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Removal of Fluoride Ions by Adsorption onto Fe_2O_3/Areca Nut Activated Carbon Composite

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Abstract: The possibility of Fe_2O_3/Areca nut activated carbon composite as an adsorbent for removal of fluoride from water is presented. Activated carbon (AC) was prepared from Areca nut by chemical activation with phosphoric acid at 400°C under nitrogen atmosphere. The resultant AC was characterized by adsorption of methylene blue and iodine. As indicated by iodine and methylene blue adsorption, the AC was highly micro and meso porous in nature. The adsorbent was prepared by compositing the AC with ferric oxide. Batch adsorption experiments were conducted to describe the effect of pH, contact time and adsorbent dose on fluoride removal from water. Percentage removal of fluoride by the adsorbent was ~75 % at contact time of 180 minutes. The maximum adsorption of fluoride was observed at pH 2 with adsorbent dose of 20 gm/L. The adsorption equilibrium data was analyzed by Langmuir and Freundlich adsorption isotherms. The adsorption data was fitted Langmuir better than Freundlich isotherm. The adsorption capacity of the Fe_2O_3/Areca nut activated carbon composite was found to be 4.8 mg/gm. The composite adsorbent prepared from Areca nut AC could be an efficient adsorbent for removal of fluoride from water.

Keywords: Fe_2O_3/Areca nut carbon composite, Adsorption, Fluoride

1. Introduction

Fluoride is an important micro-nutrient for the production and maintenance of healthy bones and teeth. However it has long been known that, excessive fluoride intake cause adverse health effect and the major source of fluoride intake is through drinking water. Continuing intake of higher concentrations can cause dental fluorosis and in extreme cases even skeletal fluorosis [13]. According to WHO, the maximum permissible limit of fluoride in drinking water is 1.5 mg/L [22].

Ground water is one of the important source of drinking water in many regions of the world. High fluoride concentrations in groundwater, up to more than 30 mg/L, occur notably in the United States of America, Africa and Asia [15]. High concentration of fluoride is observed in the various region of India. It is reported that high concentration of fluoride is found in the territories of Nepal and fluorosis cases have also been observed [5] but no in depth studies have yet been made so far. If fluoride concentration of water used for drinking purpose is higher than permissible limit, it should be lower down to permissible limit. Precipitation and adsorption are common method applied for fluoride in developing countries. Precipitation method is applied for fluoride removal of water containing high concentration of fluoride. Adsorption has proved to be the effective fluoride removal method, particularly in treating low concentrations of water. This technique has been quite popular in recent years, due to their simplicity as well as the availability of wide range of adsorbents. Different adsorbents have been used for the removal of fluoride such as activated carbon [4], activated alumina, [10] bone charcoal [1], silica gel [16] etc.

Commercial activated carbon is one of the commonly used adsorbent for fluoride removal. However, its widespread use is restricted due to its relatively high cost led to research on the alternative non-conventional and low-cost adsorbents. Agricultural wastes are considered to be potential precursors due to their availability at a low price. Agricultural waste materials such as coconut shell [18] groundnut shell [2] tamarindus indica fruit shells [19] rice straw [9] etc have been used to prepare AC for fluoride removal. In general, the carbon adsorption is not nearly effective at removing inorganic ion like fluoride as it is at removing organic compounds. For this reason, modification techniques were used to enhance fluoride removal capacity of AC. Recently, considerable work has been conducted in developing new adsorbents loaded with metal ions for the purpose of adsorptive removal of fluoride. Fluoride ion has strong affinity toward multivalent metal ions like Al^{3+}, Fe^{3+}, Zr^{4+} due of the high electronegativity and small ionic size. A composite matrix has been recognized as the new and advanced technology in the preparation of adsorbent from carbon. Carbon composites such as Carbon/Pottery Composite [12], alumina supported carbon composite [14] are studied as adsorptive removal of fluoride.

Areca nut is the seed of the oriental palm Areca catechu Linnaeus. It is commonly known as betel nut because it is mostly chewed wrapped in betel leaves. Areca nut has been used in traditional, cultural, and ritual practices in some regions of south and south-east Asia. The literature survey reveals that Areca husk carbon [6] Areca nut heartwood [11] and Areca nut coir (7) had been used for the preparation of AC for various application. There is no report available in the literature on fluoride removal with AC prepared from Areca nut. Hence this study deals with the preparation of the Fe_2O_3/Areca nut activated carbon composite for adsorption of fluoride from water.

2. Experimental

2.1 Materials

Areca nuts were purchased from food Industry, Kathmandu, Nepal. The chemicals used for the analysis were all analytical grade purchased from Qualigen, India. Ultra high pure (UHP) nitrogen was used for inert atmosphere during carbonization. Fluoride stock solution was prepared by dissolving 221 mg of anhydrous sodium fluoride in 1000 mL distilled water. Standard solutions of fluoride were prepared by subsequent dilution of the fluoride stock solution. Solutions of 0.1M NaOH and 0.1 HCl were used for pH adjustment. Fluoride ions in aqueous solution were determined by using Orion ionplus Fluoride Electrode Orion 94-09, 96-09, Thermo Electron Corporation, USA.

2.2 Characterization

Thermo gravimetric analysis (TGA) of Areca nut was carried out by a thermogravimetric analyzer (EXSTAR 6300 SEIKO TG/DTA, Korea). Characterization of activated carbon was performed by adsorption of iodine and methylene blue. The iodine number of AC was determined according to ASTM D4607-94 method [3]. Methylene blue number of AC was determined according to the Method [17]. The surface area of AC was estimated by iodine and methylene blue numbers using multiple regressions [8].

2.3 Preparation of the Adsorbent

Areca nuts were washed with distilled water and dried in oven at 110°C for 24 hrs. The nuts were then washed dried and crushed into powder. The powder was then sieved to obtain the fraction of size 212 µm. Twenty grams of dried, crushed, powdered Areca nut was mixed with phosphoric acid (H_3PO_4) in the ratio of 1:1 by weight and stirred with magnetic stirrer at 70°C until partly dried. Then, sample was oven dried at 110°C for 24 hours. After drying, the sample was carbonized in a horizontal tubular furnace at 400°C under a continuous nitrogen flow of nitrogen (75 ml/min) for 3 hrs. The prepared AC was treated with 0.1N NaOH, subsequently washed with warm distilled water until it became neutral. The sample was then dried at 110° C for 24 hrs and sieved to get the particles of size 106 µm. The resulting H_3PO_4 activated carbon sample was used for characterization.

Adsorbent was prepared by compositing Areca nut AC with ferric oxide (Fe_2O_3) according to the procedure [21]. Two grams of AC was added to 8 mL of 2 M $Fe(NO_3)_3 \cdot 9H_2O$ solution, then 0.1 mL 10 M sodium hydroxide was added to increase the pH to form precipitate of ferric hydroxide. The mixture was heated at 105ºC overnight. Upon cooling, the AC was observed to be covered with a thick layer of orange-colored iron oxide. The Fe_2O_3/Areca nut AC composite was sieved and washed with distilled water until the brown color was removed, dried at 110 °C for 24 hrs.

2.4 Adsorption Experiments

Adsorption experiments were carried out in batch mode. A definite amount of Areca nut AC was suspended with 50 ml of fluoride solution in 100 ml plastic conical flasks. The suspension was agitated on Digital VDRL Rotator-RPM-S at 225 rpm at room temperature. After equilibrium, the suspension was filtered and fluoride ion concentration before and after adsorption was measured with a fluoride ion selective electrode. The adsorption studies were conducted for the optimization of various experimental conditions like pH, contact time, adsorbent dose, adsorption Isotherm. Amount of fluoride ions adsorbed was calculated by the following equations.

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

$$q_e = \frac{(C_o - C_e) \times V}{M} \tag{2}$$

Where, C_o = initial concentration of fluoride ions (mg/L); C_e = equilibrium concentration of fluoride ions (mg/L); V = volume of fluoride solution (L) and M = mass of adsorbent (gm).

3. Result and Discussion

3.1 Characteristics of Precursor and Carbon

3.1.1 Thermogravimetric Analysis (TGA) of Areca nut

In order to predict thermal behavior of the Areca nut, the rate of weight loss of the sample as a function of temperature was studied. TGA graph of Areca nut is shown in Fig. 1.

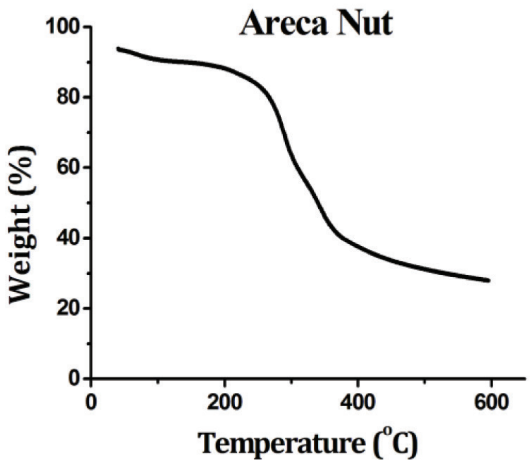

Fig. 1: TGA graph of Areca nut

Thermal degradation of Areca nut occurs in three steps. There is a little mass loss takes place from 30 to 200°C which is due to the release of moisture. After that, mass loss decreases significantly from 200 to 400° C. It might be caused by decomposition of cellulose, hemicellulose. From 400 to 600°C, there is a very little mass loss which is due to degradation of lignin with the release of tar and less volatiles materials trapped in carbon network. Therefore, 400°C was selected as the carbonization temperature in this study.

3.1.2 Iodine number and methylene blue number of activated carbon

Iodine number and methylene blue number of Areca nut AC is shown in Table 1.

Table 1 Iodine number and methylene blue number of AC

Activated carbon	**Iodine number**	**Methylene blue number**	**Surface area**
Areca nut AC	888 mg/gm	369 mg/gm	936 m^2/gm
Commercial AC	955 mg/gm	420 mg/gm	1049 m^2/gm

Iodine number is the amount of iodine adsorbed (in milligrams) by 1gm of carbon [3]. It is a measure of micropore content of the activated carbon and reflects its ability to adsorb low molecular weight substances. Methylene blue number is defined as the milligram of methylene blue adsorbed onto 1.0 gm of adsorbent [17]. It is a measure of mesopore content and indicates ability of adsorbing high molecular weight substances. Iodine number, methylene blue number and surface area of Areca nut AC were found to be higher and comparable to that of commercial activated carbon. It suggested that, the microporosity and mesoporosity of the AC were better developed with high surface area.

3.2 Adsorption Studies

3.2.1 Effect of pH

pH of the solution has a significant role in fluoride adsorption, since it determines the surface charge of the adsorbent and the degree of ionization. So adsorption of fluoride onto the adsorbent was studied over a pH range of 2-10 at room temperature. Effect of pH on the percentage of fluoride removal is shown in Fig. 2.

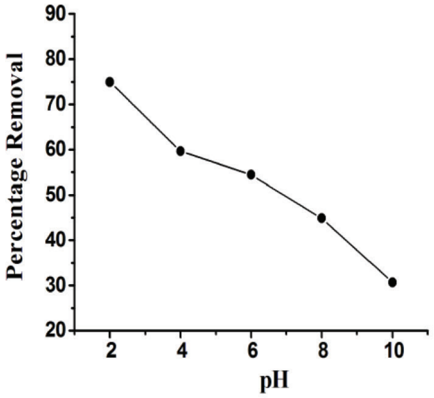

Fig. 2: Effect of pH on the percentage of fluoride removal

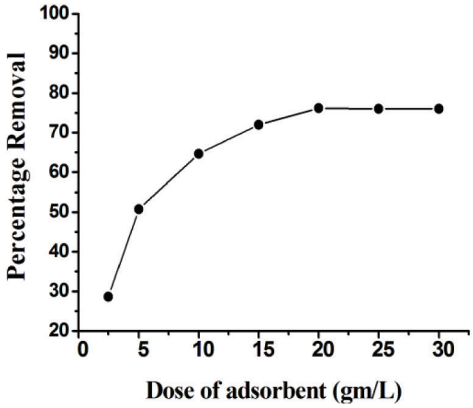

Fig. 3: Effect of adsorbent dose on percentage of fluoride removal

The adsorption of fluoride increases with decrease in pH of solution. At pH 2, the percentage of removal by adsorbent was ~75 %. It shows that, the maximum percentage of removal by the Fe_2O_3/Areca nut AC composite was observed at pH 2. At a low pH, the AC surface is more positive charged and attracts fluoride ions by electrostatic force of attraction. It led to a high adsorption rate. The percentage of adsorption rate was reduced at higher pH value. At high pH, the surface of modified AC acquires negatively charge and there is increasing repulsion between the negatively charged fluoride ions and modified AC surface. The same trend of the adsorption of fluoride at different pH was also observed in commercially available activated charcoal [20].

3.2.2 Effect of Adsorbent Dose

The plot of percentage of percentage removal of fluoride onto the adsorbent against adsorbent dose is shown in Fig. 3. Fluoride uptake increased with increasing adsorbent dose upto 20 gmL and no significant change was observed beyond this dose. The increased fluoride uptake with the increase of adsorbent dose is caused by the availability of larger number of adsorption sites. Further addition of the adsorbents did not show a does not show any considerable increase in removal capacity. This is due to overlapping of the active sites at higher adsorbent dose resulting in reduction of surface area. It indicates that an optimum dosage of 20 gm/L was required for a maximum removal by Fe_2O_3/Areca nut AC composite.

3.2.3 Effect of contact time

The plot of percentage of percentage removal fluoride onto the adsorbent against contact time is shown in Fig. 4. The percentage removal of fluoride ions is increasing linearly up to 180 min and thereafter it remained constant. It indicates the adsorption equilibrium was achieved. Initially, there are a large number of vacant surface sites are available for adsorption so the adsorption rate is very fast. But with the passage of time, the remaining vacant surface sites are difficult to be occupied due to the repulsive forces between the fluoride ions on the solid surface and in solution. These lead to a decrease of adsorption rate, shown by plateau lines after 180 min adsorption. Hence, the minimum contact time for maximum removal of fluoride onto the Fe_2O_3/Areca nut AC composite was found to be 180 min.

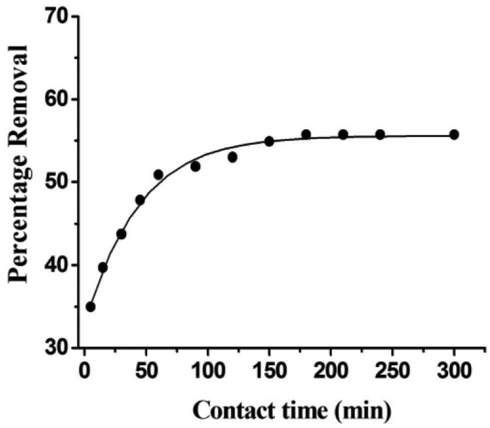

Fig. 4: Effect of contact time on the percentage of fluoride removal

3.2.4 Adsorption Isotherms

Adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The adsorption equilibrium data was analyzed by adsorption Freundlich and Langmuir isotherms. Langmuir adsorption isotherm commonly applied in solid/liquid system to describe the saturated monolayer adsorption where as Freundlich adsorption isotherm describes the adsorption equilibrium, based on adsorption on heterogeneous surface.

The linearized form of the Langmuir equation can be represented as:

$$\frac{C_e}{q_e} = \frac{1}{b\,q_m} + \frac{C_e}{q_m} \tag{3}$$

where C_e is the equilibrium concentration of fluoride in solution (mg/L); q_e is the amount of fluoride adsorbed (mg/gm); q_m is maximum adsorption capacity (mg/gm) and b is the Langmuir constant. The Langmuir constant (b) and maximum adsorption capacity (q_m) were calculated from slope and intercept of the plot.

The linearized form of The Freundlich equation is represented as.

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

where q_e is the amount of fluoride adsorbed (mg/gm); C_e is the equilibrium concentration of fluoride in solution (mg/L); K are constant respectively. The value of adsorption intensity (n) and Freundlich constant (K) determined from slope and intercepts of the plots. The applicability of the isotherm equations was compared by judging the coefficients of determination R^2.

A Langmuir isotherm for the adsorption of fluoride on the Fe_2O_3/Areca nut AC composite was analyzed by plotting C_e/q_e v_s C_e. The values of Langmuir constant, maximum adsorption capacity and coefficients of determination are given in the Table 2.

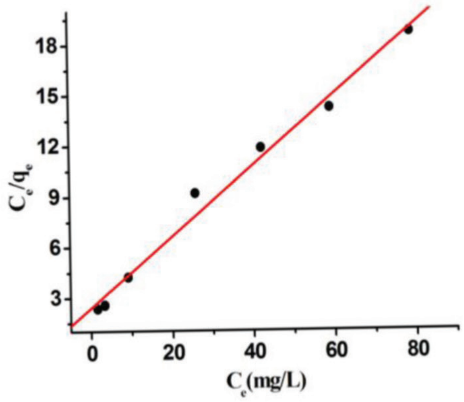

Fig. 5: Plot of C_e/q_e v_s C_e for Langmuir isotherm

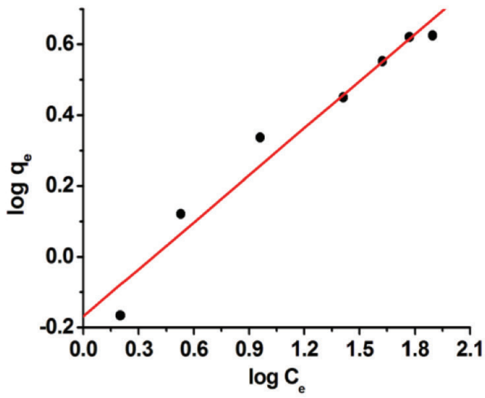

Fig. 6: Plot of log qe vs log Ce for Freundlich isotherm

Similarly, Freundlich for Langmuir adsorption isotherm for the adsorption of fluoride on the Fe_2O_3/Areca nut AC composite was analyzed by plotting log q_e vs log C_e. The value of adsorption intensity, Freundlich constant and coefficients of determination are given in the Table 2. It shows that, value of coefficient of determination is slightly higher compared to the Freundlich isotherm. Hence, Langmuir isotherm is more applicable for fluoride adsorption by Fe_2O_3/Areca nut AC composite. It suggested that, adsorption of fluoride takes place through the formation of monomolecular layer on the surface of the adsorbent.

Table 2 Langmuir and Freundlich parameters for adsorption of fluoride ion onto Fe_2O_3/Areca nut AC composite

Langmuir parameters		**R^2**	**Freundlich parameters**		**R^2**
q_m (mg/gm)	b		K (mg/g)(L/mg)$^{1/n}$	n	
4.8	0.08	0.987	2.3	1.5	0.963

The values for Langmuir and Freundlich parameters for adsorption of fluoride ion onto Fe_2O_3/Areca nut AC composite are also compared to that of other adsorbents. Maximum adsorption capacity (q_m), Langmuir constant (b) and coefficient of determination (R^2) for adsorption of fluoride by various adsorbents is shown in Table 3.

The adsorption capacity of Fe_2O_3/Areca nut AC composite was higher than that of Zr-Imp. groundnut shell carbon and commercial activated carbon. Hence Fe_2O_3/Areca nut AC composite is better in the adsorption of fluoride in comparison to Zr-Imp. groundnut shell carbon and commercial activated carbon.

Table 3 Maximum adsorption capacity (q_m), Langmuir constant (b) and coefficient of determination (R^2) for adsorption of fluoride by various adsorbents

Fluoride Adsorbents	Langmuir parameters		R^2	Source
	q_m (mg/gm)	b		
Zr-Imp. groundnut shell carbon	2.3	5.77	0.954	Alagumuthu & Rajan,2010
Commercial activated carbon	1.2	0.429	0.984	Tembhurkar and Dongre, 2006
Fe_2O_3/Areca nut AC composite	4.8	0.08	0.987	Present study

4. Conclusion

Areca nut AC is prepared by chemical activation with phosphoric acid. Microporosity, mesoporosity and surface area of AC is comparable to that commercial AC. The adsorbent prepared by compositing AC with Fe_2O_3 shows maximum adsorption capacity of 4.8 mg/gm for fluoride. Adsorption capacity is dependent on the pH of the solution. The adsorption of fluoride follows more to Langmuir isotherm than to Freundlich isotherm. It indicates the monomolecular layer adsorption of fluoride on the surface of the adsorbent. Adsorption capacity of the Fe_2O_3/Areca nut AC composite is comparatively higher than that of Zr-Imp. groundnut shell carbon and commercial activated carbon. The composite adsorbent prepared from Areca nut AC can be a promising adsorbent for fluoride removal from water.

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