Adsorption of Fluoride Ion onto Zirconyl–Impregnated Activated Carbon Prepared from Lapsi Seed Stone

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Abstract

The potentials of activated carbon derived from Lapsi (Choerospondias axillaries) seed stone after impregnation with zirconium for adsorptive removal of fluoride is presented. Activated carbons from Lapsi seed stone were prepared by three different techniques. Firstly by directly burning in limited supply of air, secondly by treating with a mixture of conc. H_2SO_4 and HNO_3 (in the ratio of 1:1 by weight) and thirdly by activation with zinc chloride (in the ratio of 1:1 by weight) followed by carbonization at 400°C and 500°C under nitrogen atmosphere. Thus prepared carbons were impregnated with zirconyl oxychloride and effects of pH, adsorbent dose, and contact time and adsorbate concentration for the removal of fluoride were evaluated by batch mode. The optimum pH for adsorption of fluoride was observed at pH 3-4, and a minimum contact time for the maximum defluoridation was found to be 180 min. The Langmuir and Freundlich isotherms were used to describe adsorption equilibrium. Zirconium impregnation increased the fluoride adsorption capacity of carbon to considerable extent. Among carbon prepared by three different techniques, the carbon prepared from zinc chloride activation followed by carbonization showed relatively higher fluoride adsorption capacity. From the experiment it is concluded that activated carbon prepared from Lapsi seed is an efficient, low-cost alternative to commercial activated carbon for defluoridation of water.

Keywords: Adsorption, zirconium impregnated, Lapsi seed stone activated carbon, fluoride, adsorption Isotherms

Introduction

Fluoride (F^-) contamination in groundwater has been recognized as one of the serious problems worldwide [1]. Fluoride is classified as one of the contaminants of water for human consumption by the World Health Organization in addition to arsenic, which causes large-scale health problems[2]. Fluoride is widely distributed in the geological environment and generally released into the groundwater by slow dissolution of fluorine-containing rocks such as granite, basalt, syenite, and shale et. al.[3] Besides the natural geological sources, various industries are also contributing for fluoride enrichment in groundwater[4]. The industries which discharge wastewater containing high fluoride concentrations include glass and ceramic production, semiconductor manufacturing, electroplating, coal fired power stations, beryllium extraction plants, brick and iron works, and aluminum smelters[5]. The effluents of these industries have higher fluoride concentrations than natural waters, ranging from ten to thousands of mg/L[6]. Elevated fluoride concentrations in the groundwater occur in various parts of the world[7].

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Depending on the concentration and the duration of continuous uptake, the impact of fluoride in drinking water can be beneficial or detrimental to mankind. Fluoride in drinking water has a profound effect on teeth and bones. Up to a small level (1–1.5 mg/L) this strengthens the enamel of teeth. Concentrations in the range of 1.5–4 mg/L result in dental fluorosis and with prolonged exposure and higher fluoride concentrations (4–10 mg/L) progresses to skeletal fluorosis. The distribution and health effects of fluoride have recently been reviewed[8]. Hence, the WHO provisional guideline value of 1.5 ppm (1.5 mg/l) for fluoride has been adopted[2], and the same value has been adopted in Nepal as drinking water standard. However it is estimated that more than 200 million people are using drinking water containing more than 1.5 mg/L of fluoride[2] concentrations.

In the groundwater fluoride concentrations of more than 30 mg/L was observed in different parts of the world, notably the arid parts of China, India, Sri Lanka, West Africa (Ghana, Ivory Coast, Senegal), North Africa (Libya, Sudan, Tunisia), South Africa, the East African Rift Valley (Kenya, Uganda, Tanzania, Ethiopia, Rwanda), Northern Mexico, and Central Argentina[9]. About 260 million people in the world, mostly in India and China are facing the problem of excess fluoride in drinking water[2]. In Nepal, practically, only little works exists on ground water contamination by toxic elements other than arsenic. Limited surveys were conducted in the low land of Terai region. It has been reported that, the ground water in Kailali district was contaminated with arsenic, iron together with fluoride, lead, molybdenum, boron and zinc[10]. Since, groundwater is a significant source for drinking water in Nepal[11], and any contamination of groundwater could lead to severe consequences.

To assess this fluoride risk, quantification of fluoride ions in ground water must be performed and adaptation of effective defloridation methodology. Most prevalent de-fluoridation technologies involve adsorption[4], ion exchange[12], precipitation[13], Donnan dialysis[14], electrodialysis[15], reverse osmosis[16] nano-filtration[17] and ultra-filtration[18]. Owing to various drawbacks associated with conventional defluoridation techniques, adsorption-based fluoride removal is emerging as a feasible option. Furthermore, the technique is robust, environmentally benign, and simple[19]. This technique offers satisfactory results especially with surface modified and/or mineral-based adsorbents. Various types of adsorbents namely alumina[20], activated carbon [21], bone charcoal[22] synthetic ion exchangers[23] and other materials[24, 25] have been used with different degrees of success. Among these adsorbents, activated carbons and modified activated carbon have great potential due to their strong affinity for fluoride[26].

Recently, considerable work has been conducted in developing new adsorbents impregnated with metal ions (surface modified) for the adsorptive removal of fluoride. Activated carbon when impregnated with metal ions has their fluoride adsorption capacity multiplied by 3 to 5 times compared to plain activated carbon.[27]. Because of the high electro-negativity and small ionic size of the fluoride ion, it has a strong affinity towards multivalent metal ions including Al (III), Fe (III) and Zr (IV) [28]. The adsorbents that use rare earth elements are attracting more and more attention because of their selective affinity to fluoride, high adsorption capacity, little induced pollution, and easy operation [28]. Zirconium and its metal complexes have been conventionally used for the colorimetric determination of fluoride due to the high affinity of zirconium for fluoride ion [26].The high charge density of the fluoride ion enables it to form stable fluoro-complexes with tetravalent metal ions like zirconium (IV)[29]. Furthermore, a detailed literature survey has revealed that, zirconium impregnated activated carbon have already been used for treating phosphate, arsenic, selenium, mercury and chromium (VI) from water samples. The presence of these co-ions (anions and cations) interfere with fluoride ion uptake by principle of competition for the adsorption sites on the zirconium impregnated activated carbon and fluoride ion decreased the co-adsorption of As (V), Se (IV),and Hg (II)[30] . Similarly, experimental results has also shown that, fluoride adsorption capacity of zirconium impregnated coconut shell carbon is 25 to 30 times that of plain activated carbon.[31]. It shows that zirconium has high affinity towards fluoride ion [32]. In addition, study on fluoride adsorption using zirconium impregnated coconut shell fiber carbon[33]. Zirconium impregnated ground nut shell carbon and zirconium impregnated cashew nut shell

carbon[34] and zirconium impregnated Collagen fiber[35] also have shown promising results in fluoride adsorption.

However, widespread use of commercial activated carbon is sometimes restricted due to its higher costs. Attempts have been made to develop inexpensive adsorbents utilizing numerous agro-industrial and municipal waste materials. Hence, biomass mainly derived from agricultural and industrial waste is a preferable option for low cost activated carbon precursors. These precursors include coconut shell and wood, olive stones, sugarcane bagasse, pecan shells, palm seeds, apple pulp, and rubber seeds etc.[36]. Use of these waste materials as low-cost adsorbents is attractive due to their contribution in the reduction of costs for waste disposal, therefore contributing to environmental protection. Lapsi (*Choerospondias Axillaries*) is one of the popular fruits in Nepal whose fleshy part is used to make candy, pickles etc. Its seed stones are used only as fuel in brick kilns.[37] Recently Lapsi fruit stone had been used as a precursor for preparation of activated charcoal for adsorption arsenic and heavy metals [38,39]. The present study deals with the preparation of activated carbon from Lapsi seed stone as an adsorbent for the removal of Fluoride from water.

Experimental method

Lapsi seed stones, as waste-products of the Lapsi fruit, were used to prepare fluoride adsorbent in this study. For the better research output, the different methods were applied to prepare adsorbent of Lapsi seed stone. The adsorbent was then characterized and used as adsorbent for fluoride ion. The method used in this study can be explained as follows.

Preparation of activated carbon from Lapsi seed stones as an adsorbent

The Lapsi seed stone were washed several times with distilled water and dried in sunlight for a week. Then it was dried at 105°C. After drying, it was crushed in a grinder to obtain raw powdered of Lapsi seed stone. The dried powdered Lapsi seed stones were processed to obtained different types of activated carbon as described below.

1st type: By burning directly in air: The dried Lapsi seed stones were burnt in air till blue flame ceases. The charcoal obtained was cooled and grounded in a mortar and sieved for 40 mesh.

2nd type: By treating with conc. H_2SO_4: 100 gm of crushed powdered was taken and 50 gm of sulfuric acid was added gradually. The mixture was subjected in an air oven at 110° C for 24 hours. The carbonized material was washed with distilled water to remove excess sulfuric acid and dried at 110° C for overnight. The sample was then ground in a mortar and sieved using 40 mesh.

3rd type: By treating with a mixture of conc. H_2SO_4 and HNO_3: 50 gm of sulfuric acid was gradually added to 100 gm of crushed powdered and cooled. 30 gm of nitric acid was then added slowly with continuous stirring. The mixture was subjected in an air oven at 100 ° C for 24 hours. The carbonized material was washed with distilled water to remove excess acid and dried at 85° C for overnight. The sample was then ground in a mortar and sieved using 40 mesh.

4th type: By activation with zinc chloride followed by carbonization: 20 gm of crushed powdered was mixed with $ZnCl_2$ in the ratio of 1:1 by weight. Then 50 ml distilled water was added to the mixture. The impregnation process was performed by shaken in magnetic stirrer at temperature about 70°C until the excess water had evaporated. The impregnated sample was dried in an oven at 110 °C overnight. The sample was placed inside a quartz tube and inserted horizontally into the middle of a tubular electric furnace. The carbonization and activation were carried out at 400 °C under N_2 gas flow for 3 hours. The resulting activated carbon was washed with 1M HCl followed by distilled water until traces of chloride ions were no longer detected. The sample was then dried at 110° C for overnight and stored in desiccator.

Metal Impregnation

Among the different carbons prepared, the activated carbon prepared from zinc chloride activation followed by carbonization has shown slightly higher iodine number. Hence this activated carbon was taken for metal impregnation. pH and iodine Numbers of different types of Carbons are listed in Table 1.Activated carbon obtained from section 2.1 was immersed in 1% solution of sodium carbonate ($Na_2CO_310H_2O$) solution then washed with distilled water to remove excess alkali. Zirconium metal impregnation was carried out by mixing Lapsi Seeds Activated Carbon (LSAC) with 5% $ZrOCl_2\ 8H_2O$ solution in the ratio of 1:2 by weight. The mixture was stirred for 3 days at room temperature (298 K) then filtered. The zirconium concentration in the effluent was determined using ammonia. Then Zirconium Impregnated Lapsi Seed Stone Carbon (ZILSSAC) was dried in an oven at 383 K and subsequently used for defluoridation studies.

Characterization of activated carbon

The characterization of the active carbons requires information on properties of the materials. Activated carbons from section 2.1 were characterized for pH, moisture content, Ash content [in accordance with American Standard of Testing Material, ASTM D3838-80 (pH) 1999ASTM D3173 (moisture) and ASTM D3174 (ash)][41]. Quantification of Oxygen containing functional groups present on the activated carbons prepared was determined by Boehm titration method[43]. Iodine number of the carbons was determined to get the information about the surface area (ASTM D4607 – 94)[43]

Adsorption studies

A fluoride ion stock solution of 1000 mg/L was prepared by dissolving 221 mg of anhydrous sodium fluoride in 100 mL distilled water in volumetric flask. Standard solutions of fluoride ion were prepared by subsequent dilution of the fluoride stock solution. Solutions of 0.1M NaOH and 0.1 HCl were used for pH adjustment.

The fluoride adsorption capacity of adsorbent (activated Carbon) was investigated using batch experiments. The defluoridation experiment was performed by mixing certain amount of adsorbent with sodium fluoride solution containing various concentration of fluoride concentration. The mixture was agitated in a thermostatic shaker at a speed of 200 rpm at room temperature for a prescribed time to attain the equilibrium. At the end of each equilibrium time, the solution were filtered and fluoride ion concentration in water samples was measured by SPANDS method using UV/VIS spectrophotometer as per the procedure of standard methods of examination of water and waste water[40]. The defluoridation studies were conducted for the optimization of various experimental conditions like contact time, dose, pH.

Fluoride uptake (q_e) was determined from eq. (1)

$$q_e\ =\ (Co\ -\ Ce)\frac{V}{m} \qquad (1)$$

Where, C_o is the initial concentration (mg /L), C_e the concentration at equilibrium (gm/L), q_e the amount adsorbed at equilibrium (mg /g), *m* the adsorbent mass (gm) and *V* is the solution volume (L).

Results and Discussion

Determination of pH and Iodine Number

Four types of activated carbon prepared as described in section 2.1 were subjected for the determination of pH and iodine number. For the pH determination, 1.0 gm of activated carbon was taken in a beaker and 100ml of distilled water was added then stirred for one hour. Samples were allowed to

stabilize and then pH was measured using a pH meter (Corning 250 pH/ion anlyzer). For determination of iodine number, 10 ml of 5 % by weight of HCl was added to 1 g of activated carbon and was allowed to boil. The solution was cooled to room temperature then 100 ml of 0.1N iodine solution was added. The content was shaken vigorously and filtered. 25 ml of the filtrate was titrated with 0.1 N sodium thiosulphate in the presence of starch as indicator. pH and iodine numbers of four types of activated carbons are listed in Table 1. It has shown that iodine number of 4th type activated carbon is higher than other types of activated carbon which is attributed to the complete carbonization of Lapsi seed stone powder. The higher value of iodine number indicates that the carbon is highly porous with better effective surface area. Therefore, 4th type activated carbon was selected to prepare an adsorbent in this study.

Table 1: *pH and Iodine numbers of different types of Activated carbons*

Types of Activated Carbon(AC)	pH	Iodine number (mg/gm)
1st type (Air burnt AC)	5.9	259
2nd type (H_2So_4 activated AC)	5.5	377
3rd type (H_2So_4 and HNo_3 activated AC)	5.4	398
4th type ($Zncl_2$ impregnated Carbon)	6.8	745

The physiochemical properties of the adsorbent

The 4th type activated carbon was characterized in more detail by measuring moisture content and ash content. The values are tabulate in Table 2. Moisture content of the samples was measured by thermal drying method. 1.0g of the dried activated carbons were taken in a crucible and dried in an oven at 110^oC for 4 hrs for constant weight and moisture content was calculated.

Ash content shows the amount of inorganic substituent present in the carbon. High ash content is undesirable for activated carbon since it reduces the mechanical strength of carbon and affects adsorptive capacity. A crucible was pre-heated in a muffler furnace to about 500^oC, cooled in a desiccator and weighed. 1.0g of activated carbon samples were transferred into the crucibles and reweighed. The crucibles containing the samples were heated to 500^oC in a muffler furnace. It was removed and allowed to cool in a desiccator to room temperature and reweighed again. The ash content was calculated using the equation 2. Table 2 shows that ash content and moisture content of 4th type activated carbon are low which indicates that activated carbon is suitable for adsorption process.

$$Ash (\%) = \{wt. of \ ash \ (gm)/dry \ wt.of \ activated \ charcoal(gm)\} x100 \qquad (2)$$

Table 2: *The physiochemical properties of the adsorbent*

Parameters	4th type activate Carbon
Moisture Content	0.24%
Ash Content	3.51 %

Determination of oxygen containing functional groups

Acidic functional groups such as carboxyl, phenolic and others on the surface of carbon present in the 4th type activated carbon were determined by Boehm titration method. For the process, 0.2 gm of samples in 50 mL of 0.05 M NaOH, Na_2CO_3 and $NaHCO_3$ was shaken separately for 24 hr and filtered through Whatman No 40 filter paper. After filtration, 5 mL of each solution were titrated with 0.05 M HCl solution using phenopthalein as indicator. The number and type of acidic sites were calculated by considering that NaOH neutralizes carboxyl, lactonic and phenolic groups, Na_2CO_3 neutralizes carboxylic and lactonic groups and that $NaHCO_3$ neutralizes only carboxylic groups. Table 3 shows the presence of acid functional groups such as carboxyl, phenolic and lactonic in milliequivalent/gm.[43] It is considered that the hydrogen ions present in the functional groups may replaced by zirconyl ion on metal impregnation of the activated carbon.

Table 3: The acidic surface functional groups in the ZnCl_2 impregnated activated carbon

Adsorbent	Functional groups in millequivalent per gram (meq/g)		
	Carboxyl	Phenol	Lactones
4th type activated carbon	0.104	0.213	0.326

Effect of contact time

Contact time was carried out by mixing 0.2 gm of adsorbent with 100 ml of sodium fluoride containing 10 mg/L as initial fluoride concentration. The mixture was agitated in a thermostatic shaker at a speed of 200 rpm at room temperature. Figure 1 illustrates the amount of fluoride adsorbed per gm of adsorbent (Zirconium Impregnated Lapsi Seed Stone Activated Carbon, ZILSSAC) as a function of contact time in the range of 25 –400 min at room temperature. The values are increasing linearly up to 150 min and thereafter it remained almost constant indicating the attainment of adsorption equilibrium. Therefore 150 min was fixed as minimum contact time for the maximum defluoridation of the sorbent. The zirconium impregnated Lapsi seed stone carbon recorded a maximum amount of fluoride adsorbed per gm of adsorbent (q_e) was found to be 1.6 mg/gm. The sudden rise in removal of fluoride indicates that the adsorption of fluoride probably takes place due to the diffusion taking place into the pores on the surface of the adsorbent. The removal of fluoride ions from water, increases with increase in agitation time to some extent, after which, increase in agitation time does not increase the fluoride uptake due to deposition of fluoride ions on the available adsorption sites on ZILSSAC[34].

Effect of pH

The pH of the solution has a significant impact on the uptake of fluoride ions, since it determines the surface charge of the adsorbent, the degree of ionization and speciation of the adsorbate. In order to establish the effect of pH on the adsorption of fluoride ion, the batch equilibrium studies at different pH values were carried out in the pH range of 2-9 (Figure 2). At higher pH values the fluoride removal by the sorbents was found to decrease. The pH of the solution was adjusted by using 0.1M sodium hydroxide or hydrochloric acid. At pH 3, the maximum amount of fluoride uptake was observed to be 3.25 mg/gm respectively. It is due to the availability of more H^+ ions in the surface of the adsorbent leading to greater adsorption of the fluoride. Hence, fluoride adsorption increases at low pH levels as more of the surface sites are positively charged. The adsorption of fluoride onto the surface of the material is may be due to the development of positively charged surface sites.
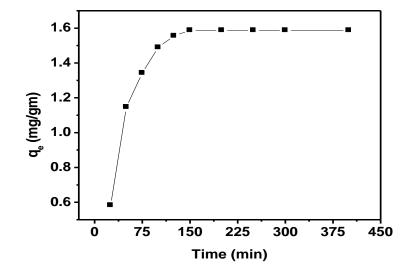
Figure 1: *Effect of contact time on fluoride adsorption by ZILSSAC*

Effect of Adsorbent Dose

One of the parameters that strongly affect the adsorption capacity is the concentration of the adsorbents. The effect of adsorbent dosage on the removal of fluoride from drinking water was studied at ambient pH and fluoride concentration of 10 mg/l for 150 min. The adsorption loading is calculated based on equation 1.

Figure 3 indicates that, increasing adsorbent dosage increases fluoride uptake, indicating that for a fluoride removal an optimum ZILSSAC dosage of 2.0 g/L was required. The result indicates that the fluoride removal efficiency increases up to this optimum dosage beyond which fluoride uptake has no significant change with ZILSSAC dosage. With the increase in the adsorbent dosage provides greater surface area and hence increases the adsorption. However, by increasing the adsorbent dosage beyond the optimum dosage, there may be a slight improvement in fluoride removal efficiency but the adsorption capacity decreases.

Adsorption isotherms

The sorption isotherm expresses the specific relation between the concentration of adsorbate and its degree to accumulation onto adsorbent surface at constant temperature[44]. The fluoride adsorption capacity of ZILSSAC was evaluated using two different isotherms namely Langmuir (Figure 4) and Freundlich (Figure 5) isotherms. The maximum adsorption capacity of the ZILSSAC was investigated at various concentrations from 5 ppm to 50 ppm of fluoride ion. The plot C_e/qe verses C_e and plot of log C_e versus log q_e are shown in Figure 4 and Figure 5.
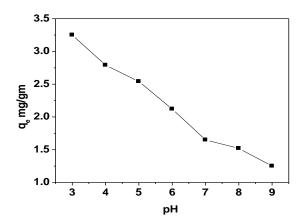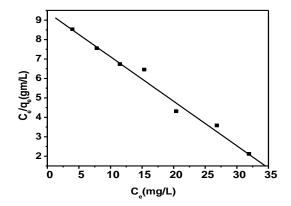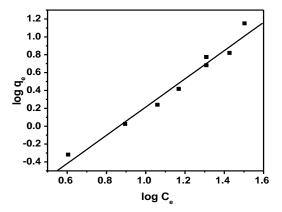
Fig.2: *Effect of pH on fluoride adsorption fluoride onto ZILSSAC*

Fig.3: *Effect of adsorbent dose on adsorption onto ZILSSAC*

Fig.4 *Plot of the Langmuir isotherm for fluoride fluoride adsorption on ZILSSAC. (R^2 =0.9768)*

Fig.5 *Plot of the Freundlich isotherm for sorption on ZILSSAC (R^2 =0.8828)*

Langmuir Isotherm

The linearized Langmuir adsorption isotherm, is expressed as

$$\frac{Ce}{qe} = \frac{1}{qmax}Ce + \frac{1}{b}qmax \qquad (3)$$

Where q_e is the amount adsorbed at equilibrium (mg/g); C_e is the equilibrium concentration of fluoride ions in solution (mg/l).

Freundlich Isotherm

The linearized form of Freundlich equation is

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

Where, K_f and $1/n$ are Freundlich isotherm constants, indicating the adsorption capacity and adsorption intensity, respectively.

The adsorption curves for ZILSSAC were applied to both Langmuir and Friendlich isotherms. The adsorption by adsorbent (ZILSSAC) was better fitted to Langmuir's isotherm which confirms monolayer adsorption. Hence the Langmuir's isotherm is applicable for adsorption of fluoride by ZILSSAC.

Conclusion

In this study, the possibility of utilization of Zirconium Ion Impregnated Lapsi Seed Stone Activated Carbon (ZIGNSC) as adsorbent for removal of fluoride from water was studied. Fluoride adsorption capacity is higher in acidic pH. It decreases with increasing pH of the solution. The rate of removal (adsorption) of ZILSSAC is also influenced by pH. Minimum contact time for maximum adsorption of fluoride was found to be 150 min. The adsorption of fluoride onto Zirconyl Impregnated Carbon follows Langmuir isotherm i.e. Maximum adsorption corresponding to a saturated monomolecular layer of solute molecules on the adsorbent surface. From the experiment it is concluded that activated carbon prepared from Lapsi seed is an efficient, low-cost alternative to commercial activated carbon for defluoridation of water. This is a strong indication for its great potential application in fluoride removal from water as ZILSSAC provides a cost-effective working solution to the defluoridation problem in the developing countries.

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