Kinetic Studies and Adsorption of Fluoride from Drinking Water using Tamarind Shell as Adsorbent

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ABSTRACT
The excessive intake of fluoride in drinking water is a serious health concern in most of the states in India and in the world. The regular consumption of drinking water containing fluoride leads to a disease called as fluorosis. The Present work of this paper explores the removal of fluoride from synthesized aqueous solution of fluoride using Tamarind fruit shell powder. The Adsorption of fluoride by Tamarind fruit shell is cost effective method and gives high efficiency than other adsorbents. In the present study, The pretreatment for moisture removal from the tamarind shell powder given also we have shown the Kinetics and comparative study to find highest fluoride removal efficiency. In the Kinetic study, the the controlling parameters for adsorption like pH, Adsorbent concentration, Contact time relation on the removal efficiency is studied. The data obtained is fitted in the Langmuir and Freundlich Adsorption Isotherms. The work shows the selective adsorbing property of tamarind shell powder for fluoride removal. The comparison of removal efficiency of fluoride by using tamarind shell powder with wheat straw is done

Keywords: Fluoride, Tamarind Fruit Shell Powder, Wheat straw, Adsorption, Langmuir Isotherm, Freundlich Isotherm.

INTRODUCTION

Water is essential for human environment and his health. Consumption of contaminated water causes adverse effect on their health. Nowadays various contaminants present in water are fluoride, nitrates, arsenic and heavy metal like calcium, zinc, lead, mercury etc. All these components are tolerable in water upto some concentration but higher concentration may leads to health problem. Fluoride in water is desirable upto 0.7-1.5ppm. World Health Organization (WHO) sets allowable consumption of fluoride in drinking water is 0.5-1.5 ppm. 0.4-1.5 ppm is useful for small children as it protects them from dental decay. But excessive consumption caused fluorosis. Dental fluorosis weaken the gums and forms yellowish layer on teeth. It is caused by higher concentration more than 1.5ppm[1]. Prolonged consumption also leads to skeletal fluorosis for above 4ppm. Skeletal fluorosis causes pain and damage bones and joints. Other effect includes kidney problem, nervous system disorder, nausea, pregnancy problem and respiratory problem [8]. The ground water and surface water contains upto or more than 30 mg/l fluoride. The recent report on fluoride includes that many states in India is affected by excess of fluoride including Maharashtra [2].

There are various techniques available for defluoridation. This technique includes reverse osmosis (RO), ion exchange, electrodialysis, nanofilteration, coagulation and precipitation, adsorption[15-18]. Reverse osmosis gives high efficiency for fluoride removal but having high operational cost and may cause clogging, scaling or fouling problems [8]. Ion exchange can be effective for low fluoride concentration but resins increase the cost and not effective against all anion. Electrodialysis gives excellent removal but required skilled labor for work and may cause polarization problem [15]. Nanofilteration is also used for de-fluoridation but it is expensive compared with other techniques. Adsorption technique is cost effective, efficient and eases in operation. It is effective for removing low fluoride, gaining popularity nowadays. Agricultural biomass wastes are use as adsorbent which is easy available, having low cost, prolong high porosity and surface area[17]. Various adsorbents such as activated wheat straw, charcoal, rice husk, biochar, nano composites, egg shell, alga biomass, tamarind shell, pipal leaves are used for fluoride removal[4][6-13]. This work explores the Tamarind shell and wheat straw as adsorbents for removal of fluoride from aqueous solution of fluoride.

MATERIALS AND METHODS

All reagents used for analysis were of AR Grade. Fluoride solution was prepared using sodium fluoride (Merck, 98% purity) in double distilled water. 0.221g anhydrous sodium fluoride dissolved in 1L double distilled water to prepare 100ppm stock fluoride solution. 5ml of stock solution was taken and volume make up to 100ml for preparation of 10ppm fluoride solution. Aim of work is to reduce fluoride concentration from 10ppm to desirable level of 0.5-1.5ppm. Analysis of fluoride concentration was done by SPADNS method using UV- VIS Double Beam spectrophotometer (Systronics, Model no. 2205, λ range 190-1100 nm, Bandwidth 1nm) at wavelength of 570 nm[21].

Synthesis of adsorbents

Tamarind shell and Wheat Straw was collected from farm area of Jalgaon. It dried in sun light for removal of moisture and grinded into fine powder. Pre-treatment was done to remove colour of wheat straw by treating it with 1% of formaldehyde in the ratio of 1:5 ratio (w/v) at 45°C for 5 hours was suggested by A.K. Yadav *et. al* [3]. Treated materials were cleaned with double distilled water to remove formaldehyde traces and filtered out. Filtrate adsorbent calcined in hot air oven for 24 h at 75°C. Activated wheat straw (WS) sieved in several particle sizes in range of 500-75 micron BSS. Tamarind shells were washed with double distilled water several times for removal of brown color. It was dried at 100°C for half hour. Same procedure given by Kumar N. et al. was followed [19]. Activated Tamarind Shell (TS) sieved from 250-75 micron BSS particle size.

Adsorption Experiment

Batch Adsorption process was studied. Known weight of adsorbent was added to 100ml of fluoride solution of known concentration (10 ppm). Fluoride solution was taken in 250ml conical flask to determine effect of various parameters such as contact time, number of doses at different pH and constant speed of rotation of 250 rpm on magnetic stirrer. pH adjusts by using 0.1 N NaOH & 0.05N HNO_3; checked on digital pH meter[14]. It was important to check influence of adsorption capacity of fluoride by increase in adsorbent dosage and particle size. Smaller particle size having large surface area provided high porosity for adsorption.

Analysis of fluoride concentration

Analysis of fluoride solution was done by SPADNS method. SPANDS reagent was prepared by dissolving 479 mg SPANDS (Merck) in 250 ml of distilled water. 66.5 mg of Zirconyl chloride octahydrate (Merck. 98% purity) dissolved in 15 ml distilled water added to 15 ml conc. HCl & mixture dilute to 250 ml for preparing Zirconyl acid reagent. Reference solution was prepared by diluting 10 ml of SPANDS solution in 100 ml distilled water used to set spectrophotometer to zero absorbance. If test solution containing residual chlorine removed by adding 2 drops of 0.1N sodium thiosulphate. For analysis on spectrophotometer each 50 ml test solution added with 5 ml of SPANDS solution followed by 5 ml of zirconyl acid reagent. Fluoride ion reacts with zirconium ion to form a stable complex ZrF_6 & this results in bleaching the reddish color of zirconium & alizarin combination. Intensity of colour decreased is directly proportional to fluoride concentration. Absorbance was measured at 570 nm on UV- VIS Double Beam spectrophotometer[5].

Fig.1. The Zirconium and Alizarin Combination after reaction

RESULT & DISCUSSION

Effect of pH

Fig 3 illustrates the effect of pH on % removal of fluoride. It indicates that the Tamarind Shell (TS) shows higher removal efficiency at acidic pH 2 and then decreasing upto pH 10. In case of wheat straw (WS) % removal was found to be decreasing at increasing pH and increases at pH 8. Negative fluoride ions may enhance adsorption in presence of positive H ions at acidic pH. Besides that negative hydroxyl ions can effect adversely to removal of fluoride. Adsorption capacity of both adsorbent decreased at basic pH.

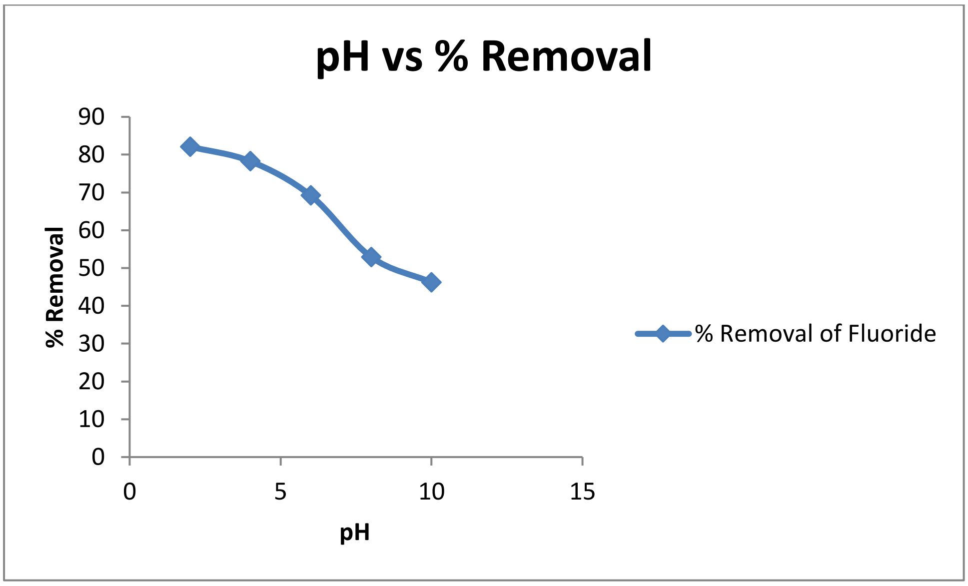

Fig. 2. The Effect of pH on Removal Efficiency

Effect of contact time & particle size

To examine effect of particle size on adsorption; Tamarind Shell and Wheat Straw sieved in different sizes. Wheat straw sieved from 500 micron to 75 micron, BSS. Batch Adsorption study carried out at 250rpm, neutral 7 pH for adsorbent dose of 1gm per 100ml of stock solution for varying time of contact from 60, 90, 120 and 150min. Tamarind shell powder sieved in different sizes from 250 to 75 micron, batch study done with same parameters use for wheat straw. As reported, 250 micron size gives highest removal efficiency. Study of contact time on defluoridation is explained in fig 3. For Tamarind Shell powder (TS), fluoride removal increases with increase in time of contact. The optimum time we obtained is 120 minutes at particle size 250 micron. In case of Wheat straw WS, fluoride removal for 500micron size increases with increase in contact time, but for smaller sizes very little increase in removal for more time of contact. For WS adsorbent optimum time of contact is select as 60min; because removal is not very effective of more time.

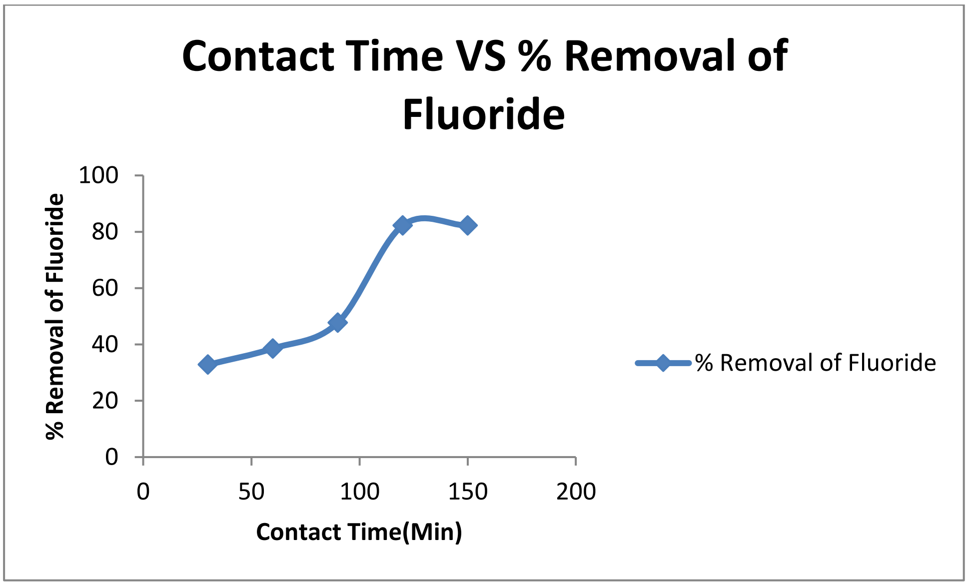

Fig.3. The Effect of Contact Time on Removal Efficiency

Effect of adsorbent dose

To study effect of adsorbent dosages; dosages varies from 0.4 to 1.2 gm at 250 rpm speed, neutral pH and contact time of 60min. For WS 250 micron adsorbent has taken and 150 micron taken for ES. Fig 5 indicates results of % removal of fluoride with variation in adsorbent dosages. Percent defluoridation increases with increase in adsorbent dose. This is because increased adsorbent dose provide more active sites for adsorption [3]. Initially removal goes on increasing progressively upto 1gm adsorbent. For higher dose increase in removal is only 1%. This may happen because fluoride accommodate on adsorbent surface it blocks active sites; this restricts further increase in removal efficiency. Hence adsorbent dose optimized to 1gm. It is worthless to increase adsorbent dose for such small increment in efficiency.

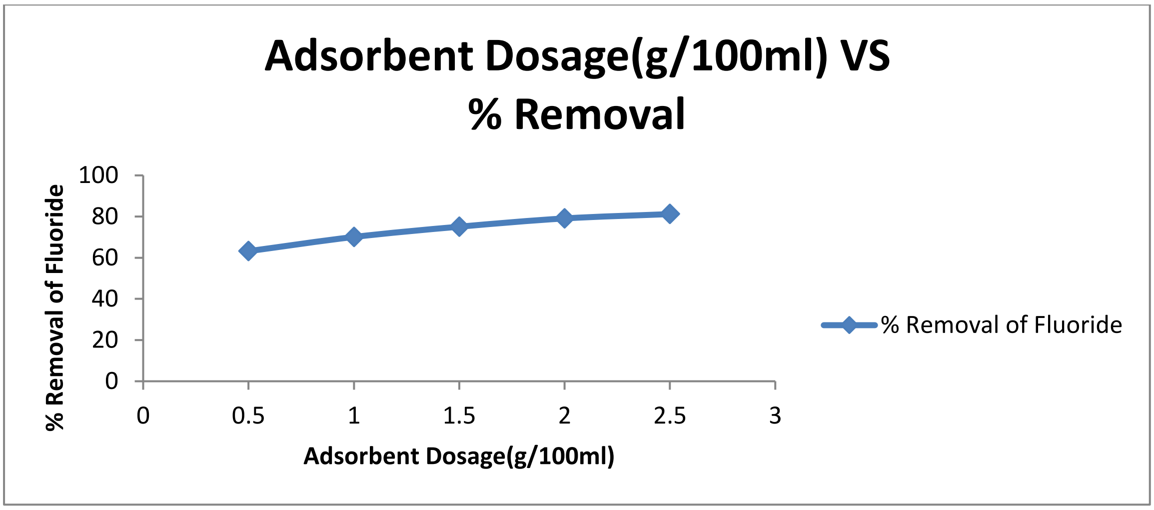

Fig.4. The Effect of Adsorbent Dosage on Removal Efficiency

Study of Adsorption Isotherm

The relation between the amounts of fluoride adsorbed at constant temperature and equilibrium concentration can be expressed by adsorption isotherm [3][11]. The equilibrium isotherm is well reported by Langmuir isotherm for both adsorbent; Tamarind Shell as well as wheatstraw powder. Langmuir isotherm equation obtained by fitting of all experimental data is given by,

$$1/q_e = 1/n + 1/nKlC_e$$

where q_e was the amount of fluoride adsorbed per mass of adsorbent used (mg/g), Ce was equilibrium solute concentration in solution, Kl was Langmuir isotherm constant (mg/g) and n was adsorption intensity [20][22]. Langmuir isotherm plot of $1/q_e$ vs $1/C_e$ shown in fig 5 for defluoridation using Tamarind Shell. The value of intercept gives K_l and slope 1/n were calculated from linearized equation obtained from experimental data. For wheat straw, K_f= 1.967 and slope 1/n is 0.925 which means adsorption intensity n is above 1. In case of Tamarind shell, Kl= 0.09424 and slope value is 9.0797 giving value of adsorption capacity n below 1. Langmuir isotherm shows acceptability from R^2 value, as for Isotherm curves R^2 values exceeding 0.95.

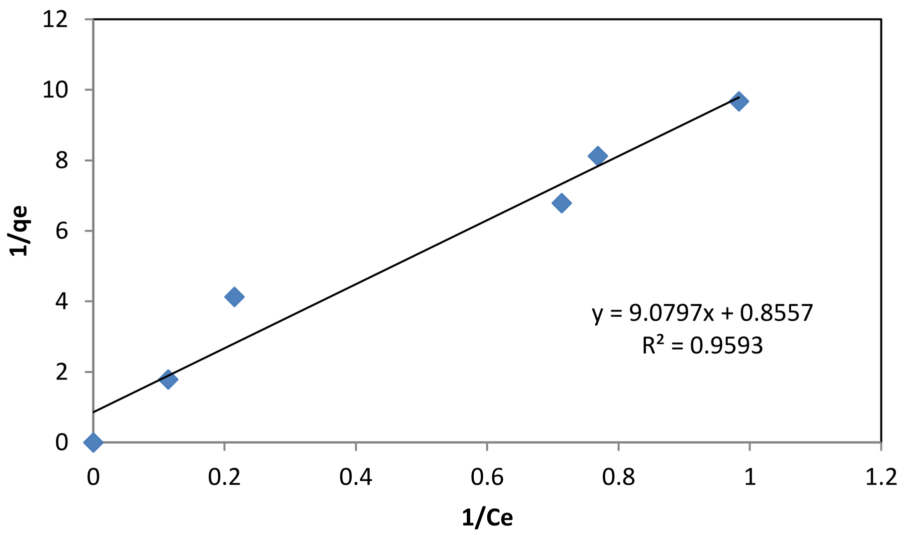

Fig.5.Langmuir isotherm for tamarind fruit shell

Table 1: Adsorption Isotherm Constants

Adsorbent	Freundlich and Langmuir Constant		
	K_l/K_f	1/n	R^2
Wheat Straw	Kf=1.967	0.925	0.9992
Tamarind Shell	Kl=0.094	9.079	0.9593

It was stated that lower the value of Langmuir isotherm constant K_l implies rate of adsorbate removal is low. Lower value of slope 1/n indicates a stronger bond between adsorbate and adsorbent and helps for better adsorption . Hence it was beneficial if value of adsorption intensity n greater than 1 but in tamarind shell case it comes as 0.11 so it is cooperative adsorption. Dada *et al* had explained if value of 1/n is below one it indicates a normal adsorption and if 1/n is above one showing cooperative adsorption [20].

CONCLUSION

In present work, adsorption studies on defluoridation of aqueous solution of fluoride of 10ppm using agricultural waste adsorbents Tamarind Shell and Wheat straw clearly shows such adsorbent can offer high adsorption capacity. These adsorbent are low cost material, easily available so its use can be economical. Avoiding use of hazardous toxic chemicals can be advantageous by accepting these materials as an adsorbent. Tamarind Shell and Wheat straw succeed to give 82.25% and 88.23% fluoride removal respectively at rotational speed 250rpm, contact time of 120min and 60min, neutral pH and room temperature. TS and WS work efficiently at adsorbent dose of 2.5g and 1g. Higher amount of adsorbent restricts adsorption by blocking the active sites of surface and hence adsorbent dose optimized to 2.5g and 1g. It was found that adsorption equilibrium can be explained using Freundlich isotherm for wheat straw as reported and Langmuir isotherm for Tamarind shell. Functional group like –OH, C=O, C-H plays important role in fluoride removal mechanism. Bed of adsorbent in adsorption column can be recommended for effective removal.

REFERNCES

1. Mohapatra M, Anand S, Mishra B, Giles D, Singh P. Review of fluoride removal from drinking water. *Journal of Environmental Management* 2009; **91**; 67–77.
2. Meenakshi, Maheshwari R. C. Fluoride in drinking water and its removal. *Journal ofmHazardous Materials* 2006; **B137**; 456–463.
3. Yadav A. K, Abbassia R, Gupta A, Dadashzadeh M. Removal of fluoride from aqueous solution and groundwater by wheat straw, sawdust and activated bagasse carbon of sugarcane. *Ecological Engineering* 2013; **52**; 211– 218.
4. Bhaumik R, Mondal N. K, Das B, Roy P, Pal K.C, Das C, Banerjee A, Datta J. K. Eggshell Powder as an Adsorbent for Removal of Fluoride from Aqueous Solution: Equilibrium, Kinetic and Thermodynamic Studies. *E-Journal of Chemistry* 2012; **9(3)**; 1457-1480.
5. Standard Methods of Examination of Water and Wastewater, APHA, 1998.
6. Daifullah A.A.M, Yakout S. M, Elreefy S. A. Adsorption of fluoride in aqueous solutions using KMnO4-modified activated carbon derived from steam pyrolysis of rice straw. *Journal of Hazardous Materials* 2007; **147**; 633–643.
7. Chakrabarty S, Sarma H. P. Defluoridation of contaminated drinking water using neem charcoal adsorbent: Kinetics and equilibrium studies. *International Journal of ChemTech Research CODEN*

(USA): IJCRGG 2012; **4(2)**; 511-516.
8. Loganathan P, Vigneswarana S, Kandasamy J, Naidu R. Review Defluoridation of drinking water using adsorption processes. *Journal of Hazardous Materials* 2013; **248– 249**; 1– 19.
9. Li Y, Wang S, Cao A, Zhao D, Zhang X, Xu C, Luan Z, Ruan D, Liang J, Wu D, Wei B. Adsorption of fluoride from water by amorphous alumina supported on carbon nanotubes. *Chemical Physics Letters* 2001; **350**; 412–416.
10. Hernández-Montoya V, Ramírez-Montoya L, Bonilla-Petriciolet A, Montes- Morán M. Optimizing the removal of fluoride from water using new carbons obtained by modification of nut shell with a calcium solution from egg shell. *Biochemical Engineering Journal* 2012; **62**; 1– 7.
11. Alagumuthu G, Rajan M. Kinetic and Equilibrium studies on fluoride removal by Zirconium (IV)-impregnated groundnut shell carbon. *Hem. Ind.* 2010; **64 (4)**; 295–304.
12. Mohan D, Sharma R, Singh V. K, Steele P, Pittman C. U. Fluoride Removal from Water using Bio-Char, a Green Waste, Low-Cost Adsorbent: Equilibrium Uptake and Sorption Dynamics Modeling. *Ind. Eng. Chem. Res.*2012; **51**; 900–914.
13. Mohan S. V, Ramanaiah S. V, Rajkumar B, Sarma P. N. Removal of fluoride from aqueous phase by biosorption onto algal biosorbent *Spirogyra* sp.*-IO2*: Sorption mechanism elucidation. *Journal of Hazardous Materials* 2007; **141**; 465–474.
14. Ezzeddine A, Bedoui A, Hannachi A, Bensalah N. Removal of fluoride from aluminum fluoride manufacturing wastewater by precipitation and adsorption processes. *Desalination and Water Treatment* 2014; 1–13.
15. Arda M, Orhan E, Arar O, Yuksel M, Kabay N. Removal of Fluoride from Geothermal Water by Electrodialysis. *Separation Science and Technology* 2009; **44**; 841–853.
16. Engeloglu Y, Kır E, Ersoz M. Removal of fluoride from aqueous solution by using red mud. *Separation and Purification Technology* 2002; **28**; 81–86.
17. Mwakabona H, Machunda R, Njau K. The influence of stereochemistry of the active compounds on fluoride adsorption efficiency of the plant biomass. *American Journal of Chemical Engineering* 2014; **2(4)**; 42-47.
18. Sing K, Lataye D. H, Wasewar K. L, Yoo C. K. Removal of fluoride from aqueous solution: status and techniques. *Desalination and Water Treatment* 2013; **51**; 3233–3247.
19. Kumar N.P., Kumar N.S., Krishnaiah A. Defluoridation of water using tamarind (tamarindus indica) fruit cover: kinetics and equilibrium studies. *J.Chil.Chem.Soc* 2012; 57; 1224-1230
20. Dada A.O, Olalekan A.P, Olatunya A.M, Dada O. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of zn^{+2} unto Phosphoric Acid Modified Rice Husk. *IOSR Journal of Applied Chemistry* 2012; 38-45.
21. Agrawal A., Shanmukha G., Manish K. Defluoridation of Drinking Water Using Tamarind (Tamarindus Indica) Fruit Shell by Dip-In-Technique *Indian Journal of Appiled Research* 2015, 5; 548-549.
22. Ramanjaneyulu V.,Jaipal M., Yasovardhan N., Sharada S. Kinetic Studies on Removal of Fluoride from Drinking Water by using Tamarind Shell and Pipal leaf Powder *International Journal of Emerging Trends in Engineering and Development* 2013; 5; 146-155.