REMOVAL OF FLUORIDE FROM SYNTHETIC WASTE WATER BY USING "BIO-ADSORBENTS"

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Abstract

The aim of this research work is to design and develop a novel, cost effective strategy for fluoride removal from industrial waste water. This study investigates the feasibility of three low-cost biomass based adsorbents namely: banana peel, groundnut shell and sweet lemon peel for industrial waste water defluoridation at neutral PH range. Action of these adsorbents on fluoride was compared with commercially available adsorbents. It was found to be much better, high removal efficiency at higher concentration (20 mg/l) of fluoride in industrial waste water. The banana peel, groundnut shell and sweet lemon peel removed 94.34, 89.9 and 59.59 %respectively. Contact time for banana peel, groundnut shell, and sweet lemon peel are 60.0, 75.0, and 40 min respectively at doses of 14, 12 and 16 gm/l respectively. Mechanism of adsorption kinetics was found pseudo-second order reaction, and the mechanism of fluoride removal on adsorbents was found to be complex. The surface adsorption as well as intra-particle diffusion contributes to the rate-determining step.

***Keywords**: Sodium Fluoride, hydrochloric acid, sodium hydroxide, pore milli water, Bio-adsorbents, SPDNS solution*

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1. INTRODUCTION

Fluoride is important as well as toxic for the human health. Its higher concentration in water creates health problems. The concentration between the ranges of 0.8 mg/l to 1.0 mg/l is beneficial for reducing dental caries and helps in improvement of bones [1-4]. Many evidences prove that higher concentration of fluoride in water produces harmful effects on dental system. The lack of Ca, protein and vitamins in the diet are due the adverse effect of high concentration of fluoride [5-6].High F^- concentration also leads to various diseases like osteoporosis, arthritis, brittle bones, cancer, infertility, brain damage, alzheimer syndrome, and thyroid disorder [7-8].The suitable fluoride concentration in drinking water is in the range of 0.5 mg/l to 1.5 mg/l (WHO). World-wide 200 million people are affected by the dental fluorosis (Mohan et al., 2012).In India, the maximum permissible limit of fluoride according to World Health Organization is 1.5 mg/l. Safe disposal of fluoride from the industrial waste water is very critical environmental task for the industries. Large part of the waste water is treated by lime softening method to reduce the excess fluoride concentration. It reduces the fluoride concentration by approximately 10-20 mg/l from the waste water. Thus, further operation is necessary to reduce the fluoride concentration to acceptable level (1.5 mg/l). For further removal of F^-, co-precipitation of fluoride with Al^{3+}isextensively employed but this method generates very large amount of sludge [9-10]. Glass and ceramic production, semiconductor manufacturing, electroplating, coal fired power stations, beryllium extraction plants, brick and iron works, and aluminium smelters etc release high fluoride concentration in waste water [11-12].

Ion exchange method and membrane technologies including reverse osmosis and nano-filtration have been successfully implemented in the removal of trace fluoride concentrations. However, these methods are expensive and energy consuming [13–14]. All these processes are not much efficient as comparable to the adsorption techniques. Adsorption process, quite attractive, simple and low cost of design and more variety of adsorbent make its convenient method for defluoridation. Conventional adsorbents have been used for defluoridation for long. These adsorbents cause adverse effect on health and are highly costly but the use of bio-adsorbents have no adverse effects on health and render good water quality.

2. MATERIALS AND METHODS

2.1 Preparation of Banana Peel Adsorbent Treated with Hydrochloric Acid

Banana peels are collected from the local seller of banana. After the collection of peel it is washed three times from the tape water to remove the dust. Banana peels are primarily dried in the sun light for two days and then dried in hot air oven in the range of 80^oC-100 ^0C for 36 h. Dried banana peels crushed in a jaw crusher and then sieved by 510 μm ASTM mesh. Screened material is treated with 0.1 M hydrochloric acid for 24 h. After treatment with acid, treated material is washed many times to make it neutral. Washed material is then dried in hot air oven at 110°C for 24 h. The material is subsequently placed in an airtight container for further use.

2.2 Preparation of Sweet Lemon Peel Adsorbent

It's collected from the juice making shop of Rookie, washed in tape water and dried in sun light for four days. This material is dried in the hot air oven for two days at 120 ᶜo. Dried Material crushed in jaw crusher and then sieved in 510 µm mesh ASTM. Sieved material is collected for further use.

2.3 Preparation of Groundnut Shell Adsorbent

Collected shell of groundnut simply washed with tape water and dried in sun light for two days. Dried sample is again dried in hot air oven at 100 ᶜo for 24 hr. This material is crushed in jaw crusher and screened in 510 µm mesh ASTM, screened material is then placed in container for further use.

2.4 Adsorption Experiments

The stock solution of 100 mg L^{-1} fluoride was prepared by dissolving 221 mg of anhydrous NaF in one litre of distilled water. Test solution of 20 mg L^{-1} fluoride concentration was prepared from stock solution. Selected concentration is the normal fluoride concentration in industrial waste water.250 ml conical flask is used for the experimental work for batch studies .Experiment is carried out with 50 ml of the test solution at (30±1) ᶜo in conical flask in horizontal incubator shaker. At the end of desired contact time, the conical flasks were removed from the shaker. Subsequently, samples were filtered using Whatman No. 42 filter paper and filtrate was analysed for residual fluoride concentration by SPADNS method. Batch study was conducted to determine the optimum condition for the fluoride removal to make the efficient technique. Optimization and the effects of adsorbent dose, pH, contact time and initial fluoride concentration on adsorption were studied by varying various parameters. pH was adjusted using 0.1 N HCl or 0.1 N NaOH.

3. RESULTS AND DISCUSSION

3.1 Effect of pH

The effect of pH on removal of fluoride was studies in the range of 2-12 and results are illustrated in the Fig-1.

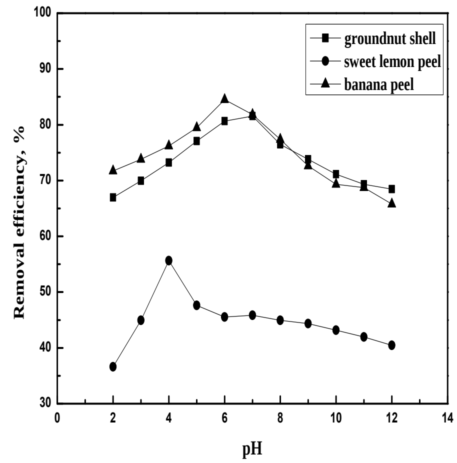

Fig-1: Removal efficiency verses pH

pH plays an important role in adsorption process on bio adsorbents. The removal efficiency of the adsorbents is concluded that, it is depending on the pH of the test sample of fluoride, as shown in Fig.1. The results confirm a strong dependence between the adsorption of fluoride and pH, whereby adsorption appears to increases with increasing pH, within a pH range of 1–7. Maximum adsorption was observed at a pH of 7, 6and 4 for groundnut shell, banana peel and sweet lemon peel respectively in 1.5 hr. Several researchers reported that biosorption process is reliant on the aqueous phase pH, and the functional groups on the biosorbent, and their ionic states (at particular pH) [15, 16, 17].In most of the biosorption process micro molecules have groups such as amino, carboxyl, thiol, alcohol, phenol, and phosphate. Biosorption is carried out by the protonation and deprotonation of functional groups on the surface of bio adsorbent [18].pH of the solution governed the ionic form of fluoride in solution and the electrical charge (i.e. functional groups carrying polysaccharides and proteins) on the biosorbent. Where it shows that the overall charge on the surface of bioadsorbent is positive. Positive charge binds the negatively charged fluoride ions. In the case of groundnut no effect of pH was observed because it shows the adsorption at neutral pH of 7.It means the surface of groundnut is cationic type ($H^{+)}$ [19]. At the lower value of pH (< 7) the surface of the adsorbent gets positively charged and sorption of fluoride occurred, probably anionic exchange sorption. In acidic medium because of the protonation, action on the surface functional groups such as amino, carboxyl, thiol, etc., imparts positive charge on the surface.

Relative sorption inhibition occurred at basic pH (>7) range, might be assign to the increase of hydroxyl ion leading to formation of aqua-complexes; thereby, desorption occurred [19].

According to the study of pH optimization, adsorption of bio adsorbent mostly observed in the acidic range of the pH But removal of fluoride in our case has observed in less acidic range which is more beneficial and cost effective for the removal.

3.2 Dose Optimization

Removal efficiency of fluoride is strongly dependent on concentration of adsorbent dose in test sample. Removal of fluoride increases as increasing dose of adsorbent in the sample as shown in Fig-2.

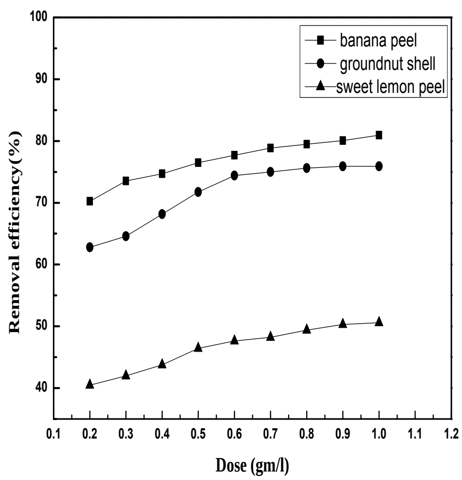

Fig-2: Removal efficiency verses dose

At the starting, removal of fluoride increases as increasing the dose until a some extent after that very slightly change in the removal of fluoride it means, the curve lapse as flat indicating the higher fluoride adsorption occurs at their maximum dose and the removal remains constant. Adsorbents have a higher availability of surface and pore volume because of this adsorption increases after that adsorption of fluoride is constant at higher dose because of saturation of pore volume and surface. Efficiency for groundnut, banana peel and sweet lemon peel increases from 62.79 to 76.59, 70.23 to 80.95 and 40.47 to 50.59 respectively for the dose range 2-20 gm/l. But there are no significant changes in removal efficiency for fluoride from the dose 12-20,16-20 and 14-20 gm/l for groundnut, sweet lemon peel and banana peel respectively. This is happened because of the overlapping of active sites at higher dosage, thus reducing of the net surface area [20].

3.3 Effect of Contact Time

It is observed that the exclusion of fluoride ions increases with increase in contact time to some level at optimum pH and dose. Further increase in contact time does not increase the uptake due to deposition of fluoride ions on the available adsorption pore volume and surface area on bio adsorbent materials as shown in Fig.3

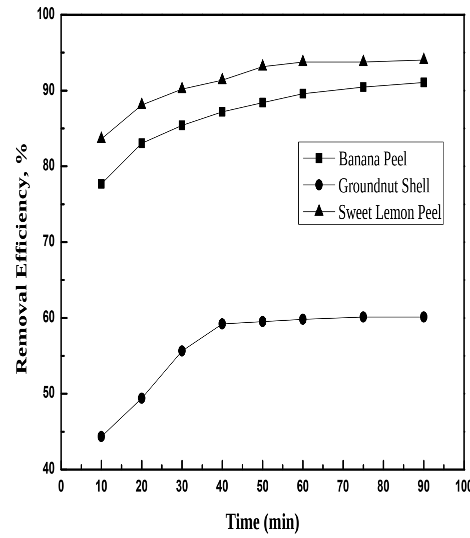

Fig-3: Removal efficiency verses time

Fig-3 explains the optimum percentage removal of fluoride by three considered bio adsorbents at different contact times. However, it progressively approached an almost steady value, denoting accomplishment of equilibrium. In the current case, the equilibrium times were obtained at 40, 60, and 75 min for sweet lemon peel, banana peel and groundnut shell correspondingly. The initial peak portion revealed the high sorption uptake of the fluoride ions on to adsorbents. The second stage assigns the sluggish uptake of fluoride ions that showed the utilization of all active sites over the adsorbents surface and accomplishment of saturation or equilibrium stage. The third stage indicated the equilibrium stage in which, the sorption uptake was relatively small [21].

3.4 Effect of Initial Fluoride Concentration

The outcome of initial fluoride concentration was investigated at their optimum dose, pH and contact time on adsorbents onto different concentration of fluoride solutions (10, 15, 20, 25, 30 mg L^{-1}). Fig.4 describes the effect of initial fluoride concentration on the fluoride removal efficiency, the results illustrated that fluoride removal efficiency was decreased by increasing the initial fluoride concentration because of the fixed dose of adsorbent capacity adsorbents gets saturated at high concentration.

Pore volume and active sites of the adsorbents filled by the fluoride finally its removal is decreased. Similar trend has been reported for fluoride removal by using Neem charcoal (Chakrabarty and Sarma, 2012) [22].

Where Ci and Ce are initial and final fluoride concentrations respectively is the volume of the solution (L), and m is mass of the adsorbent (g).

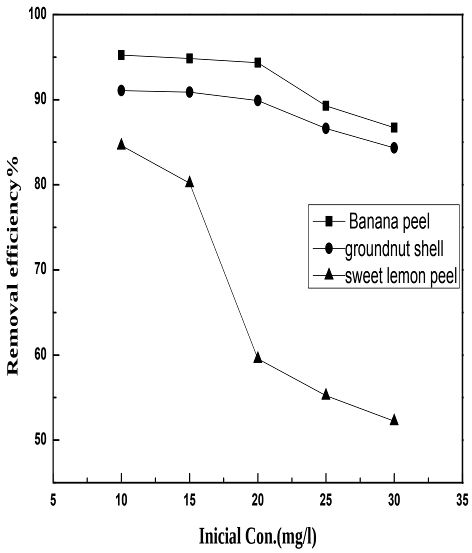

Fig-4.1: Removal efficiency verses Initial concentration

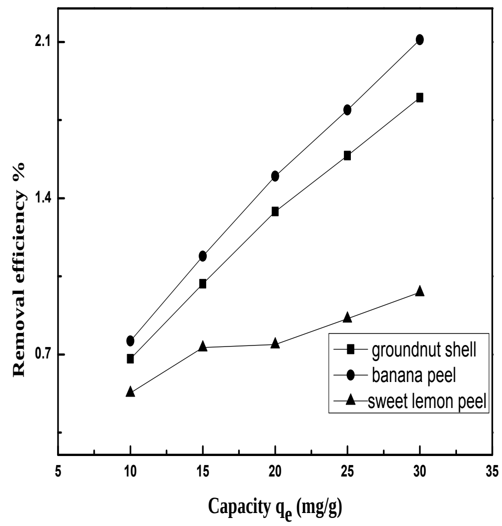

Fig-4.2: Removal efficiency verses Equilibrium capacity

The adsorption capacity of fluoride adsorbed per unit adsorbent (q_e) (mg g^{-1}) was calculated according to following Equation:

$$q_e = \frac{(C_o - C_e)}{m} V$$

The results of Fig. 4.2 reveal that the quantity of adsorbed fluoride increased with the increase in fluoride initial concentrations. Adsorption capacity of groundnut shell is maximum out of three adsorbent because of its lower adsorbent dose (mg) and high removal efficiency of banana peel

Table-1: Table for optimization parameters for different adsorbents

Adsorbents	pH	Contact time(min)	Dose (gm/l)	Concentration (mg/l)	Adsorption Capacity (mg/g)	Removal Efficiency (%)
Groundnut shell	7.0	75	12.0	20.0	1.498	89.90
Banana peel	6.0	60	16.0	20.0	1.340	59.55
Sweet lemon peel	4.0	40	14.0	20.0	0.744	94.34

3.5 Adsorption Kinetics

Mechanism of adsorption of fluoride is explained by the adsorption kinetics. Adsorption kinetics models are pseudo-first-order, pseudo-second-order and intraparticle diffusion. Studies of these models explain the adsorption behaviour of fluoride on bio adsorbents.

Pseudo-first order model:

$$\log(qe - qt) = logqe - \frac{K1}{2.303} t$$

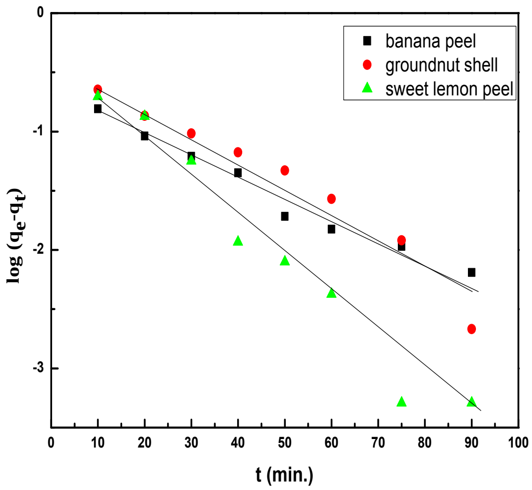

Fig-5: Plot for pseudo first order kinetics

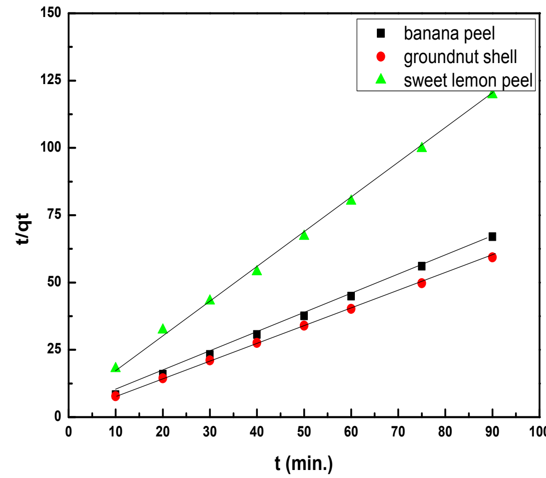

Fig-6: Plot for pseudo second order kinetics

Pseudo-second-order model:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2\, q_e^2}$$

Where q_e and q_t (both in mg g−1) are the amount of fluoride adsorbed at equilibrium and at time correspondingly. K_1 (min−1) and K_2 (g mg^{-1} min^{-1}) are the kinetics rate constants for the pseudo first- and second order models, correspondingly.

By using the above graph the rate contant (k) of fluoride sorption for all adsorbents were calculated with the help of ploting the graphwhich are given below in table

Table 2:kinetics parameters for pseudo first order and second order reaction

Adsorbents	Pseudo first order			Pseudo second order		
	K_1	**q_{ecal}**	**R^2**	**K_2**	**q_{ecal}**	**R^2**
Banana peel	0.039	0.202	0.974	0.434	1.369	0.999
Groundnut shell	0.053	0.485	0.948	0.254	1.557	0.999
Sweet lemon peel	0.086	0.509	0.966	0.295	0.795	0.998

From the above table, data show that the best model for the adsorption for all adsorbent is pseudo-second-order. Adsorption follows the pseudo-second-order kinetic because of the better result for all adsorbents

Rate limiting step is necessary to determine for adsorption study. External mass transfer, Intra-particle diffusion are two methods to explain the solid –liquid adsorption process for a solute. Intra-particle diffusion occurs in the case of high speed of agitation (120 rpm) of solid liquid test sample during the experiment. At very high agitation speed, it was reasonable to assume that mass transfer occurred from bulk of liquid to the particle adsorbents, external surface was not limiting the rate. Yadov et al. explain the rate limiting step might be both surface and Intra particle diffusion [24]. The double nature of the diffusion was explained by the McKay in his research, first linear portion of the plot depicts the boundary layer diffusion and second part of the linear portion depicts the intra-particle diffusion[25]

$$q(t) = Xi + Kp * t^{0.5}$$

Where q (t) adsorption capacity (mg/g), Kp(mg×g−1×min−$^{0.5}$) diffusion constant and Xi (mg/g) is maximum capacity in case of intra particle diffusion.

From the Fig-7 we have calculated the values of equation parameters (Xi, Kp) for all the adsorbents which are given in table 3

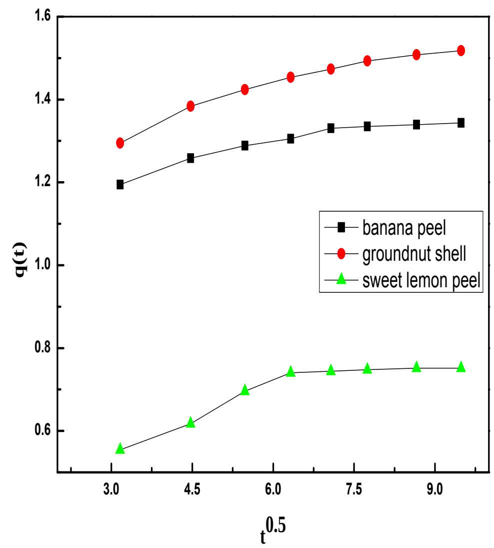

Fig-7: Adsorption Capacity verses time.

Table 3: Model parameter for intraparticle diffusion

Adsorbent	Kp	Xi R^2
Banana peel	**0.026**	**1.1320.921**
Groundnut peel	**0.033**	**1.221 0.929**
Sweet lemon peel	**0.494**	**0.494 0.803**

3.6 Isotherm Model

All the models are explained in their linearized form. We have study three models for the adsorption characteristics, Langmuir, Freundlich and Temkin.

Langmuir model in linearized form:

$$\frac{Ce}{qe} = \frac{Ce}{q_m} + \frac{1}{bq_m}$$

Where Ce (mg/l) is equilibrium concentration, q_m(mg/g)maximum adsorption capacity b is a constant. The magnitude of *b* reflects the slope of the adsorption isotherm which is a measure of adsorption affinity coefficient (Lmg^{-1}).

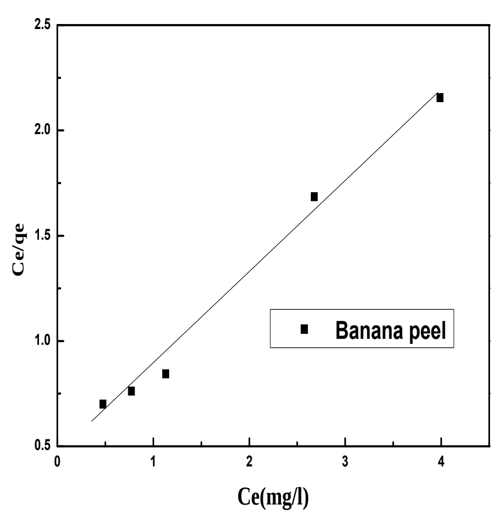

Fig-8 a: Langmuir isotherm model plot for banana peel

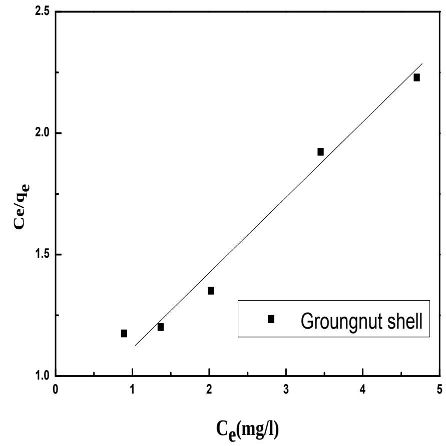

Fig-8 b: Langmuir isotherm model plot for grountnut shell

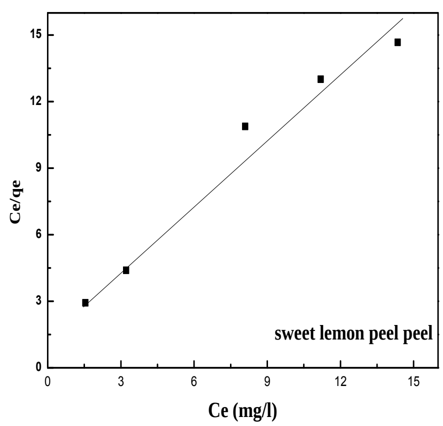

Fig-8 c: Langmuir isotherm model plot for sweet lemon peel

Fig-8a,b and c linear plots of the langmuir isotherm model for banana peel, ground nut shell and sweet lemon peel.

By comparing the slope of the line ($1/q_m$) and intercept ($1/bq_m$) with above plots, we have calculated the values of adsorption parameters q_m (mg/g) and b (Lmg^{-1}) for all adsorbents which are tabulated in table 4.

The linearized Freundlich equation is given as:

$$\log(x/_m) = logKf + \frac{1}{n}\log(Ce)$$

where *x* is the amount of solute adsorbed (mg), *m* the mass of adsorbent used (g), *C*e the equilibrium solute concentration in solution (mg/l) and *K*f (g^{-1}) a constant, which is a measure of adsorption capacity and 1/*n* is a measure of adsorption intensity. The values of *K*f and *n* were obtained from the slope and intercept of the plot between log (*x*/*m*) and log*C*e. The Freundlich equation deals with physico-chemical adsorption on heterogeneous surfaces.

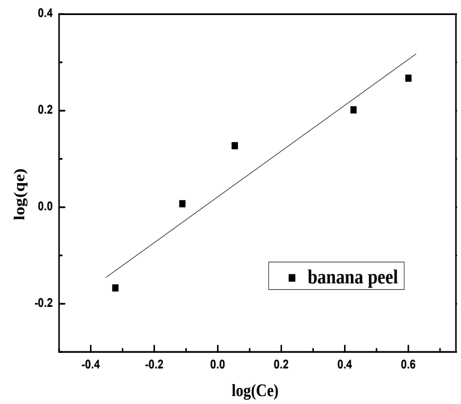

Fig-9 a: Fruendlitch isotherm model plot for banana peel

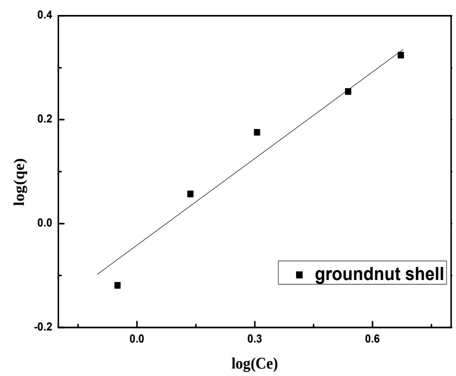

Fig-9 b: Fruendlitch isotherm model plot for groundnut shell

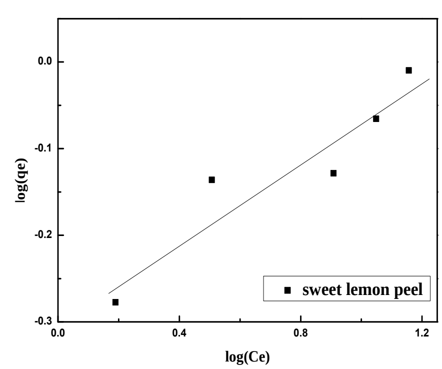

Fig-9 c: Fruendlitch isotherm model plot for sweet lemon peel

Fig.9.a,9.b and 9.c linear plots of the freundlich isotherm model for banana peel, ground nut shell and sweet lemon peel. By comparing the slope of the line (1/n) and intercept (log kf) with above plots, we have calculated the values of adsorption parameters n and Kf (g^{-1}) for all adsorbents which are tabulated in table 4.

Temkin model equation is given as:

$$qe = \frac{RT}{b_T}\ln(A_T) + \frac{RT}{b_T}\ln(Ce)$$

Where R is the gas Constant, T is temperature (K), Ce equilibrium concentration (mg/l) and A_T, b_T are the adsorption constants.

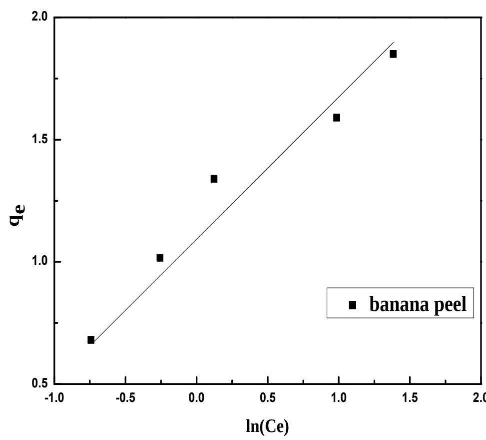

Fig-10 a: Temkin isotherm model plot for banana peel

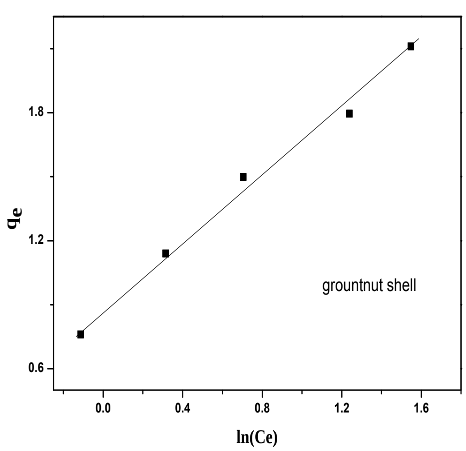

Fig-10 b: Temkin isotherm model plot for groundnut shell

Fig-10 a, 10 b and 10 c linear plots of the Temkin isotherm model for banana peel, ground nut shell and sweet lemon peel.By comparing the slope of the line (RT/b_T) and intercept ($RT/b_T \ln(A_T)$) with above plots, we have calculated the values of adsorption

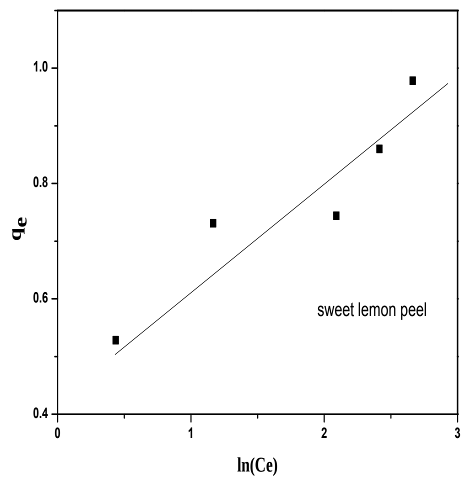

Fig-10 c: Temkin isotherm model plot for sweet lemon peel

Parameters b_T and A_T for all adsorbents which are tabulated in table 4.

All the adsorption parameters have calculated from the linear plots of models which are given below in table 4.

Table-4: Isotherm parameter for all adsorbents

Adsorbent	Langmuir			Freundlich			Temkin		
	b	q_m	R^2	K_F	n	R^2	A_T	b_T	R^2
Banana peel	**0.993**	**2.283**	**0.989**	**1.037**	**2.314**	**0.914**	**9.032**	**4860.86**	**0.967**
Groundnut shell	**0.359**	**3.344**	**0.979**	**0.893**	**1.709**	**0.959**	**3.060**	**3207.55**	**0.992**
Sweet lemon peel	**0.544**	**1.037**	**0.971**	**0.500**	**4.291**	**0.883**	**16.693**	**14987.6**	**0.872**

By comparing the correlation coefficients R^2 values, we can see the correlation coefficients are more than 0.97 for Langmuir and other rest of the model have less value as compare to langmuir isotherm model. So the best fit model for all adsorbents is Langmuir adsorption model. It informs the adsorption experimental data was fitted well by the Langmiur isotherm.

4. COMPARATIVE DATA OF DIFFERENT BIO ADSORBENTS

Table-5: Comparison of the defluoridation efficiency of different biomass based sorbents

Adsorbent	Initial Fluoride Conc.(mg/l)	pH	% Removal	References
Sawdust raw	5	6.0	49.80	K.Y.Ashishet.al
Wheat straw raw	5	6.0	60.20	K.Y.Ashishet.al
Activated bagasse carbon	5	6.0	56.40	K.Y.Ashishet.al
Neem peepal	5	2.0	84.90	A.R.Tembalkar
Available activated Carbon	5	6.0	57.60	K.Y.Ashishet.al
Sweet lemon peel	20	4.0	59.55	Current
Groundnut shell	20	7.0	89.90	Current
Banana peel	20	6.0	94.34	Current

5. CONCLUSIONS

Biomass adsorbents were studied for the removal of fluoride on synthetic waste water assuming as industrial waste water. The conclusion drained from the experiment is given below:

1. The banana peel, groundnut shell and sweet lemon peel removed 94.34, 89.9 and 59.59 %respectively from an aqueous solution of 20 mg L^{-1} fluoride at pH of 6.0, 7.0 and 4.0 respectively.Contact time for banana peel, groundnut shell, and sweet lemon peel are 60.0, 75.0 and 40 min and dose 14,12 and 16 gm/l respectively.
2. Mechanism of adsorption kinetics was found pseudo-second order reaction, and themechanism of fluoride removal on adsorbents was found to be complex. The surface adsorption as well as intra-particle diffusion contributes to the rate-determining step.
3. High removal efficiency of adsorbent banana peel and groundnut shell,andpresence of others ions in groundwater did not significantly affect the deflouridation process
4. Adsorption isotherm models langmuir, fruendlich and temkin were studies,out of these the best plots for adsorption isotherm was langmuir model.

REFERENCES

[1]. N.C.R. Rao, Fluoride and environment—a review, in: M.J.V. Bunch, M. Suresh,T.V. Kumaran (Eds.), Proceedings of third international conference on environment and health, York University, Chennai, India, 2003.
[2]. P.T.C. Harrison, Fluoride in water: a UK perspective, J. Fluorine Chem. 126(2005) 1448–1456.
[3]. M.W. Edmunds, P.L. Smedley, Fluoride in natural waters, in: O. Selinus (Ed.),Essentials of Medical Geology, Elsevier Academic Press, Burlington, MA, 2005,pp. 301–329.
[4]. J. Doull, K. Boekelheide, B.G. Farishian, R.L. Isaacson, J.B. Klotz, J.V. Kumar et al.,Fluoride in drinking water: a scientific review of EPA's standards, Committeeon Fluoride in Drinking Water, Board on Environmental Studies and Toxicology, Division on Earth and Life Sciences, National Research Council ofThe National Academies
[5]. G. Jacks, K. Rajagopalan, T. Alveteg, M. Jonsson, Genesis of high-Fgroundwaters, Southern India, Appl. Geochem. 2 (1993) 241–244.
[6]. Y. Li, C.K. Liang, P.B. Katz, S. Niu, S. Cao, G.K. Stookey, Effect of fluoride exposure and nutrition on skeletal fluorosis, J. Dent. Res.75 (1996) 2699

[7]. N.J. Chinoy, Effects of fluoride on physiology of animals and human beings, Indian J. Environ. Toxicol. 1 (1991) 17–32.
[8]. P.T.C. Harrison, Fluoride in water: a UK perspective, J. Fluorine Chem. 126 (2005) 1448–1456.
[9]. C.J. Huang, J.C. Liu, Precipitation floatation of fluoride containing waste water Fromsemiconductor manufacturer, Water. Res. 33 (1999) 3403–3412.
[10]. S. Meenakshi, N. Viswanathan, Identification of selective ion-exchange resin for fluoride sorption, J. Colloid Interface Sci. 308 (2007) 438–450.
[11]. L.A. Richards, M. Vuachere, A.I. Schafer, Impact of pH on the removal of Fluoride, nitrate and boron by nanofiltration/reverse osmosis, Desalination 261 (2010) 331–337.
[12]. B.D. Turner, P. Binning, S.L.S. Stipps, Fluoride removal by calcite: evidence of Fluoride precipitation and surface adsorption, Environ. Sci. Technol. 39 (2005) 9561–9568.
[13]. F. Shen, X. Chen, P. Gao, G. Chen, Electrochemical removal of fluoride ions from industrial wastewater, Chem. Eng. Sci. 58 (2003) 987–993
[14]. G. Zhang, Y. Gao, Y. Zhang, P. Gu, Removal of fluoride from drinking water by membrane coagulation reactor, Desalination 177 (2005) 143–155.
[15]. S. Meenakshi, R.C. Maheswari, Fluoride in drinking water and its removal, J. Hazard.Mater. B137 (2006) 456–463.
[16]. Prakasam, R.S.,Chandrareddy, P.L.,Manisha, A., Ramakrishna, S.V., 1998. Defluoridation of drinking water using eichhornia sp. IJEP 19, 119–124. fluoride increases the skeleton and dental fluorosis.
[17]. Mohan, S.V., Bhaskar, Y.V., Karthikeyan, J., 2003. Biological decolorization of simulated azo dye in aqueous phase by algae Spirogyra species Int. J. Environ Poll 21, 211–222
[18]. Mohan, S.V., Karthikeyan, J., 1997. Removal of lignin and tannin aqueous solution by adsorption onto activated charcoal Environ Poll 97, 183–197.
[19]. Ilhami, T., Gulay, B., Emine, Y., Gokben, B., 2005. Equilibrium and kinetic studies on biosorption of Hg(II), Cd(II) and Pb(II) ions onto micro algae Chlamydomonasreinhardtii. J. Environ. Manag. 77, 85–92.
[20]. Mohan, S.V., Karthikeyan, J., 1997. Removal of lignin and tannin aqueous solution by adsorption onto activated charcoal Environ Poll 97, 183–197.
[21]. Killedar, D.J., Bhargava, D.S., 1993. Effects of stirring rate and temperature on fluoride removal by fishbone charcoal Ind. J. Environ. Health 35, 81–87.
[22]. Ramanaiah, S.V., Mohan, S.V., Sarma, P.N., 2007. Adsorptive removal of fluoride from aqueous phase using waste fungus (Pleurotusostreatus 1804) biosorbent: kinetics evaluation. Ecol. Eng. 31, 47–56.
[23]. Chakrabarty, S., Sarma, H.P., 2012. Defluoridation of contaminated drinking waterusingneem charcoal adsorbent: kinetics and equilibrium studies. Int. J. Chem.Tech. Res. 4, 511–516.
[24]. Yadav, A.K., Kaushik, C.P., Haritash, A.K., Kansal, A., Rani, N., 2006. Defluoridation of groundwater using brick powder as an adsorbent. J. Hazard. Mater. 128, 289–293.
[25]. McKay, G., Otterburn, M.S., Sweeny, A.G., 1980. The removal of color from effluent using various adsorbents III. Silica: rate processes. Water Res. 14, 15–20.