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Determination and Removal of Fluoride in Various water samples at Khairagarh Block of Rajnandgaon district

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Abstract

Drinking water contamination by fluoride is recognized as a major public health problem in many parts of the world. Fluoride is an essential trace element for animals and humans, excessive fluoride intake may cause adverse health effects. The present survey highlights on efficiency of different materials for the removal of fluoride from water. The most important results of extensive studies on various key factors (pH, agitation time, initial fluoride concentration, temperature, particle size, surface area, presence and nature of counter ions and solvent dose) fluctuate fluoride removal capacity of materials. Hanna multi parameter instrument is used for determination of fluoride in drinking ground water. This paper investigates the potential health risks involved with both lower and higher concentrations of fluoride in drinking water, as well as posing possible measures of mitigation to eliminate such harmful threats. Also, this paper describes brief discussions on various low cost adsorbents used for the effective removal of fluoride from water.

Keywords: bioadsorbent, citron peel, vetiver root, vaivirang seeds

1. Introduction

Nature of drinking water is a major task in advanced days because of expansion in pollution of water bodies [8]. Fluoride is one such pollutant that undermines living life forms, specifically people [7] Fluoride is found in all natural waters. Drinking-water is typically the largest single contributor to daily fluoride intake. Fluoride has both beneficial and harmful effects on the human health depending upon its level. It occurs in waters from trace to high concentration. WHO (2006) [1] has considered fluoride as one of the very few chemicals that have been shown to cause significant effects in people. There is a narrow margin between the desired and harmful doses of fluoride [2]. Low concentration of fluoride in drinking water have been considered beneficial to prevent dental carries [3], but excessive exposure to fluoride can give rise to a number of adverse effects such as causing fluorosis [1,4,5]. WHO has set a limit value of 1.5 $mg \cdot L^{-1}$ for fluoride in drinking water [6]. Addition of fluoride to tooth paste and to drinking water has done much to reduce the occurrence of dental caries (cavities). Although addition of fluoride s certainly effective, too much fluoride can be harmful; therefore, it is important to have a convenient method for monitoring fluoride levels. Half of the 20th century showed that naturally occurring fluoride in water could be beneficial (caries reduction) and detrimental (fluorosis) to dental health. Work to find the fluoride concentration that offered an acceptable balance between these effects eventually led to the introduction of fluoride into drinking-water supplies as a public health measure.

Surplus of fluorides in organism can provoke teeth and skeleton fluorose. Fluorides inhibit many enzymes. Affected enzyme contains metal ion which unites with fluoride and creates metal-fluoride complex. Fluor in organism has its optimal, security-tolerant and toxic dose, which depends of person's age, weight and health. In the first year of life the optimal content of fluor is 0.045 mg/kg of body mass, tolerant 0.073 mg/kg, chronically toxic 0.150 mg/kg. Optimal dosage of fluor for adults is 0.020-0.025 mg/kg of body mass.

The sources of water pollution with fluorides are above all industrial waste waters from the production of aluminium, copper and nickel, steam- generating stations, then phosphate minerals treatment, production and usage of phosphorus fertilizers, usage of fluor – based pesticides, production of glass, cement, glues and adhesive means. Transport and form of fluorides in water depends on environment pH value, water hardness and the presence of ion changeable substances, such as alumina. In waste waters fluorides can be present in the form of weak and highly toxic hydrofluoric acid (HF) whose toxicity can be seen in its characteristic to penetrate in to tissue, because small molecules of HF quickly move through skin to tissue and damage it permanently.

The most important electro analytic method for determination of fluoride ion in water solution is usage of ion selective electrode for fluorides. Fluoride selective electrode is very sensitive. In this paper, fluoride is analyzed by the usage of fluoride selective electrode of Hanna multi parameter HI5521 & 5522 for determination of fluoride ion content in the samples of sample drinking water from water-supply system in Rajnandgaon district. A simple and widely used method uses a fluoride ion selective electrode. This electrode in combination with a suitable reference electrode forms an electrochemical cell whose electrical potential is a function of fluoride ion concentration. To minimize the effects of varying ionic strength and interference from other ions, a buffer referred to as a total ionic strength adjusting buffer (TISAB) is added to all standards and the sample(s). The electrode is calibrated using a series of known concentrations of fluoride. The response of the sample is obtained in a similar manner and the concentration is then determined from the calibration curve.

2. Material and methodology

2.1 Sampling

Various water sample from tube well, well municipal water were collected in clean plastic bottles which were pre-rinsed with distilled water. Various parameters like temperature are determined by thermometer, and pH, TDS, salinity Conductivity by Hanna Multiparameter instrument.

2.2 Chemical Required

Standard Fluoride solution for calibration, TISAB-2 (Total ionic strength adjusting buffer)

2.3 Fluoride determination by Hanna Multi parameter instrument

For the determination purpose Hanna multi parameter HI5521 and HI5522 is used to accurately measure total fluoride concentration, it is important that the pH and ionic strength of the standards and sample be adjusted to a constant value. The total ionic strength adjustment buffer (TISAB) ensures that the solution pH is between pH 5 and 8 and that the activity coefficient is constant. The TISAB solution also preferentially complexes with various metal ions, such as aluminum and iron, which tend to form complexes with fluoride ions. TISAB thus ensures that these metal ions do not interfere, permitting an accurate total fluoride measurement. Measuring all solutions with a constant pH and ionic strength reduces the margin of error between measurements. The HI5521 and HI5522 fluoride solid state ion selective electrodes can measure from 1µM (0.02 mg/L) to saturated F$^-$.

3. Removal of Fluoride by Bio-adsorbent

3.1 Bio-adsorbent used

1. **Citron peel**- It’s collected from the juice making shop of Durg, washed in tape water and dried in sun light for four days. This material is dried in the hot air oven for two days at 120 c o. Dried Material crushed in jaw crusher
2. **Dry vetiver root** - vetiver root are simply washed with tape water and dried in sun light for a week. Dried sample is again dried in hot air oven at 100^{0}C for 24 hr. This material is crushed in jaw crusher.
3. **Dry Karanj leafs**- Karanj leafs are simply washed with tape water and dried in sun light for a week. Dried sample is again dried in hot air oven at 100^{0}C for 24 hr. This material is crushed in jaw crusher.
4. **Vaivirang seeds**- were collected from Bhilai regional and dried for a week and again dried at 100^{0}C for 24 hr and finally crushed with jaw crusher.
5. **Rice Husk-** Rice husk was obtained from a local mill and was sieved through IS sieves of 150 µm and 300 µm size.

3.2 Methodology

For experiments the required concentration were prepared by dilution. The concentrations of F$^-$ in solution were determined by multi parameter employing HI5521 and HI5522. Experimental procedure Fixed bed column were prepared by carried out using a glass column of 50 cm in height and its diameter is approximately 2 cm. In the column bottom is packed with glass wool and adsorbent were packed above it. Three flow rates (1, 2 and 3 ml/min) were pumped in up flow mode using a peristaltic pump with initial ion concentrations of 50, 75 and 100 mg/L. The effluent samples were collected at regular intervals and analyzed it.

15 gm of all the above bio-adsorbents are taken and then screened by adding it with 150 ml stock solution of fluoride. For removal of fluoride we choose bio adsorbent and apply adsorption method because these methods are cheaper and ecofriendly. Some food material and its waste are used for removal of high concentration of fluoride. It is suitable when fluoride concentration is present in low concentration. For this purpose, 100 ppm of 150 ml aqueous solution of fluoride with various concentrations is taken in 500 ml Stoppard bottles. In each bottle 15 gm of adsorbents is added to the solutions. Batch process are carried out by the help- of Peristaltic Pump at room temperature, a contact time of 24 hours is maintained. The initial and final concentration of aqueous solutions of fluoride was determined by using spectrophotometer and by analyzing value we determined percentage of removal of fluoride. [23].

Table 1: Analysis of fluoride and various other associated parameters in drinking water of Different villages in Rajnandgoan district.

S.N.	Sample code	Fluoride concentration (ppm)	pH	TDS	Conductivity (µS/cm)	ORP (mV)	Temp (^{0}C)	Salinity (ppm)
1	RV-1	0.876	7.38	321.1	621	-32.8	30	120
2	RV-2	0.821	7.41	415.3	854.5	-24.4	28	200
3	RV-3	0.934	7.32	318.5	564.5	-21.1	28.5	130
4	RV-4	0.882	7.15	488.1	889.5	-11.1	28.5	190
5	RV-5	0.814	7.20	852.2	998	-16.9	29	340
6	RV-6	0.952	7.15	319.2	542	-18.9	30.5	130
7	RV-7	0.756	7.32	150	421	-32.6	28.5	60
8	RV-8	0.85	7.15	225	352.9	-15.2	33	90
9	RV-9	0.834	7.01	302	449.2	14.7	29	120
10	RV-10	0.882	7.32	271.5	423.1	-20.6	29.5	110
11	RV-11	0.769	7.16	622.2	1100	-9.4	29	240
12	RV-12	0.925	7.25	352	692	-36.5	32	140
13	RV-13	0.894	7.39	228.3	521.1	-31.5	29.5	90
14	RV-14	0.845	7.23	750	1200	-15.2	30.5	330

15	RV-15	0.76	7.28	289	684	-25.4	29.5	130
16	RV-16	0.921	7.12	701	1208	-9	29.5	280
17	RV-17	0.876	7.41	284.7	663.3	-26	28.5	120
18	RV-18	0.889	7.15	398	945.3	-19.7	29.5	190
19	RV-19	0.928	7.22	302.4	611.7	-24.4	29	120
20	RV-20	3.5	7.29	221.8	469.8	-26.2	29.5	90
21	RV-21	0.754	7.15	332	712.5	-21.5	28	150
22	RV-22	0.820	7.13	747.6	1503	-13.9	28.5	340
23	RV-23	0.719	7.21	189.1	385.2	6.3	27.5	70
24	RV-24	0.821	7.31	379.4	826.8	-59.4	32.5	160
25	RV-25	0.788	7.14	390.5	791.7	-23.4	30	160

4. Results and discussion

1. **Effect of adsorbent dosage-**In the batch study a series of 10 mL samples of water were shaken for 1 hr with bio-adsorbent at varying doses. In batch study it is very necessary to find optimum adsorbent dose of the adsorbent.
2. **Effect of pH** pH plays an important role in adsorption process on bio adsorbents. The removal efficiency of the adsorbents is concluded that, it is depending on the pH of the test sample of fluoride. The results confirm a strong dependence between the adsorption of fluoride and pH, whereby adsorption appears to increases with increasing pH, within a pH range of 1–7. Maximum adsorption was observed at a pH of 4 for citron peel in 1.5 hr
3. **Dose Optimization** Removal efficiency of fluoride is strongly dependent on concentration of adsorbent dose in test sample. Removal of fluoride increases as increasing dose of adsorbent in the
4. **Effect of Contact Time** It is observed that the exclusion of fluoride ions increases with increase in contact time to some level at optimum pH and dose. Waste water (10ml) with fixed adsorbent dose and pH was shaken for 1 hr after allowed to settle, filtered through whatmann paper no 42.
5. **Effect of Agitation Time** The effect of agitation time was found to be increased up to a certain period of time after which the rate of sorption was found to be constant.

Table 2: show comparative analysis of removal of fluoride by use of various bio-adsorbent

Adsorbent	Initial Fluoride Conc.(mg/l)	pH	% Removal	References
Sawdust raw	5	6.0	49.80	K.Y.Ashishet.al
Wheat straw raw	5	6.0	60.20	K.Y.Ashishet.al
Activated bagasse carbon	5	6.0	56.40	K.Y.Ashishet.al
Neem peepal	5	2.0	84.90	A.R.Tembalkar
Available activated Carbon	5	6.0	57.60	K.Y.Ashishet.al
Sweet lemon peel	20	4.0	59.55	Current
Groundnut shell	20	7.0	89.90	Current
Banana peel	20	6.0	94.34	Current

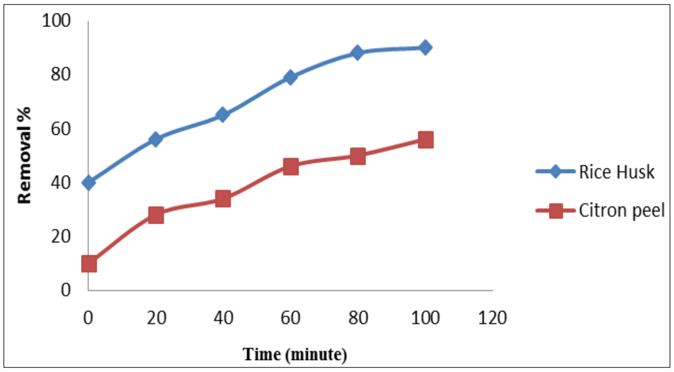

Fig 1: Adsorption capacity of citron peel and Rice Husk at different Contact time

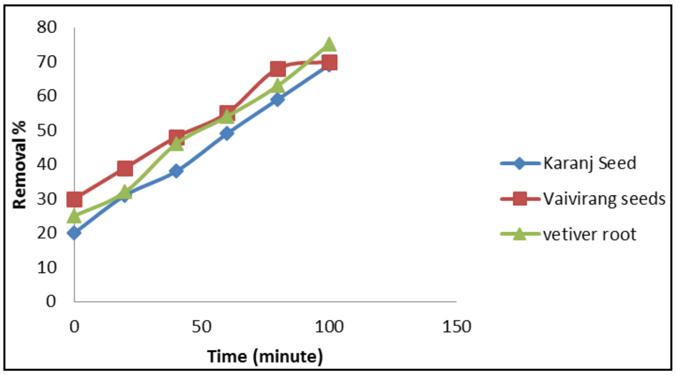

Fig 2: Adsorption capacity of Karanj seed, Vetiver root and Vaivirang seeds at different contact time.

5. Adsorption isotherms

The adsorption data were analysed with the help of the following linear forms of Freundlich and Langmuir isotherms:

Freundlich isotherm:

$$\log q_e = \log K_f + (1/n) \log C_e$$

Langmuir isotherm:

$$q_e = a\, b\, C_e / (1 + b\, C_e)$$

where log k_f is a measure of the adsorption capacity and 1/n, is an indicator of adsorption electiveness; *qe* is the amount of fluoride adsorbed per unit mass of adsorbent (mg/g), *a* and *b* are the Langmuir constants which are the measures of monolayer (maximum) adsorption capacity (mg/g) and energy of adsorption (g/ L), respectively. The values of Freundlich and Langmuir parameters were obtained respectively, from the linear correlations between the values of (i) log q_e and log C_e and (ii) (C_e/q_e) and C_e. The observed statistically significant (at 95% confidence level) linear relationships as evidenced by the r-values (close to unity) indicate the applicability of these two adsorption isotherms and the monolayer coverage on adsorbent surface [24].

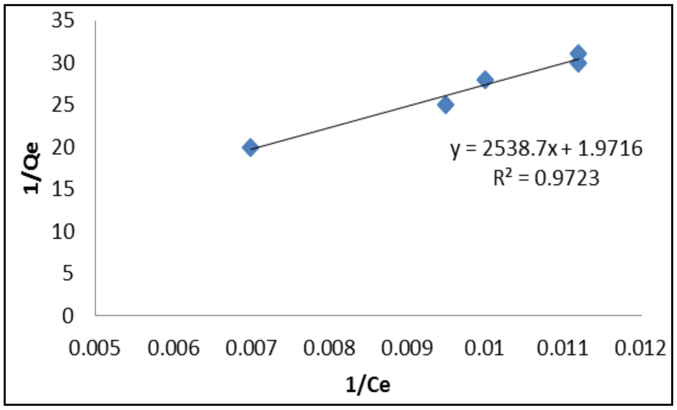

Fig 3: Langmuir isotherm for vetiver root

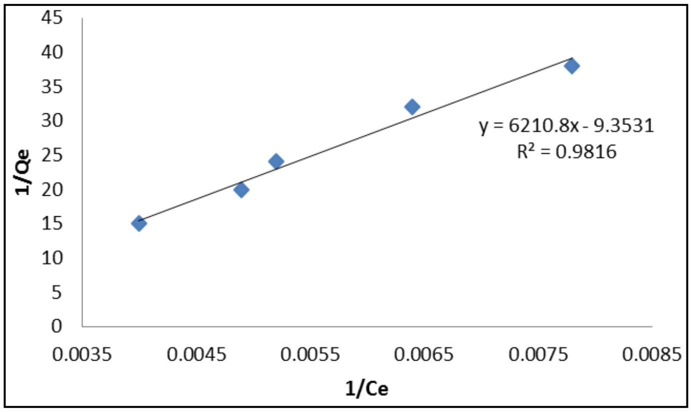

Fig 4: Langmuir isotherm for Karanj Seed

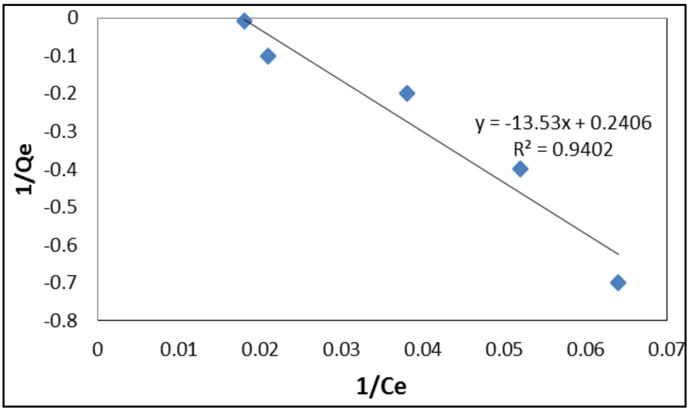

Fig 5: Freundlich isotherm for Rice husk

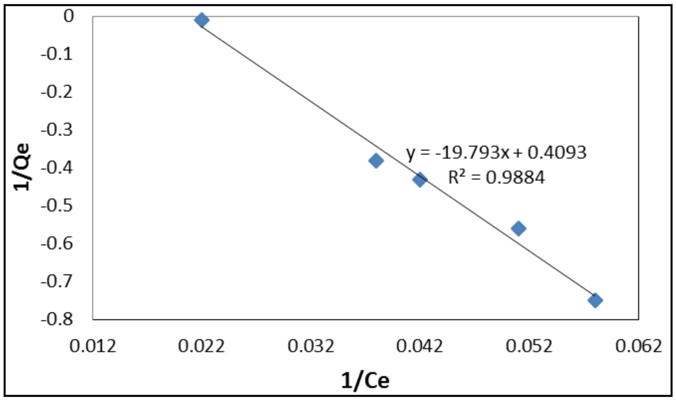

Fig 6: Freundlich isotherm for Ciron peel

6. Conclusion

This paper shows that adsorption process is one of the best methods for the removal of fluoride from water. For this process we use fruit peel like citron peel, some medicinal plants and also waste part of wheat's, this is a low cost adsorbents. Most of the bioadsorbent is temperature and pH dependent. During this review article, an assay has been made to specialize in the recent developments associated with fluoride removal by low-cost adsorbents utilizing fruit peel and medicinal plants bioadsorbents. More studies should be carried out for low-cost adsorption process to promote large scale use of nonconventional adsorbents. Our results predict that the bioadsorbents taken as filter media are highly potential in their work. For RH (rice husk) the degradation percentage is 90% for the initial fluoride concentration of 5 mg/L. The sorption process of fluoride ion on activated Vetiver root was influenced by many experimenttal conditions. The equilibrium data obtained fitted well with Langmuir and Freundlich isotherms.

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