Drinking Water Using With Reasonable Adsorbents¹Charan Singh, ²Sukhlal Chhaba^{1,2}Department of Civil Engineering¹Jayoti Vidyapeeth Women's University, Jaipur, India²Sri Balaji College of Engineering & Technology, Jaipur, IndiaE-Mail: charan.singh1216@gmail.com, sukhlal.chhaba1992@gmail.com**ABSTRACT**

The Drinking water available for daily consumption may be contaminated by natural sources or by industrial effluents. It is often the main source of fluoride intake by humans, especially in areas where their concentrations in groundwater and/or surface water is high. Endemic fluorosis is present in at least 20 states of India, affecting more than 65 million people including 6 million children. Fluoride ion (F) concentration in India's groundwater varies widely, ranging from 0.01 to 48 mg/L. Defluoridation of ground water and supply of safe drinking water is the only immediate solution to this problem. The present investigation is an attempt towards a feasible solution. The process of removal of excess fluoride from water is described as Defluoridation. One of such method is adsorption. The present study has been conducted to assess the fluoride adsorption characteristics of natural adsorbents such as red soil collected from krishnagiri district and household waste like tamarind waste from the kitchen. The experiment has followed batch process. Static studies have aimed for investigation of fluoride removal efficiency under the varying conditions of the major parameters of adsorption, viz. pH, contact time, adsorbent dose, and initial fluoride concentration, and temperature, particle size of adsorbent, stirring rate and agitation speed. Kinetic models such as Pseudo first order and second order models are used for the adsorption rate mechanism. Adsorbents are allowed to follow Freundlich, Langmuir Isotherm and finally thermodynamic analyses are going to be done for the investigation of adsorption capacity. Defluoridation capacity of the adsorbents can be explained on the basis of the chemical interaction of fluoride with the metal oxides under the suitable conditions. This study is a step in developing a general platform suitable for producing potable water.

Keywords: SVPWM, dc-dc power converter, power smoothing, PID converter.**Introduction**

Air, water and food are the three basic needs for the survival of human beings. Water is frequently referred to as a universal solvent, because it has the ability to dissolve almost all substance; that comes in its contact. Some elements are essential in trace amount for human being while higher concentration of the same can cause toxic effects. Due to rapid urbanization and growth of modern industries (anthropogenesis source of fluoride) as well as geochemical dissolution of fluoride bearing minerals (natural source of fluoride), fluoride concentration is increasing in the environment including water resources. It is also very important that the drinking water should be safe and potable. In general the public particularly in rural areas has no freedom of selection in respect of drinking water. In common with other forms of life, man has a need for water as an essential nutrient. Water is required for variety of function including regulation of the body temperature, as a solvent and as a vehicle in the transportation of other nutrients and waste products through the vascular system and through the inter and intracellular spaces. The requirement of water may vary from individual and in any one

individual from time to time under the influence of external stimuli. Therefore water intended for human consumption should be not only “Safe” but also wholesome water is defined as the water that is:

- Free from pathogenic agents
- Free from harmful chemical substances
- Pleasant to taste
- Usable for domestic purposes

Pure water is scarce and is not easily available to all. The water may be contaminated by natural sources or by industrial effluents. One such contaminant is fluoride. Fluoride naturally occurring in water can be above or below recommended levels.

Natural Sources

Fluoride is found in both surface water and ground water because some fluoride compounds present in earth’s upper crust are readily soluble in water. The average earth’s crust abundance is 300 mg/kg spread in a wide variety of minerals. The concentration of fluoride in water is normally controlled by fluorite solubility. The natural concentration of fluoride depends on the geological, chemical and physical characteristics of the aquifer, the porosity and acidity of the soil and rocks, the temperature and the action of other chemical elements. Geological formation is the main source of fluoride in the ground water. Ground water particularly in volcanic or mountainous areas can contain as much as 50 mg/l. Fluoride occurs naturally in public water systems as a result of runoff from weathering of fluoride containing rocks, soils and leaching from soil into ground water. The major sources of fluoride in ground water are fluoride bearing rocks such as fluorspar, cryolite, fluorapatite, and hydroxyl apatite. The fluoride content in the ground water is a function of many factors such as availability and solubility of fluoride minerals, velocity of flowing water, pH, temperature and concentration of calcium and bicarbonate ions in water. Although there are several sources of fluoride intake, it is roughly estimated that 60% of the total intake is through drinking water. In most drinking water, over 95% of total fluoride is the F⁻ ion, with the magnesium-fluoride complex (MgF⁺) being the next most common. Because fluoride levels in water are usually controlled by the solubility of fluorite (CaF₂), high natural fluoride levels are associated with calcium-deficient, alkaline and soft waters. Defluoridation is needed when the naturally occurring fluoride level exceeds recommended limits. In streaming surface water, fluoride concentrations are usually lower than in ground water because of the shorter contact time between water and rock. Rivers and lakes generally contain fluoride levels less than 0.5 mg/l.

Industrial Sources

The other sources of fluoride occurrence in water are industrial discharge from aluminium industries, phosphate industries, coal plants as well as due to water, food, air, medicament and cosmetics. The fluoride load in the aquatic environment due to industrial discharge is at least 100-fold high compared to that which arises due to leaching of fluoride bearing minerals. Atmospheric deposition of fluoride containing emissions from coal-fired power plants and other industrial sources also contributes to amounts food in water, either by direct deposition or by deposition to soil and subsequent runoff into water. The industrial effluent and sewage discharged from the domestic water supplies supplemented with fluoride contribute to the fluoride to the fluoride levels in aquatic systems. Combustion of coals and volcanic activity also contribute fluoride containing dust and gases to the atmosphere. The concentration of fluoride in

water is normally controlled by fluorite solubility. The natural concentration of fluoride depends on the geological, chemical and physical characteristics of the aquifer, the porosity and acidity of the soil and rocks, the temperature and the action of other chemical elements

Proposed Methods

A. Using Materials

The adsorbents used in the present study are Red soil sample and Tamarind household waste. The red soil was collected from Krishnagiri district. The red soil was washed several times with distilled water till clear water was obtained and dried in oven for 12 hours. The dried material was sieved to obtain particles, of particular sizes, for the present study. House hold waste like tamarind waste is collected from the last three months. Soluble and coloured components were removed from tamarind waste by washing with boiling water. This was repeated until the water was virtually colourless. After thorough washing, the adsorbent was sun dried and it is burned in muffle furnace at 500°C for 30 minutes and dried waste was put in a cotton jute bag and crushed manually or by mechanical crushing.

B. Characteristics of Instrument Adsorbent

The surface area of the adsorbent was measured by a surface area analyzer (Quanta orb Model, Qs.7). The porosity and density of the adsorbent were determined by mercury porosimetry and specific gravity bottles respectively elemental analysis was carried out with Perkin Elmer 2400 CHN Elemental Analyzer. PH meter (Hanna portable), and Remi shaking machine for agitating the samples for the required period at a speed of 200 strokes/minute were used. Adsorbent surface characterized by FTIR analysis (PERKINELMER, FTIR, Model-RXI Spectrometer). The pH of the solution was measured by using digital pH meter (model no. Systronic-335). Fluoride ion was estimated by Orion ion meter as per standard methods. Fluoride was measured by ion selective electrode (Thermo Orion 370 PerpHect Ion Selective Bench top Meter) and Scanning Electron Microscope.

C. Experiments Process of Adsorption

Adsorption experiments were carried out for the determination of pH, adsorbent dose variation, equilibrium time and kinetics, selection of an isotherm, effect of temperature and evaluation of thermodynamic parameters. The influence of pH (2-10), adsorbent concentration (0.2-2.4g/L) and particle size, contact time (40, 60, 120, 180, 240 and 300 min), initial fluoride concentration (1.5, 5, 7, 10, 15, 35, and 50 mg/L) and temperature (303, 313, 323 and 333K) were evaluated during the present study in a 250 mL Erlenmeyer Flask and 100 mL of fluoride solution of known concentration was added for constant shaking (at 300rpm) during 1hr in a temperature controlled magnetic stirrer at 303±1K and then the solids were separated through filtration. The solutions were collected for analysis and fluoride concentration in the solution was determined by using ion selective meter. Each experiment was conducted three times and average values are reported. Control experiments, performed without addition of adsorbent, confirmed that the sorption of fluoride on the walls of Erlenmeyer flasks was negligible. The amount of fluoride adsorbed per unit adsorbent (q_e)(mg/g) or adsorption uptake capacity of fluoride in batch system was calculated according to a mass balance on the fluoride concentration using the below equation.

$$q_e = \frac{(C_o - C_e) V}{m}$$

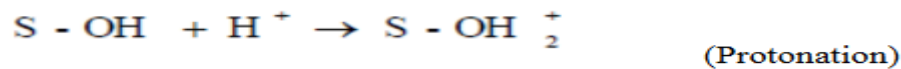
Where q_e is the amount of adsorbed fluoride onto per unit weight of the biomass in mg/g, V is the volume of solution treated in liter, C_o is the initial concentration of fluoride ion in mg/L, C_e is the residual fluoride ion concentration in mg/L and m is the mass of adsorbent in g/L. Experiments were conducted with fluoride ion solution in the absence of adsorbent and it was found that there was no fluoride adsorption by the walls of the container.

D. Effects

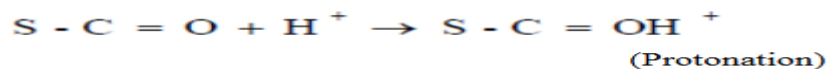
Variations in contact time, initial fluoride ion concentration, adsorbent dose, pH, particle size, temperature and agitation speed were studied. Comparative studies of both the adsorbents were carried out under same experimental conditions.

E. Sorption Mechanism

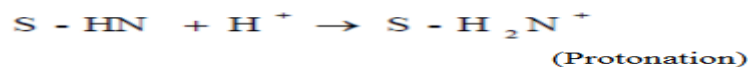
Adsorptions of the solute involve the establishment of equilibrium between the amount adsorbed on the surface and the concentration of substance in solution. The variation of extent of adsorption with concentration of solute has been correlated by the adsorption isotherms. Adsorption experiments are conducted at a constant temperature and an empirical or theoretical representation of the amount adsorbed as a function of the equilibrium gas pressure is called an adsorption isotherm. Adsorption isotherms are studied for a variety of reasons, some of which focus on the adsorbate while others are more concerned with the solid adsorbent. The surface area of a porous solid can be divided into two types, (a) the external, consisting of the geometric or outer surface of the porous particle and (b) the inner surface area made up of the surface of the walls of capillaries, crevices and cracks in the particle of the porous catalyst.



[+F-(Electrostatic attraction)]



[+F-(Electrostatic attraction)]



[+F-(Electrostatic attraction)]

Electrostatic Physisorption between Ions and Dipole (Second Strongest Among the Physical Bonds). Here, Electrostatic Attraction between Positive Poles of Partial Polar Bonds Of OH, NH And CO Groups Of Adsorbent And Anionic Fluoride Ion Took Place.

F. Thermodynamic Analysis

Thermodynamic parameters such as change in free energy (ΔG) (kJ/mole), enthalpy (ΔH) (kJ/mole) and entropy (ΔS) (JK/mole) were determined using following equations:

$$K_o = C_{\text{solid}}/C_{\text{liquid}}$$

$$\Delta G = -RT \ln K_o$$

$$\Delta G = \Delta H - T\Delta S$$

$$\ln K_o = \Delta S/R - \Delta H/RT$$

Where K_o is equilibrium constant, C_{solid} is solid phase concentration at equilibrium (mg/L), C_{liquid} is liquid phase concentration (mg/L), T is absolute temperature in Kelvin and R is gas constant. ΔG values obtained from the above equation, ΔH and ΔS values obtained from the slope and intercept of plot $\ln K_o$ against $1/T$. The negative value of ΔG indicates the adsorption is favorable and spontaneous. The low positive values of ΔH indicate Physisorption and endothermic nature of adsorption. The negative values of ΔH indicate Physisorption and exothermic nature of adsorption. The positive values of ΔS indicate the increased disorder and randomness at the solid solution interface of sorbet with the adsorbent. The adsorbed water molecules, which are displaced by adsorbate molecules, gain more transitional energy than is lost by the adsorbate molecules, thus allowing prevalence of randomness in the system. The negative values of ΔS indicate the decreased disorder and the randomness at the solid solution interface of sorbet with the adsorbent.

H. Desorption Studies

After adsorption, the adsorbate-loaded adsorbent is separated from the solution by centrifugation and the supernatant is drained out. The adsorbent is gently dished with water to remove any unabsorbed adsorbate. Regeneration of adsorbate from the adsorbate-laden adsorbent is carried out using the desorbing media-distilled water at pH 2.7 and 9 using dilute solutions of HCL. Then they are agitated for the equilibrium time of respective adsorbate. The desorbed adsorbate in the solution is separated and analyzed for the residual fluoride ions

Results and Discussion

A. Effect of pH:

The pH of the aqueous solution is a controlling factor in the adsorption process. Thus the role of hydrogen ion concentration was examined at pH values of 2, 4, 6, 8 and 10. This was adjusted by adding 0.5N HNO₃ or 0.1M NaOH with the standard solution. The pH of the water significantly affects fluoride uptake capacity. In this, the positively charged sites favor the sorption of fluoride anion due to electrostatic attraction. It also appears that the surface charge of the sorbent has a considerable influence on the fluoride ion removal. With increase in pH, the net electro negativity of the biosorbent increased due to deprotonation of different functional groups results reduction in adsorption. When the surface is positively charged, sorption is favored by electrostatic attractions between the fluoride ion and protonated sorbent surface. On the other hand, when it is charged negatively, the electrostatic repulsions involve a reduction in sorption. In acidic medium, H⁺ ions preferably get combine with active functional group sites like-OH, C=O, -HN-of surface of sorbent particles and becomes positively charged and thus ions increase in adsorption of fluoride ions due to attractive forces. An H⁺ ion on the surface of adsorbents attracts the anionic fluoride ion from the solution from the solution and preferably occupies the binding sites available in the sorbent particles. In basic medium, -OH-neutralize the functional groups of sorbents like -OH and -COOH and formation of anionic active sites on sorbents reduces the adsorption of fluoride ion due to increase in repulsive forces.

B. Effect of Adsorbent Dose

The effect of adsorbent dose on the removal of fluoride ion was studied by keeping fluoride ion concentration constant. The response of the adsorbent dose on the removal of fluoride that an increase in the adsorption occurs with the corresponding increase in the dose of the adsorbent. The factors response for the increase in the removal efficiency with the simultaneous increase in adsorbent dose to increase in the surface area, and hence more active sites available for adsorption of fluoride. The adsorbent dose was varied in the range of 1g/L to 12g/L by maintaining optimum pH, contact time and stirring rate.

C. Effect of Stirring Rate

Studies were conducted to find the effect of stirring rate on the fluoride removal efficiency. For this, the stirring rate was maintained between 20 and 75 rpm at the optimum value of pH and dose of adsorbent, with a particular contact time and initial concentration.

D. Effect of Contact Time

Studies on effect of contact time on the fluoride removal efficiency was carried by varying it from 30 to 180 minutes keeping constant range of pH, dose of adsorbent and initial concentration of fluoride of solution.. Rate of stirring was maintained to its optimum value. The progression of adsorption reaction and percentage removal of fluoride for different contact times will be shown in the figure. For further optimization of other parameters, this contact time was considered as the equilibrium time. The changes in the extent of adsorption might be due to the fact that initially all the adsorbent sites were open and the solute concentration was high. Later the fluoride uptake by the adsorbent decreased significantly due to increase in the active sites. It indicates that the possible mono layer of fluoride ions on the outer surface is formed, pores of the adsorbent are blocked and pore diffusion onto inner surface of adsorbent particles through the film due to continuous mixing maintained during the experiment is restricted.

E. Effect of Initial Concentration

The effect of initial concentration on adsorption capacity of the biosorbent was studied for optimized conditions of all other parameters by keeping pH, contact time, rate of stirring, dose of adsorbent and contact time at their optimum values respectively by varying initial concentration.

F. Effect of Particle Size

Particle size is an important factor in adsorption because adsorption is a surface phenomenon and the extent of adsorption is expected to be proportional to the surface area available for adsorption. In the present work, the effect of adsorbent particle size was investigated by using the average particle size. Experiments were conducted to evaluate the influence of adsorbent particle size for a constant weight on the removal of fluoride ions. Particle size analysis was conducted on treated adsorbent and the percentage composition of particle size was investigated.

G. Effect of Agitation Speed

Studies on the effect of agitation speed were conducted by varying speeds at optimum pH, adsorbent dose and contact time at specific temperature. The response in this effect is based on the diffusion of adsorbate towards the adsorbent surface and also better contact between the adsorbent and adsorbate is possible.

H. Effect of Temperature

It is well established that temperature is an additional factor greatly influence any adsorption process. The effect of solution temperature was investigated at 303, 313, 323 and 333K.

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