Original Research Paper

Chemistry

KINETIC STUDIES FOR THE ADSORPTION OF FLUORIDE FROM AQUEOUS MEDIUM USING AGAR-AGAR ADSORBENT.

Dr. Nilakantha Dash* Dept. Of Chemistry, Panchayat College, Dharmagarh, Odisha, India. *Corresponding Author

ABSTRACT The present study deals with ground water quality with respect to the fluoride content in water resources different district of Odisha, India. Water samples were collected in different locations covering tap water, open wells, tube wells and lake waters. Ground waters of Tube wells are highly polluted with fluoride in comparison to open wells. In tube wells contains 1.5-6.5> (mg/lit). The water supply contains objectionable fluoride content i.e. 3.88 mg/lit. In view of the severity of the problem the defluoridation techniques need to be evolve to reduce or minimize the fluoride concentration in drinking water. The fluoride removal for drinking water can be accomplished by different methods , for example , coagulation-precipitation, membrane separation process, ion exchange adsorption techniques and so on . among these procedures, membrane and ion exchange processes are not extremely regular because of its high establishment and support price. Other two techniques are extremely regular in indina. Nalgonda procedure is one of the well known strategies generally utilized for defluoridation of water as a part of developing nations, for example, India , Kenya, Senegal and Tanzania. Among different technique utilized for defluoridation water, the adsorption procedure is broadly utilized and offers acceptable results and is by all accounts more appealing techniques for the removal of fluoride regarding expense, straightforwardness of outline and operation. It is apparent from the literature study that different methods have indicated novel potential for the removal of fluoride. The purpose of study was to prepare Biosorbents (Agar-agar) from Algae collected from Chilika lake for defluoridation . The isotherm and kinetic indicated the adsorbent fitted well with Langmuir isotherm and freundlich isotherm kinetic adsorption model resepectively The result showed that the removal of fluoride by Biosorbent prepared id effective and could be used for defluoridation of drinking water.

KEYWORDS : Defluoridation,Adsorption ,Biosorbents (Agar-agar), TISAB, pH, Isotherm model

INTRODUCTION

Management of contaminants such as fluoride is a major public issue. Fluoride of geogenic origin in ground water used as a source of drinking water is a major concern because fluoride content above permissible levels is responsible for human dental and skeletal fluorosis [11,12]. Consequently, water sources containing elevated levels of fluoride have to be treated coagulation/precipitation, electro chemical, electrodialysis, reverse osmosis, adsorption and hybrid processes combining adsorption and dialysis are widely used deflu oridation techniques. Currently, however, the development of cost effective and clean processes due to economic constraints and stringent environmental policies is desired[21,22] . Adsorption technique is arguably one of the most versatile of all the defluoridation techniques due to a number of reasons such as cost , diverse end-uses, socio-cultural acceptance, regulatory compliance, environmental benignity and simplicity [6,7]. Accumulation of fluoride by algae had been studied extensively for biomonitoring or bioremediation purpose .

Having the advantages of low cost raw material, big adsorbing capacity, no secondary pollution , etc., algae may be used to treat industrial water containing heavy metals[36,37,38]. The adsorption processes were carried out in two steps: rapid physical adsorption first, and then slow chemical adsorption. pH is the major factor influencing the adsorption. The Freundlich equation fitted very well the adsorption isotherms. The uptake decreased with increasing ionic strength[9,10] . The principle mechanism of metallic cation sequestration involves the formation of complexes between a metal ion and functional groups on the surface or inside the porous structure of the biological material. The carboxy1 groups of alginate play a major role in the complexation[5,8]. Different species of algae and the algae of the same species may have different adsorption capacity. Their selection affinity for heavy metals was major criterion for the screening of a biologic adsorbent to be used in water treatment[23,24] .

The surface complex formation model (SCFM) can solve the equilibrium and kinetic problems in the biosorption. Adsorption is the bond of molecules species from bulk solution for a surface of of a solid by physical or chemical forces, Adsorption procedures include the water's entry through a contact bed where fluoride is removed by ion exchange or surface chemical reaction with the solid bed matrix. As contrast with different procedures of defluoridation ,adsorption method is prominent because of its straightforwardness and also accessibility of extensive variety of adsorbents[1,2].Adsorption onto solid surface is straightforward, flexible and suitable procedure for treating drinking water systems, particularly for small groups. Adsorption technique is efficient and can remove ions over an extensive variety of pH to a lower leftover concentration than precipitation. A few adsorbent materials have been attempted in tha past to check their possibilities and techno-economic feasibility as defluoridating specialists.

The poing of interest and restriction of adsorption are given below: Interest 1. Ease of operation 2.Adsorption procedure id worthwhile 3. High productivity for fluoride removal and can remove upto 90% fluoride. Adsorption is one of the most widely applied techniques for environmental remediation. Its kinetics is a great significance to evaluate the performance of a given adsorbent and gain insight into the underlying machanisms.An extensive increase in industrial activities and environmental accidents in recent year have greatly contributed to increasing metal pollution in water resources, thereby causing threats to terrestrial as well as aquatic life. The toxicity of metal pollution is slow and long lasting, as these metal ins are nonbiodegradable[13,14].

The most appropriate solution for controlling the biogeochemistry of metal contaminants to produce high-quality treated effluents from polluted waste waters is sorption technique. Agar-agar, a readily available seaweed, was used as sorbent for the removal of Mn (ll) and Co (ll) from aqueous media[41,42]. Batch experiments were performed to study adsorption as a function of process parameters: sorption time, initial pH, concentration of sorbate and sorbent[28,29,30].

MATERIALS AND METHODS

The sorption isotherm and kinetics experiments were performed by batch adsorption experiments and were carried out by mixing 1.25g (obtained by the study effect of adsorbent dose) of sorbent with 100 mL of sodium fluoride containing 3 mg/L as initial fluoride concentration. The mixture was agitated in a thermostatic shaker at a speed of 250 rpm at room temperature. The defluoridation studies were conducted for the optimization of various experimental conditions like contact time, initial fluoride concentration, adsorbent dose, particle size and influence of coions with fixed dosage[39,40]. The reagents used in this present study are of analytical grade. A fluoride ion stock solution (100 mg/L) was prepared and other fluoride test solutions were prepared by subsequent dilution of the stock solution. All the experiments were carried out at room temperature. Fluoride ion concentration was measured with a specific ion selective electrode by use of total ionic strength adjustment buffer ll (TISAB ll) solution to maintain pH 5-5.5 and to eliminate the interference effect of complexing ions[3,4]. The pH of the samples was also measured by Orion ion selective equipment. All other water quality parameters were analyzed by using standard methods. Kinetic studies of sorbent were carried out in a temperature controlled mechanical shaker. The effect of different initial fluoride concentration viz., 2,4,6,8 and 10 mg/L at four different temperatures viz., 303,313,323and 33k on sorption rate were studied by keeping the mass of sorbent as 1.25 g and volume of solution as 100ml in neutral pH.

Characterization of sorbents:

The X-ray diffraction (XRD) pattern of adsorbent was obtained using a Bruker AXS D8 Advance , Inst ID: OCPL/ARD/26-002 X-ray

diffractometer. Fourier transform infrared spectra were recorded using Nicolet 6700 , Thermo Electronic corporation USA made spectrophotometer. The scanning electron microscopy (SEM0) analysis performed using a Philips XL-20 electron microscope. Computations were made using Microcal Origin (Version 6.0) software[31,32,33]. The accuracy of fit are discussed using regression correlation coefficient (r) and chi-square analysis (SSE). The chi-square statistic test is basically the sum of the square of the difference between the experimental data and data obtained by calculating from the model , with each squared difference divided by the corresponding data obtained by calculating from the models[43] .

RESULT AND DISCUSSION
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 transmigration of adsorbate in the plane of a surface. The Langmuir equation is useful for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage expressed by:

$$q_e = \frac{q_m bc}{1+bc}$$

The linear of equation 1 is given as:

$$\frac{c_e}{q_e} = \frac{1}{q_m b} + \frac{c_e}{q_m}$$

Where, Ce is the equilibrium concentration of the adsorbate (mg/L), e q is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), qm and b are Langmuir constants related to adsorption capacity or the amount of a solute adsorbed per unit mass of the adsorbent for monolayer coverage of the surface and heat of adsorption or the binding strength, respectively[15,16,17]. The higher the value of b the higher is the affinity of the adsorbent for the adsorbate. The constants can be determined from the slope and intercept of the Ce/qe versus Ce plot. The slope of the straight line, gives 1/qm and the constant b can be determined from the intercept. Figure-2 shows Langmuir isotherm model fit.

for the experimental data. The result of the Langmuir isotherm model shows that the experimental data well fitted to the model with a correlation coefficient (R2) greater than 0.97. The maximum sorption capacity corresponding to complete monolayer coverage is found to be 18.62 mg F-/g and the constant b related to adsorption intensity is 0.3 83 L/mg.

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant, RL.

$$R_1 = \frac{1}{1+bc}$$

Where Co is the initial concentration in mg/L and b is the Langmuir constant (L/mg).

According to Hall *et al.* the parameter, RL indicates the shape of the isotherm such that:
if RL > 1 it is unfavorable,
if RL = 1 it is linear,
if RL = 0 < RL < 1 it is favorable.

Adsorption of fluoride on the adsorbent under the experimental conditions is favorable, as the value of RL in all cases is between 0 and 1.

Freundlich Isotherm
The basic assumption of this model is that there is an exponential variation in site energies of the adsorbent. The Freundlich equation is presented below in both the standard form and linearized form, respectively[25,26,27].

$$q_e = k_f C_e^{1/n}$$

Rearranging equation (4)

$$\log(q_e) = \log(k_F) + \frac{1}{n}\log(c_e)$$

Where,qe is the amount of fluoride adsorbed per unit mass of adsorbent (mg/g) at equilibrium, Ce is the equilibrium fluoride concentration (mg/L), KF and n are Freundlich constants indicative of adsorption capacity (mg/g) and adsorption intensity, respectively. When log (qe) versus log (Ce) is plotted a straight line with slope 1/n was obtained[19,20]. Thus, the constants adsorption intensity and adsorption capacity can be determined from the slope and intercept of the graph, respectively.

Figure-3 shows Freundlich isotherm model fit of the experimental data. TheFreundlichparameters along with correlation coefficients were obtained for the adsorbent (Table-2). The result indicated that the experimental fluoride adsorption data well fitted to this model with the correlation coefficient of 0.9529, suggesting that the average energy of adsorption is decreasing with increasing adsorption density witha minimum adsorption capacity of 4.48 mg/g and adsorption intensity, n of 1.67.The value of n obtained, lies between 1 and 10 indicating Freundlich favorable sorption[18,34,35]. Theincrease in equilibrium fluoride removal capacity with residual fluoride concentration observed indicated the heterogeneous nature of adsorbent surface which is characteristics of adsorption following Freundlich isotherm model fit.

Table-1: Pseudo-second Order Rate Constants, Rate Equations, Correlation Coefficients And Their Averages For The Three Different Initial Fluoride Concentrations Of Same Loadings

Initial F con. and adso. dose	k_2 (g mg⁻¹min⁻¹)	Rate equation	R^2
10 mg/L F with 1 g/L dose	2.1976×10^{-2}	$t/q_t = 0.5976 + 0.1146t$	0.9999
20 mg/L F with 2 g/L dose	3.6695×10^{-2}	$t/q_t = 0.3579 + 0.1077t$	0.9998
40 mg/L F with 4 g/L dose	4.5396×10^{-2}	$t/q_t = 0.2893 + 0.1040t$	0.9998
Average	3.4689×10^{-2}	$t/q_t = 0.4138 + 0.1088t$	0.9998

Table-2: Summary of Freundlich, Langmuir and Dubinin–Radushkevich isotherm model constants and correlation co efficients for adsorption of fluoride

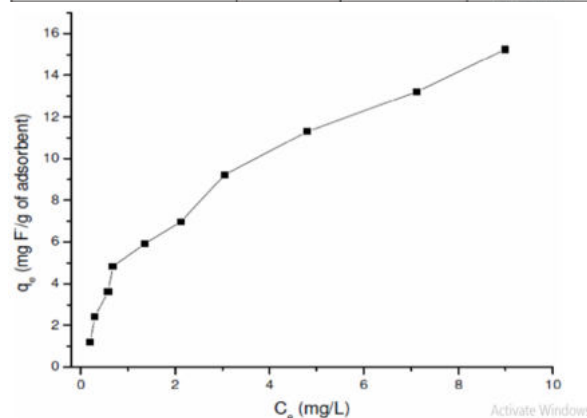| Isotherm model	Constants		Correlation coefficient (R^2)
Langmuir	b (L/mg)	q_m (mg/g)	0.9712
	0.38344	18.62	
Freundlich	K_F (mg/g)	n	0.9529
	4.48177	1.67	
Dubinin-Radushkevich (D-R)	q_s (mg/g)	E (kJ/mol)	0.9644
	99.87	9.71	

Fig.1: Adsorption isotherm of different initial F- concentration (Adsorbent dose = 4 g/L, contact time = 4 h, pH = 7.0 ± 0.20) (Data for triplicate measurements)
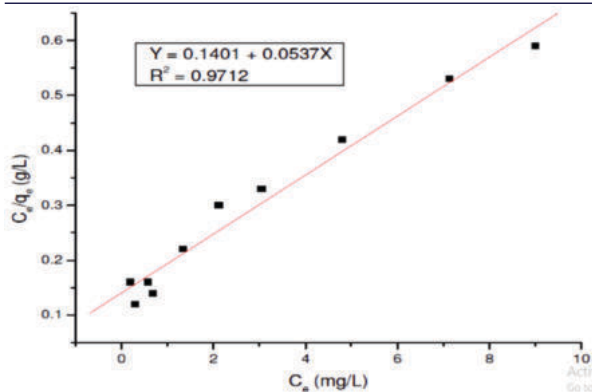
Fig. 2: Linear Langmuir isotherm (Adsorbent dose = 4 g/L, contact time = 4 h, pH = 7.0 ± 0.20)
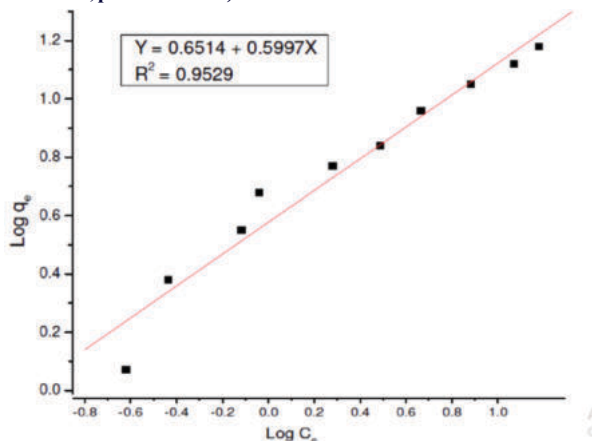

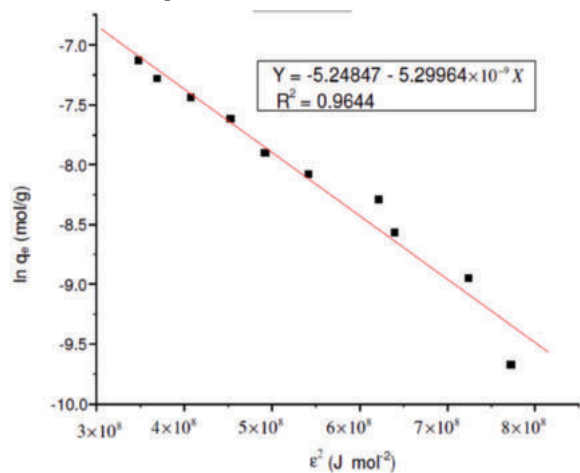**Fig.3 : Linear Freundlich isotherm (Adsorbent dose = 4 g/L, contacttime = 4 h, pH = 7.0 ± 0.20)**

Fig. 4 : Dubinin-Radushkevich isotherm (Adsorbent dose = 4 g/L, contact time =4 h, pH = 7.0 ± 0.20, T = 20°C)

CONCLUSION

Presence of excess fluoride in drinking water is responsible for various fluoride related diseases in community. The WHO prescribed limit for fluoride in drinking water is 1.5 mg L⁻¹. Ground water contributes nearly 80% of the drinking water requirement all over the world. Different processes as well as materials have been developed for removal of fluoride from drinking water/water bodies. The major techniques/methods include chemical reaction, adsorption, osmosis, and ion-exchange among which adsorption is the operationally most simple, cost effective and sustainable for use among community. Although a number of adsorbents with appreciable defluoridating capacity have been developed by various researchers/group of researchers, only a few are successful at implementation level due to various reasons. Thus, the specific conclusions can be summarized as follows:

High fluoride in ground water cause health hazard. In Odisha incidence of high fluoride content ground water (>1.5mg/L) is not

uncommon in both shallow and deeper water bearing zones. Fluoride data analysis of tube wells, open wells and river water of villages blocks and gram panchayats ranges from 1-6 (mg/L). In majority of the cases 1-1.5 (mg/L) was prevalent. However large number of cases starting from school children to old age people affected with dental and skeletal fluorosis. Fluoride concentration in water depends on several contributing factors such as pH, temperature, total dissolved solids, alkalinity and hardness. Various technologies are currently available to remove fluoride from water, but adsorption processes are generally considered attractive because of their effectiveness, convenience, ease of operation, simplicity of design and for economic and environmental reasons.

REFERENCES
1. A. M. Echavarria-Alvarez and A. Hormaza –Anaguano, "Flower wastes as a low-cost adsorbent for the removal of acid blue 9 ," Dyna, vol.81, no. 185, , pp. 132-137, 2014.
2. Agarwal, M., Rai, K., Shrivastav, R., Dass, S., (2003). Defluoridation of water using amended clay. *J. Cleaner Prod.* **11**, 439–444.
3. Alexei, G.P., Eugene, V.D., Oleg, A.S., Victor, V.A., Sergei, A.K., Roman, I.M., (2000). RO and NF membrane systems for drinking water production and their maintenance techniques. *Desalination* **132**, 315-321.
4. B. Bestani, N. Benderdouche, B. Benstaali, M. Belhakem, and A. Addou, "Methylene blue and iodine adsorption onto an activated desert plant," Bioresource Technology , Vol.99, no.17 , pp. 8441-8444,2008.
5. B. A. Fil, C. Ozmetin, and M. Korkmaz, "Cationic dye (methylene blue) removal from aqueous solution by montmorillon ite," Bulletin of the Korean chemical Society, vol. 33, no. 10, pp. 3184-3190,2012
6. Belachew, B., (1990). The occurrence and distribution of fluoride and fluorosis in Wonji Shoa Sugar Estate and adjacent areas. MA Thesis, Department of Geography, Addis Ababa University, Ethiopia.
7. Beneberu, S., Feleke, Z., Chandravanshi, B.S., (2006). Removal of excess fluoride from water by aluminium hydroxide. *Bull. Chem. Soc. Ethiop.* **20(1)**, 1–34.
8. Bishop, P.L., Sansoucy, G., (1978). Fluoride removal from drinking water by fluidized activated alumina adsorption, *J. Amer. Water Works Asso.* **70,** 554–559.
9. British Fluoridation Society, (2004). One in million, the facts about water fluoridation. British Fluoridation Society, London.
10. British Geological Survey, (2003). Water quality fact sheet: fluoride. British Geological Survey, London.
11. C. A. Nunes and M.C. Guerreiro, "Estimation of surgace area and Pore volume of activated carbons by methylene blue and iodine numbers," Quimica Nova, vol. 34, no. 3. pp . 472-476, 2011.
12. D. Das, D. P. Samal, and B. C. Melkep, "preparation of activated carbon from green coconut Shell and its characterization ,: Journal of Chemical Engineering & process Technology, vol. 6, no , pp . 1-7, 2015.
13. Fan, X., Parker, D.J., Smith, M.D., (2003). Adsorption kinetics of fluoride on low cost materials. *Water Res.* **37**, 4929 – 4937.
14. Feleke, Z., Mulugeta, E., Shimelis, B. Chandravanshi, B.S., (2008). Fluoride in groundwater in the Rift Valley Regions of Ethiopia: Problem and possible solutions. In Palanisami, K., Neupane, B., Thangarajan, M. (Eds.). Groundwater Quality and Environment (pp. 141-157). New Delhi: Rajiv Beri for Macmillan India Ltd.
15. Gaciri, S.J., Davies, T.C., (1993). The occurrence and geochemistry of fluoride in some natural waters of Kenya. *J. Hydrol.* **143**, 395-412.
16. Ghorai, S., Pant, K.K., (2005). Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina. *Separ. Purif. Technol.* **42**, 265–271.
17. Gopal, V., Elango, K.P., (2006). Equilibrium kinetics and thermodynamic studies of adsorption of fluoride onto plaster of Paris. *J. Haza. Mat.* **32**, 1-8.
18. Hall, K.R., Eaglton, L.C., Acrivos, A., VerMeulen, T., (1966). Pore and solid diffusion kinetics in fixed bed adsorption render constant–pattern condition. *Ind. Eng. Chem. Fundam.* **5(2)**, 212-223.
19. Harrison, P.T.C., (2005). Fluoride in water: A UK perspective, *J. of fluorine chem.* **126**, 1448-1456.
20. Hubaux, N., (2006). An investigation of calcium phosphate for drinking water defluoridation, MSc Thesis (unpublished), Federal polytechnic college of Lausanne, Switzerland.
21. Hem, J.D., (1989). Study and Interpretation of the Chemical Characteristics of Natural Water. Water Supply Paper 2254, 3rd edition, U.S. Geological Survey, Washington.
22. Heikens, A., Sumarti, S., Van Bergen, M., Widianarko, B., Fokkert, L., Van Leeuwen, K., Seinen, W., (2005). The impact of the hyperacid Ijen Crater Lake: risks of excess fluoride to human health. *Sci. Tot. Environ.* **346**, 56-69.
23. Hering, J.G., Chiu, V.Q., (2000). Arsenic occurrence and speciation in municipal ground water based supply system. *J. Eng.* **26(5)**, 471 – 474.
24. Hobson, J.P., (1969). Physical adsorption isotherms extending from ultrahigh vacuum to vapor pressure, *J. Phys. Chem.* **73,** 2720 – 2727.
25. I. Ali, M, Asim , and T. A . Khan , "Low cost adsorbents for the removal of organic pollutants from wastewater," Journal of Environmental Management, vol. 113. pp. 364-370, 2012.
26. M. A. Ahmad and N.K. Rahman, "Equilibrium, kinetic and thermodynamic of remazol brilliant orange 3R dye adsorption on coffee husk –based activated carbon," Chemical Engineering Journal, vol. 170, no. 5, pp .170-183,2012
27. M. Habuda –Stanic, M. E. Ravancic, and A. Flanagan , "A review on adsorption of fluoride from aqueous solution," Materials, vol7, pp . 1857-1866, 2015
28. M.E. Kaseva, "Optimization of regenerated bone char for fluoride removal in drinking water: a case study in Tanzania," Journal of Water and Health, vol. 4, no. 1, pp. 139-147,2006.
29. N. Chen, Z. Zhang, C. Feng, N. Sugiura, M. Li, and R. Chen, "Fluoride removal from water by granular ceramic adsorption," Journal of colloid and Interface Science, vol. 348, no.2, pp. 579-584,2010.
30. Q. Hu, N. Chen , C. Feng, and W.W. Hu, "Nitrate adsorption from aqueous solution using granular chitosan-Fe 3+ complex," Applied Surface Science, vol. 347,pp. 1-9, 2015.
31. R. H. Gumus and I. Okpeku, "Production of activated carbon and characterization from

snail shell waste (<> Helix</i> <i>pomatia&;/i>),)" Advances in chemical Engineering and science, vol. 5, no. 1, pp. 51-61,2015.

32. S. Mopoung, P. Moonsri, W. Palas, and S. Khumpai, "Characterization and properties of activated carbon prepared from tamarind seeds by KOH activation for Fe(III) adsorption from aqueous solution," The scientific World Journal, vol . 2015, Article ID 415961, 9 Pages, 2015

33. T. Getachew, A. Huseen, and V.M. Rao, "Defluoration of water by activated carbon prepared from banana (Musa paradisiacal) peel and coffee (Coffea Arabica) husk," International journal of Environmental Science and Techonology, vol. 12, no.6, pp. 1857-1866,2015.

34. T. Shalna and A. Yogamoorthi, "preparation and characterization of activated carbon from used tea dust in comparison with commercial activated carbon," International Journal of Recent Scientific Research, vol. 6 , no. 2, pp. 2750-2755,2015.

35. WHO (2008). Guidelines for drinking water quality. 3rd Edition. Incorporating the 1st and 2nd Addenda, Volume 1, Recommendations. Geneva: WHO.

36. Wieprecht, T., Apostolov, O., Beyermann, M. and Seelig, J. (2000). Membrane binding and pore formation of the antibacterial peptide PGLa: thermodynamic and mechanistic aspects. *Biochemistry.,* 39: 442-452.

37. Wondwossen Fantaye (2004). Dental Fluorosis in Ethiopia: An assessment of dental fluorosis and relation to dental caries as well as the social acceptance of fluorotic teeth in rural and urban areas. Faculty of Dentistry, University of Bergen, Ph.D thesis, Bergen, Norway.

38. Yalemtsehay Mekonnen (1999). Effects of ethanol extract of *Moringa stenopetala* leaves on Guinea – pig and Mouse smooth muscle. *Phytother. Res.*, 13: 1 – 3.

39. Yalemtsehay Mekonnen (2005). The multi–purpose *Moringa* tree: Ethiopia. examples of the development of pharmaceutical products from medicinal plants. *UN development program, New York,* 10: 111-117.

40. Yalemtsehay Mekonnen and Amare Gessesse (1998). Documentation on the use of *Moringa stenopetala* and its possible Antileshmanial and Antifertility Effects. *SINET: Ethiop. J. Sci.*, 21(2): 287 – 295.

41. Yalemtsehay Mekonnen and Dräger, B. (2003). Glucosinolates in *Moringa stenoptetala*. *Planta Med*, 69: 380 – 382.

42. Yalemtsehay Mekonnen, Yardley, V., Rock, P. and Croft, S. (1999). *In vitro* Antitrypanosomal activity of *Moringa stenopetala* leaves and roots. *Phytother. Res.*, 13: 538–539.

43. Zabban, W. and Jewett, H.W. (1967). The treatment of fluoride wastes. Proceedings, 23rd Purdue Industrial Waste Conference, No. 2–4: 706–715.