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Use of Al_2O_3-Areca nut activated carbon composite as an adsorbent for defluoridation of water

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Abstract

The concentration of fluoride in drinking water above 1.5 mg/L can cause adverse health effects. The present study deals with defluoridation (fluoride removal) of water using Al_2O_3-Areca nut activated carbon composite as an adsorbent. Activated carbon (AC) was prepared from Areca nut using H_3PO_4 as an activating agent at 400°C under N_2 atmosphere. The Al_2O_3-Areca nut AC composite (composite adsorbent) was prepared with the resultant AC and Al_2O_3. The effects of pH, adsorbent dosage and contact time on the percentage of fluoride removal were studied by batch mode. The percentage of fluoride removal by the composite adsorbent (~80) was much higher as compared to the plain AC (~40%). The highest percentage of fluoride removal was found at pH 2, adsorbent dose of 20gm/L and contact time of 180min. The adsorption data were fitted more to Langmuir isotherm than Freundlich isotherm. It describes a monolayer adsorption of the fluoride on a uniform composite adsorbent surface. The maximum adsorption capacity of the composite adsorbent for fluoride removal was 7.6 mg/gm. As such, it can be concluded that, Al_2O_3-Areca nut AC composite shows best performance for defluoridation and can be applied in water treatment.

Keywords: Al_2O_3-Areca nut carbon composite, adsorbent, fluoride, water.

Introduction

Low concentrations (~ 1.5mg/L) of fluoride in drinking water are necessary for human body to strengthen teeth and bones. However, high concentrations can cause dental and skeletal fluorosis. The dental fluorosis is characterized by discoloration or pitting of teeth and the skeletal fluorosis is marked by osteosclerosis, calcification of tendons and ligaments and deformities in bones. WHO guideline value of fluoride in drinking water is 1.5mg/L[1].

Groundwater constitutes the primary source of drinking water in many regions of the world. The occurrence of high concentrations of fluoride in ground water has been recorded in about 27 countries[2]. In India, millions of people are suffering from fluorosis because of drinking water with high concentration of fluoride[3]. The presence of fluoride concentration above the permissible limit in ground water has been reported in the Terai region (low land) of Nepal. However, the data are unsystematic and incomplete[4]. Since, fluoride contamination in groundwater being a common problem in several parts of the world, defluoridation of water before consumption is needed so as to prevent from health related problems.

Precipitation-coagulation[5] and adsorption[6-9] are the most commonly used defluoridation (fluoride removal) methods in developing countries. One of the common precipitation methods used for defluoridation water in India, is Nalgonda technique. In this technique, fluoride is precipitated by adding aluminium sulphate and lime. This technique is simple and reasonable. However, the concentration of fluoride in water after defluoridation depends on the solubility of precipitated fluoride and precipitating agents. It often creates difficulties in removing excess of chemicals. Therefore, adsorption is the appropriate method for defluoridation of water. This is due to reasons such as flexible operation, simple design and low maintenance cost. In this method, different adsorbents are used to remove fluoride from water. The commonly used adsorbents are activated alumina[10], activated carbon[8], bone char[11], bauxite[12], calcite[13] etc. Among these, activated carbon (AC) and activated alumina are frequently used. Activated alumina is an effective adsorbent for defluoridation of drinking water because aluminium has a strong affinity for fluoride. It can form an inner-sphere complex with fluoride ions. In the same way, activated carbon (AC) is also an adsorbent for defluoridation because of its high surface area and high microporosity.

AC is a preferred adsorbent for water treatment however it is expensive due the use of relatively high cost starting material like coal. So, small industrial units and developing countries cannot afford using AC at large scale. As such, efforts have been made in developing alternative low cost AC for defluoridation of water. In the last few years, there is increasing research interest towards the use of agricultural waste or industrial waste for the preparation of the AC. These materials are renewable, widely available and inexpensive. The utilization of these materials for preparation of AC is a promising

alternative because it reduces the cost of waste disposal and solves environmental problems. Accordingly, various agricultural wastes such as Lapsi seed stone[14], Groundnut shell[15], Peepal leaf powder[6], Areca nut[16] etc have been applied for preparation of AC.

AC can remove organic compounds easily but it is not effective at removing inorganic ion like fluoride. Therefore, in most studies, AC are modified by oxidation and impregnation with multivalent metal ions with Al^{3+}, Fe^{3+} and Zr^{4+} to enhance defluoridation capacity[15,17,18]. Recently, the use of a composite adsorbent or a combination of a single precursor into a composite matrix has been accepted as an advanced method in the preparation of the adsorbent. Because of the presence of the chemical functional groups on composite surface, it can adsorb various organic and inorganic compounds. Some of the composite adsorbent for defluoridation of water includes carbon/pottery composite[19], alumina supported carbon composite[20], Fe_2O_3/Areca nut AC composite[16].

Areca nut is the edible fruit of the Areca palm (Areca catechu) and is also known as betel nut. It is commonly found in India and Nepal and has a rich history of use throughout Asia. Areca husk carbon[21], Areca nut hearth wood charcoal[22] and betel nut coir charcoal[23] had been reported for the preparation of AC for various applications. However, no report has been found on the AC prepared from Areca nut itself for the defluoridation of water. The aim of present work was to investigate the feasibility of using Al_2O_3-Areca nut AC composite as an adsorbent for defluoridation (fluoride removal) of water.

Materials and methods

Materials: Areca nuts were purchased from local markets, Kalimati, Kathmandu, Nepal. All the chemical reagents used in this study were of analytical grade (AR). A commercial activated alumina was procured from Thermo Fisher Scientific India Pvt. Ltd. The nitrogen gas of ultra high pure (UHP) was used to create an inert atmosphere during carbonization. A stock fluoride solution was prepared by dissolving 0.221gm of anhydrous sodium fluoride (NaF) in distilled water and diluted to 1000ml. The stock solution was diluted to get the standard solutions of required concentration. The concentration of fluoride ion in the solutions is measured on Orion ionplus Fluoride Electrode Orion 94-09, 96-09, Thermo Electron Corporation, USA. pH of the solution was determined by using digital pH meter DICA, India.

Preparation of activated carbon: Areca nuts were washed several times with distilled water and dried in air oven at 110°C for 24 hrs. The nuts were then crushed and grinded with mortar and electric grinder. The nut powder was sieved to get the particles of size 312µm. 20gm of the nut powder were mixed with H_3PO_4 in the ratio of 1:1 by weight and stirred with magnetic stirrer at 70°C until party dried. Then, the resulting mixture was dried in an air oven at 100°C for 24hrs. The material was then transferred into quartz tube. The tube was placed inside an electric horizontal tube furnace and heated at 400°C under the continuous flow of N_2 gas at a rate 75ml/min for 3hrs. The prepared AC was washed with 0.1N NaOH, subsequently washed with warm water until it became neutral. The AC sample was dried in an air oven at 110°C for 24hrs, sieved to get the particle of a size 106µm. The resultant AC was used for the preparation of the adsorbent.

Preparation of adsorbent: 36.8gm of aluminum nitrate ($Al(NO_3)_3.9H_2O$) gm was dissolved in 400 ml. distilled water and 5gm AC were added. Then 5M NaOH was added dropwise till the precipitation of $Al(OH)_3$ was completed. The product was dried in oven at 110°C for 12hrs, calcined in the tube furnace at 300°C for an hour. The prepared Al_2O_3-Areca nut AC composite (composite adsorbent) was washed with distilled water till it became neutral and dried at 100°C for 24hrs. After that, the composite adsorbent was sieved to obtain a particle size of 212µm and used for defluoridation of water.

Adsorption experiments: Adsorption experiments were performed by batch method. A definite amount of Al_2O_3-Areca nut AC composite (composite adsorbent) was suspended in 50 ml of fluoride solution in 100 ml plastic conical flasks. The suspension was agitated on VDRL shaker at 225rpm at room temperature. After equilibrium, the suspension was filtered and fluoride concentration in the filtrate was measured. The concentration of fluoride ion in the sample was determined by using fluoride ion selective electrode (ISE) according to the procedure using calibration curve[24].

Adsorption experiments were carried to determine the effect of various parameters such as pH, contact time, adsorbent dose and adsorption isotherm. The effect of adsorbent dose on percentage of fluoride removal by composite adsorbent was studied by varying the adsorbent dose from 2.5gm/L to 30gm/L. During study, other parameters kept constant such as the initial fluoride concentration 19mg/L, contact time 3hrs and pH 6.5. Effect of pH on the percentage of fluoride removal by the composite adsorbent was studied in the pH range of 2 to 10 keeping other parameters constant such as adsorbent dose 5 gm/L, initial fluoride concentration 19mg/L and contact time 3 hrs. pH of the solution was adjusted by adding 0.01N HCl and 0.1N NaOH. The effect of contact time on the percentage of fluoride removal by composite adsorbent was studied at different contact time from 5min to 300min by keeping other parameters constant such as the adsorbent dose 5 gm/L, initial fluoride concentration 19 mg/L and pH 6.5. All the experiments were carried out at room temperature. The percentage removal of fluoride ions was calculated by using the following equation-1.

$$\text{Removal } (\%) = \frac{(C_o - C_e) \times 100}{C_o} \quad (1)$$

Where: C_o = initial concentration of fluoride ions (mg/L); C_e = equilibrium concentration of fluoride ions (mg/L). Adsorption isotherms study was conducted with fluoride solutions of different initial concentrations from 5gm/L to 100gm/L. The

other parameters were kept constant such as adsorbent dose 5 gm/L, contact time 3hrs and pH 6.5 during the experiment. The milligram of fluoride ions per gram of adsorbent, q_e(mg/gm) adsorbed was calculated by using the following equation.

$$q_e \text{ (mg/gm)} = \frac{(C_o - C_e) \times V}{M} \quad (2)$$

Where: V = volume of fluoride solution (L) and M = mass of the adsorbent (gm).

Results and discussion

Adsorption studies: Comparison on percentage of fluoride removal of Al_2O_3 (Alumina), Areca nut AC and composite adsorbent were carried out. The percentage of fluoride removal by Al_2O_3, Areca nut AC and composite adsorbent is presented in Figure-1.

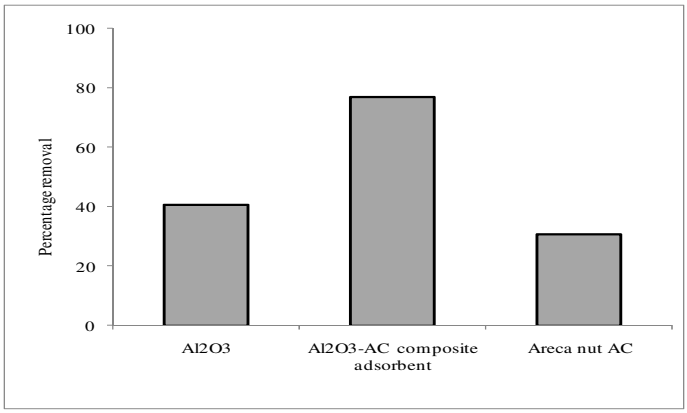

Figure-1: Percentage of fluoride removal by Al_2O_3, Areca nut AC and Al_2O_3-Areca nut AC composite.

The percentage of fluoride removal by both Al_2O_3 and Areca nut AC is found to be less than 40%, but the adsorption capacity increased to ~80% by using the composite adsorbent. It clearly indicates the synergistic effect of AC for adsorption of fluoride. Thus, the composite of Al_2O_3 and AC is much better adsorbent than individual components for defluoridation of water.

Fluoride adsorption onto the composite adsorbent is probably due to the ligand exchange reaction between hydroxyl ion on the co-ordination sphere of the composite adsorbent surface and fluoride ions in aqueous solution. It means fluoride is adsorbed onto surface of the composite adsorbent with the formation of surface complexes. The fluoride ion exchange reaction is shown as below. The metallic ion makes the connection between adsorbed fluoride and surface of the composite adsorbent.

$$\sim Al\text{-}OH_2^+ + F^- \leftrightarrow \sim Al\text{-}F + H_2O$$
$$\sim Al\text{-}OH + F^- \leftrightarrow \sim Al\text{-}F + OH^-$$

Where: ~ represents the surface of the composite adsorbent.

Effect of pH: pH of the solution is an important parameter in fluoride adsorption, since it affects the surface charge of the adsorbent. Effect of pH on the percentage of fluoride removal by the composite adsorbent is shown in Figure-2.

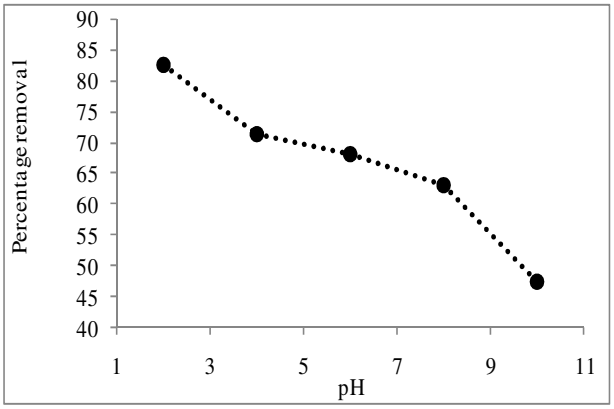

Figure-2: Effect of pH on the percentage removal.

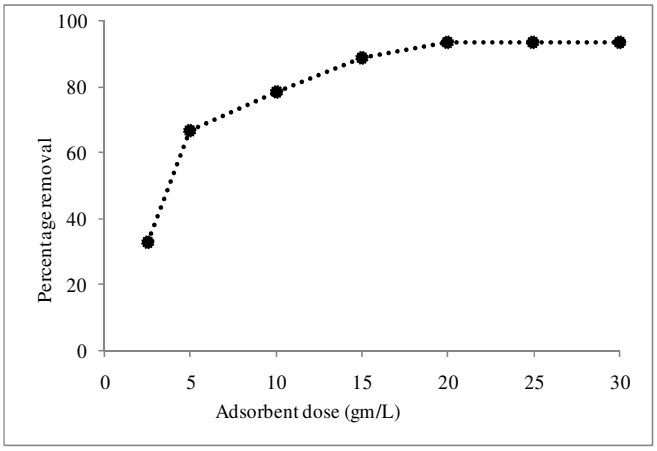

Figure-3: Effect of adsorbent dose on the percentage removal.

As shown in the Figure-2, the percentage removal decreases considerably with increasing pH from 2 to 10. Maximum percentage removal was found at pH 2. At low pH, the composite adsorbent surface is highly protonated, therefore the negatively charged fluoride ions were attracted to the positively charged surface. It enhances fluoride adsorption. At high pH, the composite adsorbent surface becomes negatively charged such that, the attraction between the composite adsorbent surface and fluoride ions is reduced. It leads to decrease in the adsorption of fluoride ions. The same trend in the adsorption of fluoride at different pH was observed in commercially available activated charcoal[8].

Effect of Adsorbent Dose: The effect of adsorbent dose on the percentage removal is shown in Figure-3. The percentage removal of fluoride increases rapidly with an increase in adsorbent dose, but beyond a dose of 20gm/L, further addition of the composite adsorbent did not change percentage removal. At the dose of 20gm/L, the system attained equilibrium. It

indicates the possibility of monolayer formation of fluoride ion at the adsorbent surface. Initially, there is the availability of a large number of adsorption sites due to increase in the adsorbent dose so fluoride adsorption is increased. However, at high dose of the composite adsorbent, there is the tendency of overlapping of the adsorption sites due to the overcrowding of adsorbent particles. As a result, further adsorption is not possible. Hence, an optimum dosage of 20gm/L is required for defluoridation of water by composite adsorbent.

Effect of contact time: The effect of contact time on the percentage removal of fluoride is shown in Figure-4. Percentage of fluoride removal sharply increased with a contact time up to 180 min and then reached equilibrium. At the beginning, a large number of vacant sites are available on the surface of the composite adsorbent so fluoride adsorption is increased. With increasing the contact time, adsorption sites are gradually saturated and further adsorption is not possible. The achievement of equilibrium indicates the possible monolayer formation of fluoride at the outer surface and its diffusion into the inner surface of the composite adsorbent. Hence, the optimum contact time for defluoridation by the composite adsorbent was 180min. Similar results were observed by Alagumutu and Rajan for adsorption of fluoride onto Zr impregnated groundnut shell AC[15].

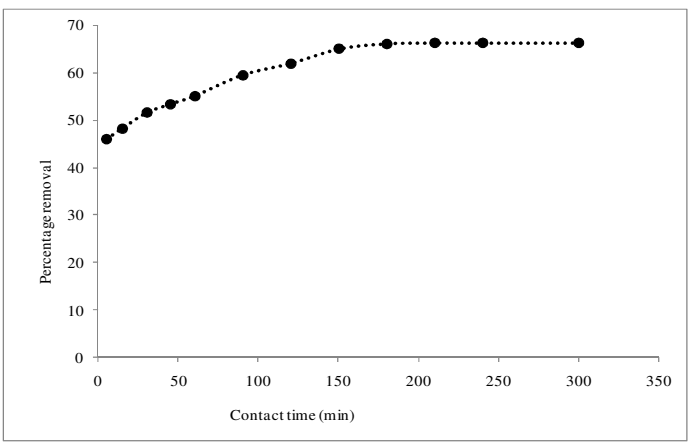

Figure-4: Effect of contact time on the percentage removal.

Adsorption Isotherms: Adsorption isotherm is the relationship between the amount of adsorbate adsorbed per unit mass of adsorbent (q_e) and the concentration of the adsorbate in the remaining solution (C_e) at constant temperature. It explains how the amount of adsorbate distributes between the liquid phase and solid phase after equilibrium is reached. Freundlich and Langmuir isotherms are most frequently used isotherms for the application of activated carbon in water treatment.

Langmuir isotherm explains saturated monolayer adsorption of solutes on the homogenous surface of the adsorbent. Freundlich isotherm explains adsorption of solutes on a heterogeneous surface of the adsorbent. Equation-3 represents the linear form of the Langmuir equation.

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (3)$$

Where: C_e is the equilibrium concentration of adsorbate (mg/L); q_e is the amount adsorbed at equilibrium (mg/gm); q_m is the maximum adsorption capacity (mg/gm) and b is the Langmuir constant (L/mg). The Langmuir constant (b) and maximum adsorption capacity (q_m) were calculated from the slope and intercept of the plot. Similarly, the equation-4 represents the linear form of Freundlich equation.

$$\log q_e = \log K + \frac{1}{n}\log C_e \quad (4)$$

Where: K and 1/n are empirical constants. They indicate the adsorption capacity and adsorption intensity respectively. The values of adsorption intensity (n) and Freundlich constant (K) were determined from the slope and intercept of the plot. The applicability of the isotherm was compared by judging the correlation coefficient (R^2) value. A Langmuir isotherm (Figure-5) was plotted with C_e/q_e vs C_e.

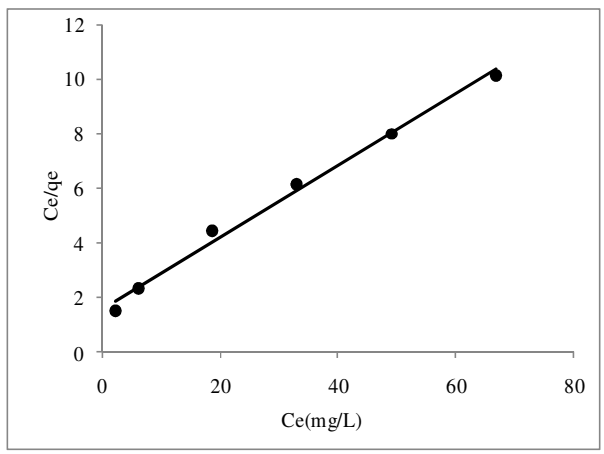

Figure-5: Plot of C_e/q_e vs C_e for Langmuir isotherm.

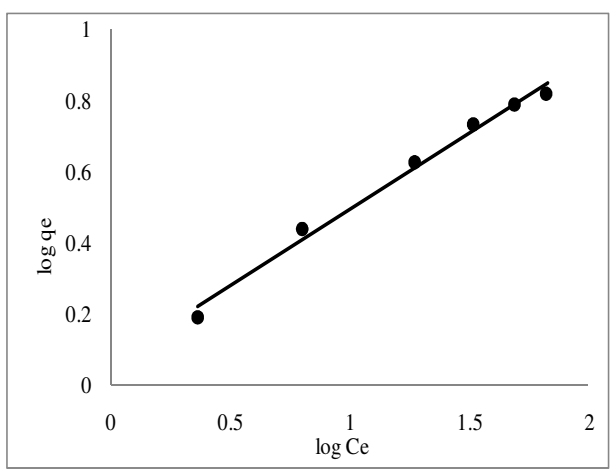

Figure-6: Plot of log q_e vs C_e for Freundlich isotherm.

Freundlich isotherm (Figure-6) was plotted with log q_e vs. log C_e. As the correlation coefficients (R^2) values are close to unity in both cases, it indicates the applicability of the both isotherms. The values of correlation coefficient, R^2 for Langmuir isotherm is marginally better as compared to the Freundlich isotherm. It suggested that the adsorption of fluoride onto composite adsorbent follows more to Langmuir isotherm. It means fluoride removal is due to the continuous monolayer coverage of fluoride on the homsogenous surface of the composite adsorbent. Values of Langmuir and Freundlich parameters for adsorption of fluoride onto composite adsorbent are shown in the Table-1.

Table-1: Langmuir and Freundlich parameters for adsorption of fluoride onto Al_2O_3-Areca nut AC composite.

Langmuir parameters		R^2	Freundlich parameters		R^2
q_m (mg/gm)	b (L/mg)		K (mg/gm) L/mg)$^{1/n}$	n	
7.62	0.084	0.993	1.150	2.3	0.988

The values of Langmuir and Freundlich parameters are also compared to that of other adsorbents. The comparison of the maximum adsorption capacity (q_m) for fluoride onto various adsorbents is shown in Table-2.

Table-2: Comparison of the maximum adsorption capacity (q_m) for fluoride onto various adsorbents.

Fluoride adsorbents	Langmuir adsorption capacity q_m (mg/gm)	Reference No.
Al, Fe dispersed charcoal	13.64	24
Fe_2O_3/Areca nut AC composite	4.8	16
Zr imp. groundnut shell carbon	2.3	15
Al_2O_3-Areca nut AC composite	7.62	Present study

The adsorption capacity of composite adsorbent was higher than that of Fe_2O_3/Activated carbon composite and Zr-impregnated groundnut shell carbon and lower than Al, Fe dispersed charcoal. Hence, composite adsorbent was found to be better adsorbent for fluoride in comparison to Fe_2O_3/Activated carbon composite and Zr-impregnated groundnut shell carbon.

Conclusion

In this study, the Al_2O_3-Areca nut AC composite has been utilized for the defluoridation of water. Activated carbon was prepared by H_3PO_4 activation of Areca nut and the resultant AC was composited with Al_2O_3. The fluoride removal capacity of the composite was much higher than the plain AC. The adsorption capacity of the composite adsorbent is dependent on the pH of the solution. The adsorption data were fitted well to the Langmuir isotherm. The maximum monolayer adsorption capacity of composite adsorbent was 7.62mg/gm. Optimum conditions of defluoridation of water by composite adsorbent are – i. pH-2, ii. adsorbent dose- 20gm/L and iii. contact time-180 min. The maximum adsorption capacity of the composite adsorbent is higher compared to Fe_2O_3/Areca nut AC composite and Zr-impregnated groundnut shell carbon. Hence, this study shows that, the Al_2O_3-Areca nut AC composite can be good adsorbent for the defluoridation of contaminated water.

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