

Removal of Fluoride in Water Using Activated Carbons Prepared From Selected Agricultural Waste Materials

John. Bentil[1]*, William Kwame Buah[2]
Department of Civil Engineering, Takoradi Polytechnic, Ghana, P.O.Box 256, Takoradi, Ghana.
[2] Department of Minerals Engineering, University of Mines and Technology, Tarkwa, Ghana.

Abstract

Water is essential to life, but many people do not have access to clean and safe drinking water and many die of water borne or water related infections. Fluoride is one of the anionic contaminants which are found in excess in both surface and groundwater due to geochemical reactions and anthropogenic sources like industrial wastewater disposal. Many methods like coagulation, precipitation, membrane processes, electrolytic treatment and ion – exchange are some of the methods used for the defluoridation of water. But the most widely used method is the adsorption process. Though various conventional and non-conventional adsorbents have been assessed for the removal of fluoride from water, this research aims to promote innovative use of local raw materials and relatively low cost techniques in the production of activated carbons for fluoride adsorption. Activated carbons were prepared from coconut shells, cocoa pod husks and palm kernel shells by carbonisation of the residues to obtain chars which were activated at 900 ^{o}C using steam as the activating agent. Analysis of fluoride was done before and after treating water with the derived activated carbons. The water treatment experiment using fluoride as a model pollutant demonstrated that activated carbons prepared from agricultural waste materials have a good potential for fluoride removal. Adsorption of fluoride was also found to be influenced by the type and concentration of other ions in the treated water.

Keywords: fluoride, adsorption, carbons, waste, pH, ions, fluorosis, Langmuir isotherms.

1. Introduction

Fluorine is the lightest in the halogens group and most electronegative of all the elements (Fawell *et al*., 2006). Fluorine occurs naturally in the environment as fluoride and accounts for about 0.06 - 0.09 percent of the earth crust (Fawell *et al*., 2006).Fluoride ions are found in significant quantities in various minerals notably fluorspar, rock phospahate, cryollite, apatite, mica, hornblende and others (Murray, 1986). Traces of some concentrations of fluoride are also found in natural water bodies, therefore the presence of naturally occurring fluoride or as an added fluoridated salt in water accounts for the presence of fluorine in the body via the gastrointestinal tract through drinking water (Habuda-Stanic *et al*., 2014).

In addition to drinking water, fluoride also enters the human body through food, industrial exposures, drugs, cosmetics etc. with lesser contributions from toothpaste (Fawell *et al*., 2006; WHO, 1984). Water is essential to life, but many people do not have access to clean and safe drinking water and many die of water borne or water related infections. Epidemiological studies conducted on the long term ingestion of fluoride via drinking water with fluoride concentrations above 1.5 mg/L have revealed that fluoride can induce birth, reproduction and immunological defects, dental and skeletal tissues fluorosis (Harrison, 2005; Fawell *et al*., 2006; Valdez-Jame'nez *et al*., 2011; Browne *et al*., 2005; Wang *et a*l., 2004; Singh *et al*., 2007; Ayoob and Gupta, 2006). Fluoride in low concentrations is also beneficial in the protection against dental carries especially in children. Due to these above-mentioned fluoride health problems, the World Health Organisation (WHO) has specified the tolerance limit of fluoride in drinking water as 1.5 mg/L (Fawell *et al*., 2006; Habuda-Stanic *et al*., 2014).

Removals of excess fluoride from drinking water are currently done by processes such as coagulation and precipitation, membrane process, electrochemical treatment, ion-exchange and its modification etc. (Habuda-Stanic *et al*., 2014; Fawell *et al*., 2006), but the adsorption process has become the generally accepted, most effective and cheapest method for the removal of pollutants like fluoride from water (Fawell *et al*., 2006; Valdez-Jame'nez *et al*., 2011; Browne *et al*., 2005; Wang *et al*., 2004; Ayoob and Gupta, 2006: ; Habuda-Stanic *et al*., 2014; Meenakshi and Maheshwari, 1997; Sujana *et al*., 1997; Bhatnagar *et al*., 2011).

Adsorptions of pollutants from liquid and gaseous streams by activated carbons have been extensively used in recent years. Activated carbons are high porosity, high surface area materials manufactured by the carbonisation and activation of carbonaceous materials.

Activation of a wide variety of carbonaceous materials is achieved by either physical activation and/or chemical activation. In chemical activation, the carbonisation and activation are accomplished in a single step by carrying out thermal decomposition of the precursor material with certain chemical agents. Several activating agents have been reported for the chemical activation process; the commonly used ones are phosphoric acid, zinc chloride and alkaline metal compounds. Physical activation involves the gasification of the char obtained from the carbonisation of the precursor materials by oxidation with steam, carbon dioxide, air or any mixture of these gases in the temperature range of 800 to 1100 ^oC. The advantages of chemical activation are low energy cost due to lower temperature (500-800 ^oC) than those needed for physical activation (McKay *et al*., 1998). Our quest to promote the innovative use of local raw materials and relatively low cost techniques in the production of activated carbons for water treatment motivated the use of activated carbons derived from cocoa pod husks, palm kernel shells and coconut shells in the removal of excess Fluoride as a model pollutant in drinking water.

2. Experimental Methods

2.1 Preparation of Activated Carbons

Activated carbons prepared from coconut shell, palm kernel and cocoa pod husks were used in this study. The coconut shells were obtained from Bas Van Buuren (BVB), a Non-Governmental Organisation (NGO) which buys coconut shells from the Nzema communities and process them for sale as organic manure. The palm kernel shells and the cocoa pod husks were obtained from Bompa a village in the Western part of Ghana. All the biomass samples were carbonised in a pyrolysis reactor to further dry and also drive off hydrocarbons and other gases present in them. Carbonisation of all the biomass was completed at a temperature of 500 ^oC. Samples of the carbonised products were activated at a temperature of 900 ^oC for 2 h in the presence of steam. The temperatures for activation were measured using a k-type thermocouple.

2.2 Application of the Activated Carbons on water

Activated carbons prepared from these agro-solid waste materials were used for the treatment of raw water spiked with a known concentration of fluorine to simulate the excess of fluoride in drinking water. Samples of the water (50 ml) containing fluoride were mixed with 1.0 g of the activated carbons in separate 250ml Erlenmeyer flask at pH of 7. The mixtures were stirred at 240 rpm mechanically for 30 mins. The solutions were then filtered to remove the carbons using a Whatman No.42 Filter paper. The Fluoride ions concentrations remaining in the various solutions were determined using Palintest Photometer. The pH of the treated water was determined using a pH meter. The procedure was also repeated using distilled water.

The results of fluoride adsorption are expressed in terms of percentage adsorption of the fluoride ions (eqn.1) and amount of fluoride adsorbed per gram of carbon (eqn.2) according to the formulae:

$$\%\ \text{adsorption} = \frac{C_o - C_e}{C_O} x100\,\% \qquad \text{(Eqn.1)}$$

$$\text{Amount Adsorbed} = \frac{C_e - C_o}{M} \qquad \text{(Eqn.2)}$$

where C_o and C_e are the initial and equilibrium concentration of fluoride (mg/L) respectively and M is the mass of adsorbent (g).

By knowing the fluoride concentrations before and after adsorption, the efficiency of fluoride ion adsorption by the activated carbons can be determined.

3. Results and Discussions

3.1 Fluoride Removal Efficiency by the Activated Carbons from Raw Water and Distilled Water

The Table 3.1 shows the results of the average of the triplicates removal efficiency of fluoride by using 1.0g of activated carbons in raw water and distilled water. In all cases, the results of the percentage of fluoride adsorbed from the distilled water were higher than that from the raw water. This is an indication of the fact that the presence of other ions in the raw water perhaps from the water treatment chemicals interacted with the adsorbent and decreases the adsorbent's surface area available for adsorption. The availability of calcium and aluminium in the raw water may have also formed insoluble complexes (Edmunds and Smedley, 1996), with the fluoride in solution decreasing its concentrations in solution. From the analysis of the adsorption percentages indicated in Table 3.1, the average values of percentage adsorption of fluoride removal from water by the three carbons derived from agricultural waste materials are in the order:

Palm kernel shell> Coconut shells> Cocoa pod husks.

Table 3.1: Removal of Fluoride from Raw water and Distilled water spiked with fluoride by the Activated Carbons.

	Raw Water	Distilled water	Raw water	Distilled water
Activated Carbon Source	Amount Adsorbed Conc.(mg/g)		Adsorption (%)	
Cocoa pod husks	0.335	0.362	10.55	14.85
Coconut shells	0.435	0.493	13.87	20.05
Palm kernel nuts	0.263	0.793	8.59	32.18

3.2 Adsorption Isotherms

The Langmuir and Freundlich isotherms were used to understand the equilibrium data and conclude on the adsorption mechanism.

The Langmuir (Langmuir, 1918)) model is linearly expressed as

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_a q_m} \qquad \text{(Eqn.3)}$$

Where C_e (mg/L) is the equilibrium concentration of fluoride

q_e (mg/g) is the amount of fluoride adsorbed at equilibrium per gram of activated carbon

q_m (mg/g) is the adsorption for a complete monolayer,

k_a (L/mg) is the adsorption equilibrium constant.

When $\frac{C_e}{q_e}$ is plotted against Ce and this data are regressed linearly,

q_m and K constants are calculated from the slope and the intercept.

The Freundlich (Freundlich, 1906) model is expressed linearly as

In q_e = In K_{f} + 1/n(In C_{e}), (Eqn.4)

The constant K_f (mg/g) is related to the adsorption capacity of the activated carbons and the 1/n is related to the surface heterogeneity. The adsorption data were fitted with these isotherms by

(a) plotting the values of C_e/q_e Vs C_e indicated in Fig. 2 and Log q_e vs log C_e, indicated in Fig. 1 and

(b) by carrying out correlation analysis between values of (i) C_e/q_e and C_e and (ii) log q_e and log C_e for both the fluoride removal in raw water and distilled water spiked with fluoride. The parameters of Langmuir and Freundlich equations for the adsorption capacity of fluoride onto the three carbons obtained as described above are given in Tables 3.2 and 3.3. The isotherms obtained using these parameters are presented in Figs. 1 and 2:

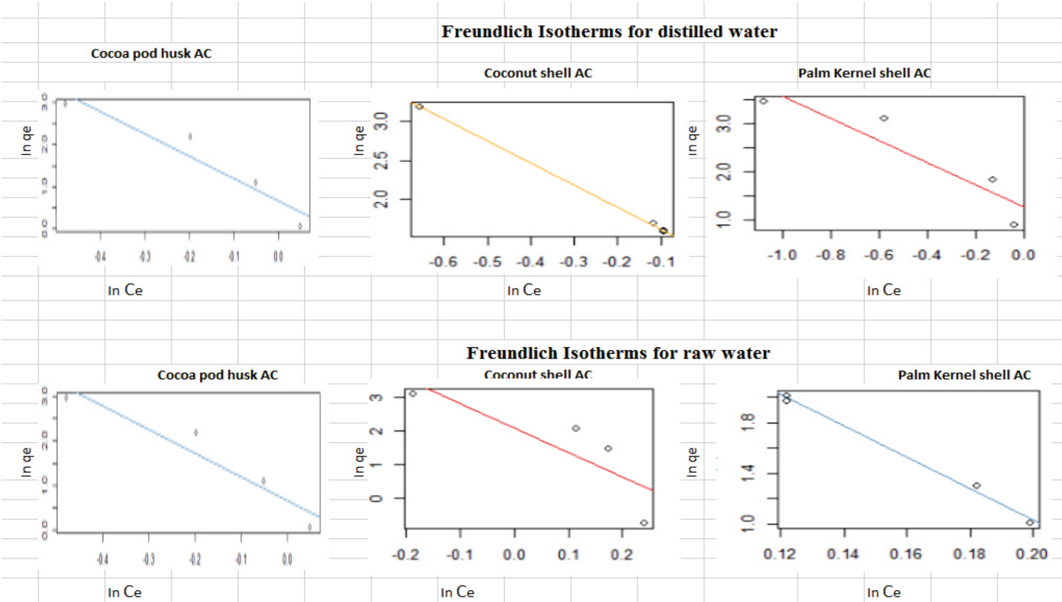

Fig. 1 Freundlich Isotherms of fluoride adsorption by the various activated carbons

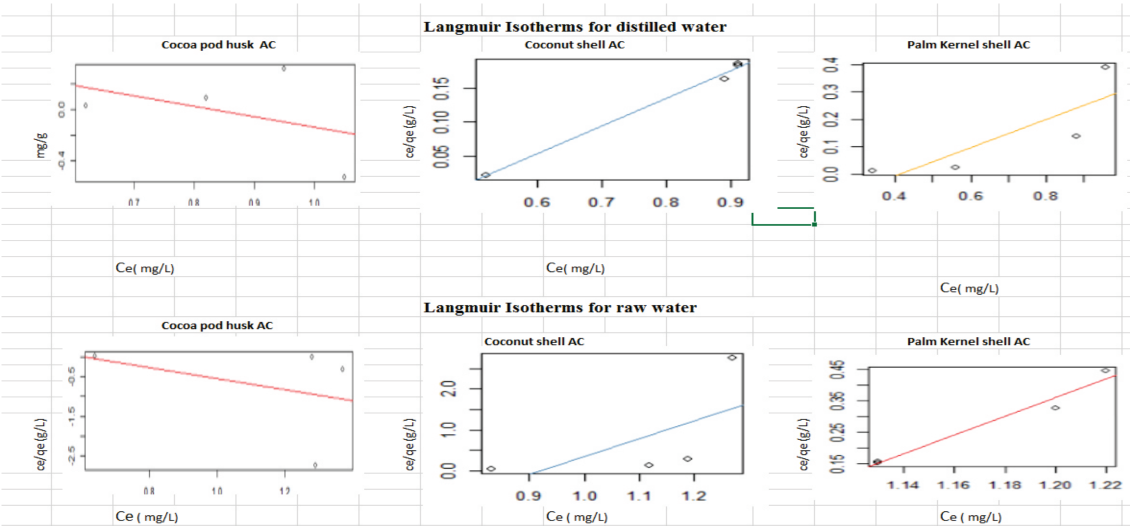

Fig. 2 Langmuir Isotherms of fluoride adsorption by the various activated carbons

Table 3.2: Adsorption Isotherms data for fluoride removal by activated carbons in raw water

S.No	Parameters	Cocoa pod husks carbons	Coconut shells carbons	Palm kernel shell carbons
Langmuir Isotherms	Slope(1/Ka)	-0.0896	0.093	0.3223
	Intercept(1/qm)	1.077	1.027	1.0823
	Correl. coef. (r)	-0.353	0.637	0.985
	R_L	1.128	0.890	0.708
Freundlich isotherms	Slope(1/n)	-7.489	-7.298	-12.440
	Intercept(log K_f)	0.2382	2.079	3.5172
	Correl. coef.(r)	-0.8384	-0.837	0.997

Table 3.3: Adsorption Isotherms data for fluoride removal by activated carbons in distilled water

S.No	Parameters	Cocoa pod husks carbons	Coconut shell carbons	Palm kernel shell carbons
Langmuir Isotherms	Slope(1/Ka)	-0.8085	0.407	0.516
	Intercept(1/qm)	1.077	-0.191	-0.2117
	Correl. coef. (r)	0.6741	0.996	0.841
	R_L	5.452	0.709	0.657
Freundlich isotherms	Slope(1/n)	-5.2928	-2.808	-2.285
	Intercept(log K_f)	0.667	1.346	1.289
	Correl. coef.(r)	-0.956	-0.996	-0.921

The values of K_f determine the adsorption capacity of an adsorbent at equilibrium concentration in solution. A high K_f value corresponds to a high adsorption capacity (Frimmel and Huber, 1996). According to the K_f values listed in Tables 3.2 and 3.3, the adsorption capacities of the fluoride studied are higher for both the coconut shells and palm kernel shells activated carbons than the cocoa pod husks activated carbons.

The slope (1/n) value in the Freundlich equation is an indicator of adsorption intensity of a given substance from water phase of adsorbent. The value of 1/n is known as the heterogeneous factor and ranges between 0 and 1; the more heterogeneous the surface, the closer 1/n is to 0 (Langmuir, 1918). The slope (1/n) values for the three carbons as shown in Tables 3.2 and 3.3 were all < 1 suggesting non linear adsorption isotherms. The Tables 3.2 and 3.3 indicate that the Langmuir equation gives a fairly good application of fluoride adsorption. Accordingly all the r-values observed are close to unity for all the three derived activated carbons. This indicates the applicability of these adsorption isotherms and the monolayer coverage of fluoride species on the carbons surfaces.

Langmuir isotherms plots indicate monolayer adsorption capabilities of the three activated carbon adsorbents are the same as established from the experimental results in Table 3.1; palm kernel shells> coconut shells> cocoa pod husks. This result can be explained in terms of the pore accessibility. It could be that palm kernel shells based activated carbons have more pores which were easily accessible to the fluoride ions than the coconut shells and cocoa pod husks activated carbons.

In addition, it could also be non-accessibility of the micropores, and sites not used for adsorption by the locating of surface groups in the pores of the coconut shells and cocoa pod husks activated carbons. All the three activated carbons are observed to possess high adsorption and hence they can be employed as locally prepared adsorbents as alternatives to commercial activated carbons and other sources of adsorbents for the removal of fluoride in drinking water.

Further, the essential characteristics of the Langmuir isotherms can be described by a separate dimensionless factor R_L (Ruthsen, 1984); which is defined by the equation:

$$R_L = \frac{1}{(1+K_a C_o)} \qquad \text{(Eqn.5)}$$

Where C_o is the initial concentration of the fluoride in mg/L and Ka is the Langmuir constant. The value of separation factor R_L indicates the nature of the adsorption process as shown in Table 3.4

Table 3.4: Nature of adsorption process

R_L Values	Nature of adsorption process
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0< R_L <1$	Favourable
$R_L = 0$	Irreversible

In this study, the computed values of R_L as shown in Tables 3.2 and 3.3 for coconut shell and palm kernel shells activated carbons are found to be in the range of 0-1, indicating that the adsorption process is favourable for these adsorbents for the removal of fluoride ions.

4. Conclusion

Three different activated carbons were prepared from agricultural waste materials namely cocoa pod husks, coconut shells and palm kernel shells and used to remove fluoride ions from both raw water and distilled water. Among these derived carbon adsorbents under consideration, palm kernel shells carbons possess the highest adsorption capacity. Hence it is the best and the most effective adsorbent in the removal of fluoride content in water. The next in the order of basis of efficacy of removing fluoride content is coconut shells and then cocoa pod husks carbons.

The Langmuir and Freundlich isotherms indicate the applicability of these activated carbons for the removal of fluoride in water. The computed values of R_L for coconut shells and palm kernel shells activated carbons were found to be in the range of 0-1, indicating that the adsorption process is favourable for these adsorbents for the removal of fluoride ions. These adsorption data suggest that activated carbons derived from coconut shells and palm kernel shells can be used as alternative locally prepared adsorbents to remove fluoride from water.

References

Ayoob S.,Gupta A. K., 2006. Fluoride in drinking water; A Review on the status and stress effects. J.*Crit. Rev. Environ. Sci.*;36: 433-487.

Bhatnagar A., Kumar E., Sillanpaa M., 2011. Fluoride removal fromwater by adsorption, A review. J.*Chem.Eng.* 171: 811-840.

Browne D., Whelton H., Mullane D.O., 2005. Fluoride Metabolism and Fluorosis.J. *Dent,*;33:177-186.

Edmunds W.M., Smedley, P.L. 1996. Groundwater geochemistry and health: an overview, In: Appleton, Fuge and McCall (Eds), Environmental Geochemistry and Health, Geological Society Special Publications, 113:91-105.

Fawell J., Bailey J., Chilton K, et al. 2006. Fluoride in Drinking-water.IWA, London, UK.

Freundlich H., 1906. Adsorption in solution. J. Phys. Chem. 57: 385-470.

Frimmel H. F., Huber L., 1996. Influence of humic substances on the aquatic adsorption of heavy metals on defined mineral phases. J. Environ.Int.; 22: 507-517.

Habuda-Stanic M, Ravancic M.E, Flanagan A,. 2014. A review on Adsorption of fluoride from Aqueous solution.J. *Materials,*7: 6317-6366.

Harrison P., 2005.Fluoride in Water: A UK Perspective. *Fluor.Chem,* 1448-1456.

Langmuir I., 1918. The adsorption of gases on plane surface of glass, mica and platinum. J.Am.Chem.Soc. 40:1361-1368.

McKay G., Allen S.J., Whitten L., 1998. The Production and Characterisation of Activated Carbons, A Review, Dev. Chem .Eng. Mineral Process, 6(5):231-261.

Meenakshi R.C., Maheshwari J., 2006. Fluoride in drinking water and its Removal. J.*Hazard Mater.*; 137: 456-463.

Murray J., 1986. *Appropriate Use of Fluorides for Human Health.* Geneva: World Health Organisation.

Ruthsen D. M., 1984.Principles of Adsorption and Adsorption processes. JohnWiley and Sons, New York.

Singh B, Gaur S, Garg V.K., 2007. Fluoride in drinking water and human urine in Southern Haryana, India. J.*Hazard Mater*;144:147-151.

Sujana M.G, Thakur R.S, Das S.N et al. 1997.Defluorination of Waste water. *Asian J.Chem.* 4: 561-570.

Valdez-Jime'nez L, Soria Fregozo C,Miranda Beltra'n M.L, et al. 2011. Effects of the fluoride on the central Nervous system.J. *Neurologia,* Volume;26: 297-300.

Wang B, Zheng B, Zhai C, et al. 2004. Relationship between Fluorine in drinking water and dental health of residents in some large cities in China. J.*Environ. Int.* 30:1067-1073.

World Health Organisation (WHO) 1984. *Fluoride and Fluorides: Environmental Health Criteria 36,* Geneva, Switzerland: World Health Organisation;.