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Preparation and Evaluation of Adsorption Effectiveness of Peanut Husk for the Removal of Fluoride Ion from Aqueous Solution

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Abstract

Fluoride is one of the largely abundant elements occurring in groundwater in Ethiopia and creates a major problem out of harm's way groundwater supply. Occurrence of fluoride above the set limit in drinking water consumed by human beings has caused multi-dimensional physical condition tribulations. The present study describes the preparation of low cost adsorbent and to evaluate its adsorption efficiency for removal of fluoride ion in artificially prepared waste water using peanut husk powder. The set adsorption study was applied to study the defluoridating effectiveness by varying contact time, adsorbent dose, adsorbate concentration, and pH. Prepared adsorbent showed better removal of fluoride by 82.3% at equilibrium contact time of 80 minutes. The adsorption information appeared to be well integral to both the Langmuir and Freundlich isotherm model. The adsorption capacity (q_m) and adsorption coefficient (b) was obtained as 22.6 mg/g and 0.14 L/mg respectively and the results are suggesting that the treated peanut husk has a reasonable defluoridating capacity and could be considered as an effective and appropriate adsorbent for a sustainable solution to mitigate the fluoride problem. This study is a step in developing a general platform suitable for producing potable water that also specifically addresses the problem of fluoride.

Keywords: Adsorption; Fluoride ion; Peanut husk; Defluoridation

Introduction

A fluoride is one of the largely plentiful elements occurring in groundwater in Ethiopia and creates a major problem out of harm's way groundwater supply. Occurrence of fluoride above the set limit in drinking water consumed by human beings has caused multi-dimensional physical condition tribulations. Most worldwide of these are dental fluorosis and undernourished fluorosis [1]. Fluoride exists moderately abundantly in the earth's crust and enters groundwater through natural procedure; especially soil at the mountains is particularly likely to be high in fluoride from the weathering and escape of bed rock with high fluoride content. Low levels of fluoride are essential for humans as it has beneficial effects on tooth structures an optimal concentration can reduce the incidence of dental caries. However, intake of more amounts of fluorides can causes dental, skeletal and a number of skeletal fluorosis. According to the WHO, the maximum acceptable concentration of fluoride ions in drinking water is 1.5 ppm so that to prevent tooth problems [2]. Concentration of fluoride below 1.5 ppm is helpful in prevention of tooth decay and such level of fluoride also assists in the development of proper bone structure in humans and animals. However, a dose of fluoride above 1.5 ppm increases the severity of tooth mottling and induces the prevalence of osteoporosis and malformed vertebrae. Fluorosis, consequential as of excessive intake of fluoride, has no healing and considered as crippling disease [2]. It is considered that probable source of high fluoride in Ethiopia waters is that during weather and circulation of water in rocks and soils, fluorine is leached out and dissolved in groundwater. Total fluoride content of groundwater varies greatly depending on the type of rocks from which they originated. Among the various minerals responsible for high concentration of fluoride, the Fluro apatite ($Ca_{10}(PO_4)_6.F_2$) is important [3]. The most important fluro apatite and Concerned with the extent of health problems due to surplus concentration of fluoride in drinking water. Several method of defluoridation of drinking water has been developed. The ion-exchange, adsorption, reverse osmosis and precipitation are the usual way of defluoridation. However, adsorption methods are most favored. Getting in touch with of the fluoride containing water with an appropriate adsorbent is important condition for effective removal of the fluoride ion. Fluoride removal way is based on the addition of chemicals and removal of precipitate of fluoride compounds as insoluble compounds. In adsorption method, diverse category of adsorbents are being used for defluoridation and studies has been shown that building materials for removal of other minerals, dyes and heavy metals among these, instant activated alumina [4] coconut shell carbon, biogases [5], chemically activated carbon [6], bone charcoal [7,8], natural zeolites, hydroxyapatite [9], burn clay [10] and crushed clay pots [11], electro dialysis [12] and other low-priced bioadsorbants like saw dust [13], second-hand tea leaves, cow dung have been found to be very much effective, inexpensive and biodegradable. The activated carbon prepared from peanut shell has been utilized for the sorption of dye such as ethylene blue and malachite green [14]. No report on the utilization of peanut husk, for adsorption of fluoride has been found in literature. Therefore, the present study intended to make use of powdered peanut husk for the adsorption of fluoride from wastewater. Finally, the Influence of operating conditions such as pH, adsorbent amount and preliminary fluoride concentrations on the adsorption process were also investigated.

Materials and Methods

Materials and apparatus

Different kinds of laboratory materials and apparatus used were: nickel crucibles, Analytical balance, spatula, pipettes, pipette fillers, hot plate, SIBATA muffle furnace (SM-200), ovens, washing bottles, 50 mL plastic beakers, magnetic stirrer, magnetic rod, 50 mL graduated plastic tubes, filter funnels, filter papers, different sizes of volumetric flasks, beakers, pH/ISE meter (Orion Model, EA 940 Expandable Ion Analyzer) equipped with mixture fluoride-selective electrode (Orion Model 96-09) glass electrode are used.

Chemicals

All solutions were prepared from analytical-reagent grade chemicals and distilled/deionized water. These includes glacial acetic acid (CH_3COOH), sodium chloride (NaCl), sodium citrate and EDTA, NaOH pellets, HCl (37% sp.gr. 1.19), buffer solutions for pH calibration, tri-sodium acetate and sodium fluoride (NaF) are use.

Preparation of peanut husk adsorbent material

Peanut husk was collected from debreberhan market, Amhara Region and washed with distilled water several times to eliminate attached dust and impurities. In addition, Soluble and colored components were removed from the husk by washing with boiling water, repeatedly until the water was almost colorless. The washed Peanut husk was dried and ground in a mechanical grinder to form a powder. The husk powder was separated in size fraction in the range of 200-300 µm. Then, 30 g/L peanut powder was soaked in 0.1 M nitric acid for 24 hr. The mixture was filtered, and the powder residue was washed with distilled water a number of times to remove any acid contents. This filtered biomass was primarily dried, at room temperature and nextily in an oven at 105°C for 6-8 hr. The dried adsorbent material was kept in air tight glass bottles to keep it from moisture.

Preparation of study solution

Prior to use, all glassware was washed off with nitric acid and rinsed thoroughly and repeatedly with distilled water before use. The preferred concentrations of operational solutions were prepared from this stock solution. A 1000 mg/L fluoride supply solution was prepared by dissolving 4 g of anhydrous sodium fluoride (99.0% NaF) in 1 L deionized water in volumetric flask. Standard and samples solutions of fluoride at a required concentration range were prepared by diluting an aliquot of the stock solution, using deionized water. Standard fluoride solutions of 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, and 6.0 mg/L were used for calibrating the instrument. The total ionic strength adjustment buffer (TISAB) solution was prepared by following a suggested procedure, except that EDTA replaced by CDTA as follows: 57 ml of glacial acetic acid, 58 g of NaCl, 7 g of sodium citrate and 2 g of EDTA were added to 500 ml deionized water, allowed to dissolve, pH adjusted to 5.3 with 6 M NaOH, and then made up to 1 L in a volumetric flask with deionized water [15].

Defluoridation technique

Batch adsorption study: All experimentation was conducted in 500 ml Erlenmeyer flask at room temperature (23 ± 2°C), to estimate fluoride removal effectiveness and ability of the adsorbent under nonstop mixing condition with magnetic stirrer. The cause of dose of the adsorbent, initial fluoride concentration, contact time and raw water pH were studied by changing any one of the parameters and keeping the other parameters constant. For each trial, a sample was occasionally taken out of the flask and filtered through a 0.2 µm filter paper (ADVATEC) for fluoride analysis. Then, residual F- concentration was measured immediately after equal volume of TISAB was added on 5 ml sample solution. All the trials were performed in triplicate and the mean values were used. The adsorption efficiency in percent (%) and the defluoridation capacity (mg F-adsorbed/g of adsorbent) at a specified contact time for the selected adsorbents were determined [16]. The precise concentrations were then used to calculate the absorption capacity (q_e) (mg/g) of the adsorbent using mass balance equation.

Effect of dose and contact time: To look into the effect of dose and contact time, experiments were conducted by varying adsorbent dose in the range of 0.5 g/L to 6.0 g/L at constant initial fluoride concentration of 10 mg/L.

The residual fluoride concentrations were measured by taking samples at different contact time (10 to180 min).

Effect of primary fluoride ion concentration: To examine the effect of starting F-ion concentration, experiments were conducted by varying fluoride concentrations ranging from 5 mg/L to 25 mg/L at constant adsorbent dose of 3 g/L.

Effect of pH: The effect of unprocessed water pH on the adsorption of fluoride onto the media was investigated by varying the initial solution pH range from 3 to 13, which were prepared by adjusting the pH to the desired level either with 0.1 M NaOH or 0.1 M HNO_3. Initial fluoride concentrations (10 mg/L), adsorbent dosages (3.0 g/L) and temperature were kept constant during the experiment. The residual Fluoride ion was determined after 1 h of contact time.

Determination of adsorption isotherm: Adsorption Isotherm experiments were carried out to check the relationship between the solid phase and the solution phase concentration of the adsorbate at stable condition under Constant temperature. Information for plotting isotherm were obtained by mixing a constant fluoride ion amount of 10 mg/L at pH of 3 with adsorbent dose of 0.5, 1.0 2, 3, 4, 5, 6, and 7 g/L. The mixture was uptight for 24 h to ensure equilibrium. A residual fluoride ion was calculated and all the values necessary to plot an isotherm were calculated from these determinations. The most commonly used equations for modeling biosorption equilibrium data are the Langmuir and Freundlich adsorption isotherms.

Langmuir isotherm: The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no trans migration of adsorbate in the plane of the surface [17]. As with the Freundlich equation, it best describes sorption at low sportive concentrations.

$$\frac{c_e}{q_e} = \left(\frac{1}{qmce} + \frac{1}{bqm}\right) \text{..........................} (1)$$

The vital characteristics of a Langmuir isotherm can be articulated in terms of dimensionless separation factor, and describe the type of isotherm defined by,

$$RL = \frac{1}{bC_O} \text{..........................} (2)$$

Where b is the Langmuir constant and Co is fluoride concentration (mg/l). The value RL indicates the type of isotherm to be either favorable (0<RL<0), unfavorable (RL>0), linear (RL=1) or irreversible when (RL=0).

Freundlich isotherm: The Freundlich isotherm is more general than the Langmuir isotherm since it does no assume ahomogeneous surface or constant sorption potential and this model has a linear expression which has been demonstrated as below [14]. It has the general form of Freundlich equation is

$$q_e = k_f Ce^{1/n} \text{..........................(3)}$$

The linearised Freundlich adsorption isotherm, which is of the form

$$\log(q_e) = \log k_f + \frac{1}{n} log Ce \text{..........................(4)}$$

Where q_e is the amount of fluoride ions adsorbed per unit weight of adsorbents (K_f (l/mg) is the constant related to the adsorption capacity of the adsorbent and 1/n is the Freundlich constant related to energy heterogeneity of the system and the size of the adsorbed molecule.

Results and Discussion

Optimum condition for fluoride ions removal

Effect of adsorbent dose and pH: Effect of dose of treated peanut husk on the removal fluoride from water was analyzed using the results obtained from the measurement of the residual fluoride concentration using initial concentration of 10 mg/L of fluoride at pH 3 and contact time of 80 min for 0.5, 1.0, 2.0, 3.0, 4.0 5.0 and 6.0 g/L of the doses of the treated Peanut husk as indicated in Table 1.

pH	3	5	6	7	8	10	12	13
Residual F^- ion Concentration	1.66	1.88	1.99	2.61	3.89	3.91	6.47	6.47
	1.68	1.86	1.98	2.62	3.88	3.93	6.47	6.48
	1.67	1.87	1.99	2.62	3.87	3.92	6.47	6.46
Mean Residual (mg/L) and Std deviation F^-	1.67 ± 0.01	1.87 ± 0.01	1.99 ± 0.01	2.62 ± 0.01	3.8 ± 0.01	3.9 ± 0.01	6.4 ± 0.01	6.47 ± 0.01
F^- Removal efficiency (%)	82.3	81.1	80.1	73.8	61.2	60.8	35.3	35.3

Table 1: Effect of pH on fluoride removal.

As shown in above Table 1, concentration of 1.67 mg/L was obtained at pH of 3 and the highest 6.47 mg/L at pH of 12.0 and 13.0. It was observed that the values were less than 2.00 mg/L for the pH between 3.0 and 6.0 and then increases progressively above 6.0 and below 3.0 pH of the solution. At contact time of 80min fluoride removal efficiency increased from 48.8% to 82.3% when dose of treated ground nut husk increased from 0.5 to 6.0 g/L. This shows that fluoride removal efficiency increases with increasing dose of sorbent. The increased in fluoride removal efficiency of the adsorbents with increasing dose might be due to the increase in surface area as result enhances active binding sites available for fluoride uptake [18,19].

Effect of contact time: Effect of contact time on the fluoride removal efficiency was studied using the mean residual Fluoride concentration results obtained from 3.0 g/L dose of the peanut husk, Fluoride concentration of 10 mg/L at pH of 3. Fluoride efficiency increased from 35.7% to 82.8% as the contact time between the fluoride and cement support increased from 20 to 180 min rapid increase in the percent of fluoride removal 82.3% was observed with in the first 80 min. More over the graph showing a horizontal curve of the initial steep rise in the curve is due existence of free adsorption sites on the surface of peanut husk. After the establishment of equilibrium, the lines in the figure become parallel to the time axis, this can be explained on the basis of reaching saturation point. The one hundredth removal of fluoride with contact time follows a flat curve which indicates the monolayer coverage [16].

Effect of initial concentration of fluoride:

Initial F^- Conc. (mg/L)	5	10	15	20	25
Mean Residual F^- (mg/L) and Std Deviation	0.54 ± 0.04	1.98 ± 0.0	6.84 ± 0.0	11.03 ± 0.0	18.11 ± 0.03
Fluoride Removal (%)	89.2	80.2	54.4	44.8	39.6

Table 2: Mean residual fluoride concentration and percentage of fluoride for the different initial concentration of fluoride.

Fluoride removal efficiency treated ground nut husk of was studied using different initial concentration of fluoride taking another parameters constant as shown in above Table 2. As the initial fluoride concentration increased from 5.0 to 25 mg/L the residual fluoride concentrations. Increased from 0.5 to 18.11 mg/L even applied at the same pH of the solution for the same length of contact time. But fluoride remove efficiency has an inverse relationship with the initial fluoride concentration. As the initial concentration of fluoride increased from 5.0 to 25.0 mg/L, there was a decreasing trend in fluoride removal efficiency from 89.2% to 39.6% when fixed dose of the peanut husk applied. At low initial fluoride concentration, the ratio of the fluoride ions to the number of available adsorption site is high and these sites are decreases with increase in fluoride concentration. As a result, the amount adsorbed per unit mass is decreases with increase in fluoride concentration.

Adsorption isotherms

In order to get additional information about the fluoride adsorption characteristics, the experimental data of equilibrium isotherm for Fluoride ions adsorption by the adsorbent were modeled using the most frequently used isotherms, such as Freundlich and Langmuir isotherms.

Freundlich isotherm: Freundlich isotherm assume unlimited sorption site which correlated better with heterogeneous surface of the adsorbent media [20]. From the experimental data the Freundlich Parameters along with correlation coefficients were obtained by plotting log (q_e) vs. log (Ce) and are shown in Figure 1. The Freundlich constants K_f and 1/n of the adsorption isotherm was 3.48 and 0.546 for nut husk respectively.

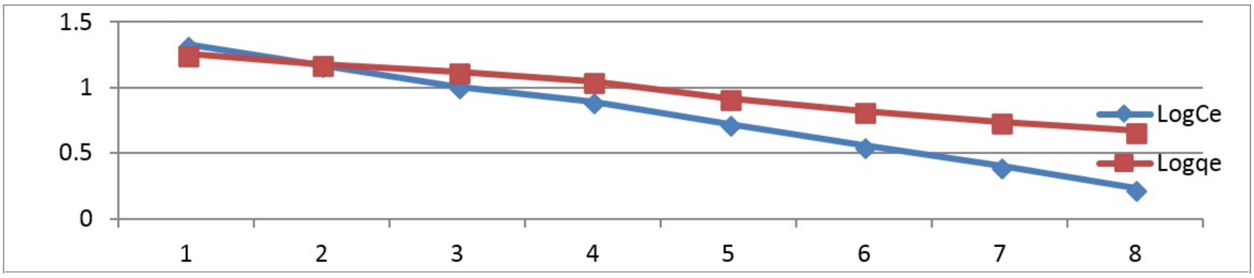

Figure 1: Freundlinch isotherm data of adsorbent treated peanut husk adsorbent.

Dose(g/L)	C_e	q_e	$LogC_e$	$Logq_e$
0.5	21.4	17.6	1.33	1.26
1	14.7	15.3	1.17	1.18
1.5	10.3	13.1	1.01	1.12
2	7.7	11.1	0.89	1.05
3	5.2	8.3	0.72	0.92
4	3.6	6.6	0.56	0.82
5	2.5	5.5	0.4	0.74
6	1.7	4.7	0.23	0.67

Table 3: Freundlinch isotherm data of adsorbent treated peanut husk adsorbent.

Langmuir Model:

Dose (g/L)	C_e(mg/L)	q_e (mg/g)	C_e/q_e (g/L)
0.5	21.4	17.2	1.25
1	14.7	15.3	0.96
1.5	10.3	13.1	0.79
2	7.7 1	1.1	0.69
3	5.2	8.3	0.62
4	3.6	6.6	0.54
5	2.7	5.5	0.45
6	1.7	4.7	0.36

Table 4: Langmuir equilibrium isotherm model of ground nut husk. C0=25mg/L, Contact time 24 h.

The Langmuir isotherm supposes monolayer adsorption onto a surface containing a finite number of adsorption sites of identical strategies of adsorption with no trans migration of adsorbate in the plane of surface [18] (Table 3). The sorption capacity, q_m, which is a measure of the highest sorption capacity corresponding to complete monolayer coverage for the pea nut husk is 22.6 mg/g. as shown in above Table 4 and the adsorption constant of Langmuir that is related to the apparent energy of sorption for fluoride ion onto nut husk is 0.14 L/mg. Necessary characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (RL) [19]. The value of RL indicates the type of the isotherm to be either favorable (0<RL<1), unfavorable (RL>1), linear (RL=1) or irreversible (RL=0). The value of RL was found to be 0.2 values for the peanut husk treated at 25°C. It indicates that the system is favorable for adsorption.

Adsorbents	q_{max} (mg/g)	References
Activated Aluminum	23.75	[16]
Rice husk	0.82	[21]
Banana peel	1.34	[22]
Bone chair	5.9	[23]
Sweet Leamon peel	0.744	[24]
Peanut husk treated	22.6	current work

Table 5: Comparison of adsorption capacity of for fluoride removal with another adsorbent.

The higher adsorption capacity for treated peanut is due to mainly that the chemical modified might have improved adsorption capacity of adsorbent in modified form, which probable because of formation of higher number of active binding sites after modification, better ion exchange properties and appearance of new function group that favors fluoride uptake as shown in Table 5.

Conclusion and Recommendations

Conclusion

This work deals with removal of fluoride ions from aqueous solution using treated peanut husk as adsorbent optimum adsorption conditions were determined as function of initial concentration of fluoride ion, pH, contact time, and adsorbent dose. Along with increase adsorbent dose from 0.5 g/l to 6 g/l the percentage removal of fluoride ion was increased due to increase in active site for adsorption with increasing dose. The results which also indicates for fluoride ion adsorption by treated peanut husk was achieved with contact time of 80min and the percentage removal of fluoride ion which decease with increasing in fluoride ion concentration, the adsorption of fluoride ion by treated peanut husk was also pH dependent in the maximum adsorption of fluoride ion. Both Langmuir and freundlich isotherms are adsorption data for wide ranges of adsorbent doses. The experimental isotherm data were analyzed using the Langmuir and freundlich equations and calculated equilibrium data were well fitted to both models, the equilibrium data of adsorption of fluoride were simply described by freundlich isotherm model. Based on this study, it is concluded that the biosorbent prepared from peanut husk has shown promising results for the removal of fluoride. The percentage of fluoride removal was found to be function of adsorbent dose and contact time at a given initial solute concentration. It increased with time and adsorbent dose. But declines with higher initial solute concentration with time and adsorbent dose.

Recommendation

The following recommendations are made for in order to make use of peanut husk adsorbent to remove fluoride from different wastewater.

- Further Studies should be carried out on the description of the surface area, pore size for adsorption by means of spectroscopic analysis involving Fourier Transform infrared.
- The studies reported here are conducted using synthetic fluoride ion solution further study should be carried out on real fluoride contaminated water samples.
- Studies effect of co-ions on fluoride removal efficiency.

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