

Defluoridation of Water Using Bioadsorbents : Kinetic Study



Chemistry

KEYWORDS : GL (Guava Leaf), NL (Neem Leaf), NB (Neem Bark), RH (Rice Husk), BB (Black Berry).

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ABSTRACT

The process of removal of excess fluoride from water is described as defluoridation. One of such method is adsorption. Present study has been conducted to investigate the efficiency of various treated natural adsorbents such as Guava leaf powder (GL), Neem leaf powder (NL), Neem bark powder (NB), Black Berry seed powder (BB), Rice husk (RH) and their same proportions as mixed bio-adsorbents. The experiment has followed batch process. The effect of contact time has been studied in detail. The adsorption kinetics has been to follow first order rate mechanism for RH, GL and NB but other adsorbents under study followed second order rate mechanism. All adsorbents followed Freundlich and Langmuir models.

Introduction

The water may be contaminated by natural sources or by industrial effluents. One such contaminant is fluoride. Fluoride is a salt of the element fluorine. Fluorine is the most highly reactive element of halogen family. Small amounts of it are found in seawater, bone, teeth and in ground water mainly as fluoride ion. Most fluoride associated with monovalent cations such as NaF and KF is water soluble, while the one formed with divalent cations such as CaF₂ and PbF₂ is generally insoluble. Fluoride is "more toxic than lead and less toxic than arsenic" and is an accumulative toxin. Fluoride has dual significance: if its content is less then it may result in problems like dental caries. World Health Organization (WHO) recommends it in the range of 0.1-0.5ppm. The standard of the United States is between 0.6 and 0.9ppm, and of India 1 and 15ppm. Fluoride is an essential mineral that in permissible guideline level (WHO, 2006) is beneficial to mankind in dental protection and excessive intake led to various disorders and diseases such as crippling skeletal fluorosis, brittle bones, cancer (lung and bladder), infertility in women, brain and hepatic damage and Alzheimer syndrome 2,4-5,7-9,12. Various treatment procedures have been reported for the removal of excess fluoride from water. These can be broadly classified into three categories namely precipitation, adsorption and membrane based. Among them adsorption is still widely accepted pollution removal technique because of its ease of operation and cost effectiveness. Recently, researchers have devoted their study on different types of low-cost but effective materials, clay 11, brick powder 13, cotton cellulose 14, spent bleaching earth 8, activated carbon 3, activated alumina 6, zeolites 10, red mud 1 etc. The objective of the present study is to investigate the effectiveness of different biomaterials for adsorption of fluoride from water.

Adsorbents

In the present study some new single and mixed adsorbents are used

- Black Berry (*Syzygium Cumini*) seed powder (BB)
- Guava (*Psidium Guajava*) leaf powder (GL)
- Neem (*Azadirachta Indica*) bark (NB) and Neem leaf powder (NL)
- Activated rice husk (*B.N.Oryza Sativa*) carbon (RH)
- Mixed adsorbents (1:1) (GL+BB) (NL+NB)

Material Development

Black Berry, Guava, Neem leaf and Neem Bark were collected and were washed with tap water to remove dirt and other particulate matter. They were dried in sunlight. The collected materials were grounded and sieved to get the particle size of 60-250 μ m. Acid treated biomasses were washed with distilled water until maximum colour was removed. Rice husk was obtained from a grocery store in M.P. Rice husk was partially carbonized in laboratory over at 250C to 300C for 4 to 5 hours. The partially carbonized material was then completely carbonized in muffle furnace at temperature 500C to 600C. The material

from muffle furnace was cooled to room temp. Material was then repeatedly washed with hot boiling water. Acid Treated biomass was washed with distilled water.

Adsorbate (Fluoride ions)

NaF salt with molecular weight 41.987 supplied by S.D.Fine Chemicals, Jaipur is used for generation of fluoride ions in aqueous solution.

Preparation of Fluoride Standard Solution

Stock solution of fluoride ions was prepared by dissolving 221mg of NaF in 1000ml of distilled water. The stock solution are diluted with distilled water to obtain the desired initial concentration.

Batch Mode Adsorption Studies

The efficiency of adsorbents is evaluated by conducting laboratory batch mode studies. Specific amount of adsorbents were shaken in 100ml fluoride standard solution at selected pH, adsorbent dose, particle size, agitation speed, initial fluoride concentration and temp. for different time periods. Variation in contact time, was studied.

Result and Discussion

Effect of Contact Time

Effect of contact time (10 to 90 minutes) on adsorption of fluoride ions from 1mg/ml initial fluoride ion concentration is presented in Fig. 1. The mixture was agitated at 25°C with 225rpm. The sample was taken at regular intervals, filtered and then analyzed. Observations were represented in Fig. 1. It was found that the fluoride removal increases with increase in contact time to some extent. The removal of fluoride ions by the adsorbents increases, reaches a maximum value and then decreases with the increase in contact time (it may be due to desorption process).

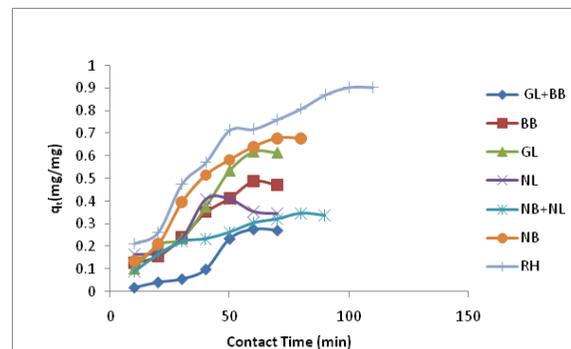


Fig.1 : Effect of contact time on adsorption of fluoride

Mechanism of adsorption was studied by using following kinetic models.

The Langergen pseudo first order rate expression is given as

$$\log (q_e - q_t) = \log q_e - (k_1/2.303) t$$

Where q_e and q_t are amounts of fluoride ions adsorbed (mg/mg) an adsorbent at equilibrium and at time t , respectively and K_1 is rate constant of pseudo first order adsorption (min). The slope and intercept of plot $\log (q_e - q_t)$ against t give values of K_1 and q_e respectively. Pseudo first order plot $\log (q_e - q_t)$ against t is shown in Fig.2. Pseudo first order rate constant (K_1), q_e , q_t and linear correlation factor values are given in Table 1. Pseudo first order plot showed reasonably good linearity till equilibrium time. Also q_e (the) values for RH, GL and NB obtained from pseudo first order plot are found to be in good agreement with q_e (exp) values than those obtained from pseudo second order plot. This indicates that RH, GL and NB followed first order kinetics and weak Vander Waal Forces (physisorptions) are playing major role in adsorption. But for other adsorbents like NL, NL+NB, BB and GL+BB there may be a possibility of chemisorptions playing a significant role in the rate determining step. The correlation coefficient (R^2) for first order adsorption model has very high values for all the adsorbents. ($R^2=1$) showed that pseudo first order adsorption equation of Langergen fit well with whole range of contact time.

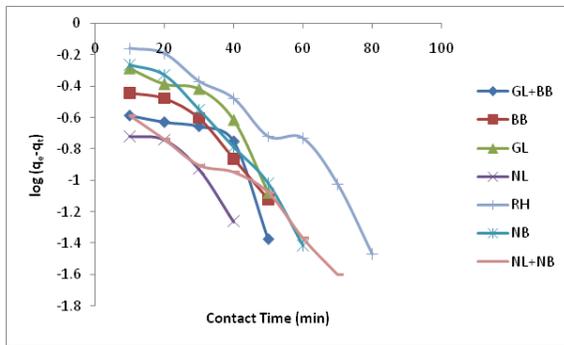


Fig. 2: Pseudo first order plot of effect of contact time on adsorption of fluoride

Table 1 Pseudo-First Order Model

Adsorbent	q_e (exp)	q_e (the)	K_1	R^2
GL	0.618	1.02	0.02	0.909
BB	0.488	1.50	0.02	0.960
GL+BB	0.276	1.95	0.02	0.820
NL	0.410	2.88	0.02	0.933
NB	0.678	1.20	0.04	0.980
NB+NL	0.374	2.45	0.02	0.978
RH	0.904	1.38	0.02	0.962

The Langergen pseudo second order kinetic model is given as

$$t/q_t = 1/(K_2 q_e^2) + t/q_e$$

Where K_2 is rate constant of second order adsorption (mg/mg/min). Slope and intercept of plot of t/q_t against t gives values of q_e (the) and k_2 respectively.

Pseudo second order plot t/q_t against t is shown in Fig. 3. Pseudo second order rate constant (K^2), q_e (the), q_e (exp) and the correlation coefficient (R^2) values are given in Table 2. q_e (the) values for BB, GL+BB, NL+NB, NL obtained from pseudo second order plot are found to be in good agreement with q_e (exp) values than those obtained from first pseudo plot. This indicates that BB, NL, NL+NB and GL+BB followed second order kinetics.

Fig. 3: Pseudo second order plot of effect of contact time on adsorption of fluoride

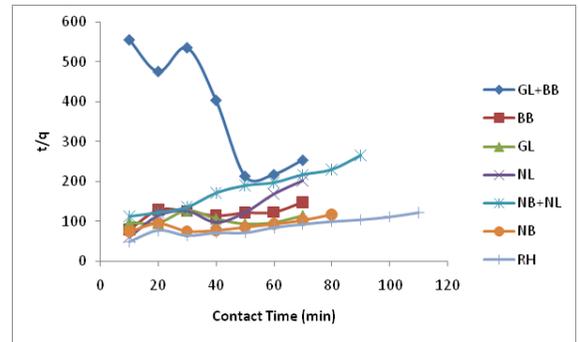


Table 2 Pseudo-Second Order Plot

Adsorbent	q_e (exp)	K_2	q_e (the)	R^2
GL	0.618	0.009	14.28	0.124
BB	0.488	0.005	1.44	0.710
GL+BB	0.276	0.061	0.160	0.897
NL	0.410	0.070	0.529	0.882
NB	0.678	0.003	2.07	0.780
NL+NB	0.347	0.041	0.526	0.990
RH	0.904	0.008	1.56	0.955

According to Weber and Morris, the intraparticle diffusion rate constant (K_i) is given by the following equation

$$q_t = K_i t^{1/2} + A$$

K_i (mg/mg/min^{1/2}) intraparticle diffusion constant value can be determined from the slope of plot q_t against $t^{1/2}$. The intraparticle diffusion rate constant k_i (mg/mg/min^{1/2}) values, Table 3 are determined from the slope of the plot q_t against $t^{1/2}$. Fig.4 showed a linear relationship after certain time but they do not pass through origin due boundary layer effect. The larger the intercept, the greater the contribution of surface sorption in rate determining step. Initial portion is attributed to the liquid mass transfer and linear portion to the intra particle diffusion.

Fig. 4 : Intra particle diffusion plot of effect of contact time on adsorption of fluoride

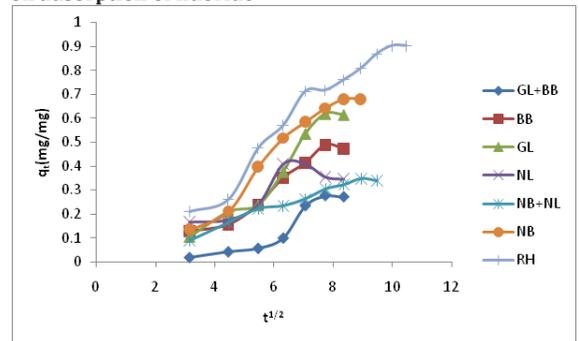


Table 3 Intraparticle Diffusion Model

Adsorbent	K_i	A	R^2
GL	0.10	-0.285	0.973
BB	0.07	-0.155	0.975
GL+BB	0.05	-0.200	0.929
NL	0.04	0.010	0.822
NB	0.10	-0.195	0.979
NB+NL	0.04	-0.011	0.986
RH	0.10	-0.102	0.980

The linearized form of Elovich kinetic equation is presented as

$$q_t = 1/\beta\{\ln(\alpha\beta)\} + \ln t/\beta$$

Found to be ≤ 0 indicates that there is no any contribution of surface sorption in rate determining step. Where α and β are the constants calculated from the intercept and slope of plot qt against $\ln t$. Elovich kinetic model constants α and β are calculated from the intercept and slope of plot Fig.5 qt against $\ln t$. Constant α depends upon initial rate of adsorption which is found to be high but constant β which is desorption constant has the low value for the same adsorbent.

Fig. 5 : Elovich plot of effect of contact time on adsorption of fluoride

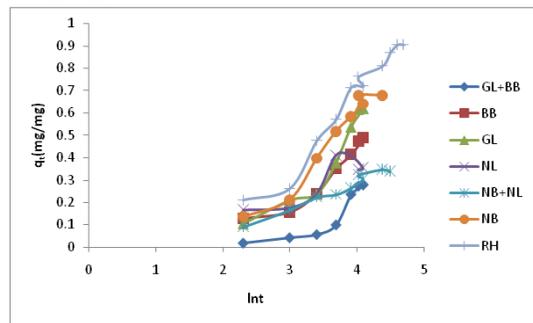


Table 4 Elovich Model

Adsorbent	α	β	R^2
GL	2.11	3.33	0.932
BB	2.92	4.76	0.945
GL+BB	4.44	6.62	0.867
NL	3.31	7.19	0.858
NB	1.98	3.28	0.972
NL+NB	4.43	8.33	0.984
RH	1.84	3.12	0.980

Freundlich and Langmuir adsorption isotherms were used to study the adsorption behaviour of fluoride ions on adsorbents.

The linear form of Freundlich isotherm equation was employed for the adsorption of fluoride onto the adsorbents was represented by

$$\log q_e = \log K_f + 1/n \log C_e$$

Where q_e is amount of fluoride ions adsorbed at equilibrium (mg/mg), C_e is the equilibrium concentration of fluoride in solution (mg/ml). A plot Fig.6 (a-g) of $\log q_e$ against $\log C_e$ gives a straight line, K_f and n are constant incorporating factors affecting the adsorption capacity and intensity of adsorption calculated from the intercept and slope of the plot respectively. The value K_f , n and R^2 are given in Table 5.

K_f values are found to be high for good adsorbents and low for poor adsorbents and follow the same order as the order of adsorption capacities of adsorbents. Values of constant n lies between 1 and 10 indicating the adsorption of fluoride ions obeys the Freundlich adsorption isotherm.

Table 5 Freundlich Isotherm Parameters

Adsorbent	K_f	n	R^2
GL	41.68	1	0.999
BB	43.65	1	0.999
GL+BB	45.70	1	0.999
NL	42.65	1	0.999
NB	43.65	1	0.999
NL+NB	47.86	1	0.999
RH	43.65	1	0.999

Freundlich ISOTHERM PLOTS

Fig. 6(a)

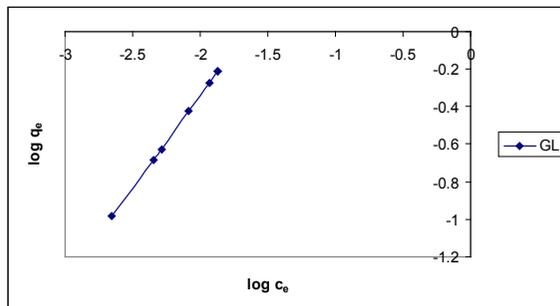


Fig. 6(b)

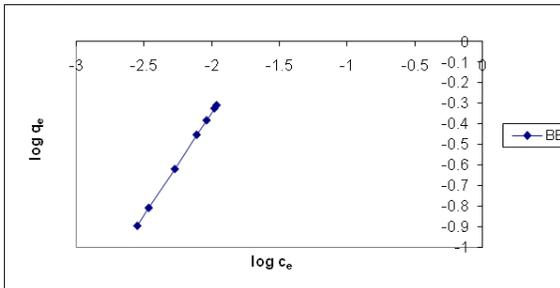


Fig. 6(c)

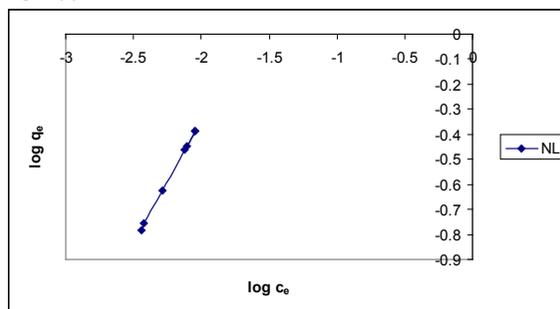


Fig. 6(d)

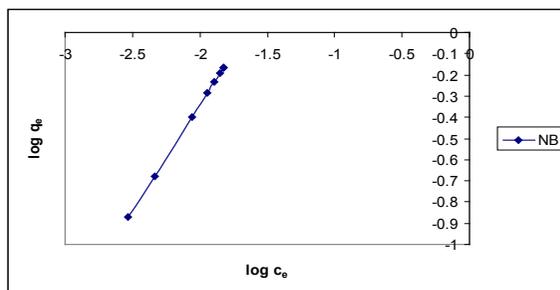


Fig. 6(e)

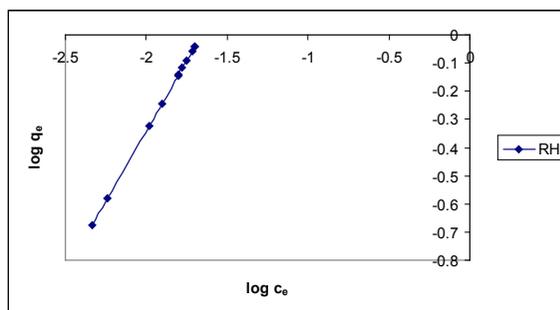


Fig. 6(f)

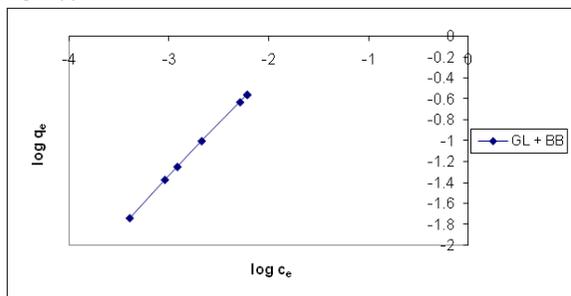
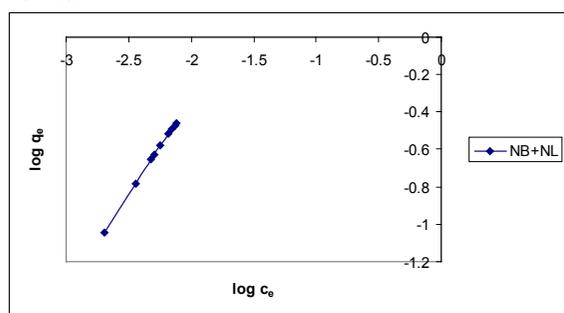


Fig. 6(g)



The linear form of Langmuir isotherm was represented by the following equation

$$1/q_e = 1/a + 1/abC_e$$

When $1/q_e$ is plotted $1/C_e$ a straight line with slope $1/ab$ is obtained which shows that the adsorption follows the Langmuir isotherm as shown Fig. 7(a-g). The Langmuir constant a and b are calculated from the slope and intercept of the linear plot. Equilibrium parameters R_L is represented as follows

$$R_L = 1/(1+bC_0)$$

Where C_0 is initial concentration of fluoride ion (mg/ml).

The values of a , b and R^2 are given in Table 6. A linear plot of $1/q_e$ against $1/C_e$ suggests the applicability of the Langmuir isotherms.

Table 6 Langmuir Isotherm Parameters

Adsorbent	a	B	R ²
GL	125	0.4	0.999
BB	10.0	0.5	0.999
GL+BB	12.5	4.0	0.999
NL	25	2.0	0.999
NB	50	1.0	0.999
NL+NB	10	5.0	0.999
RH	100	0.5	0.999

Langmuir Isotherm Plots

Fig. 7(a)

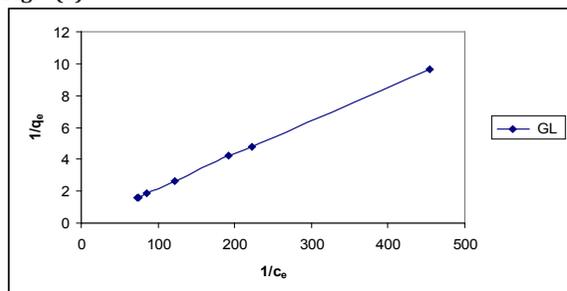


Fig. 7(b)

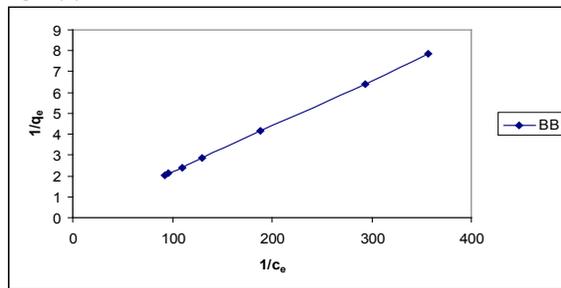


Fig. 7(c)

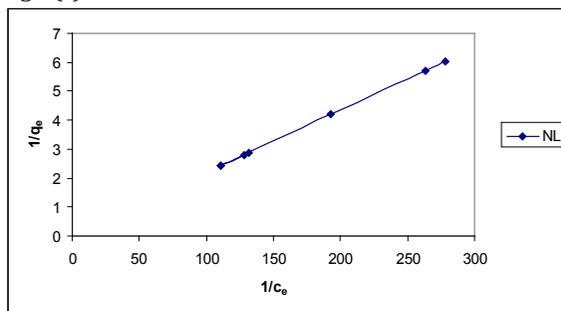


Fig. 7(d)

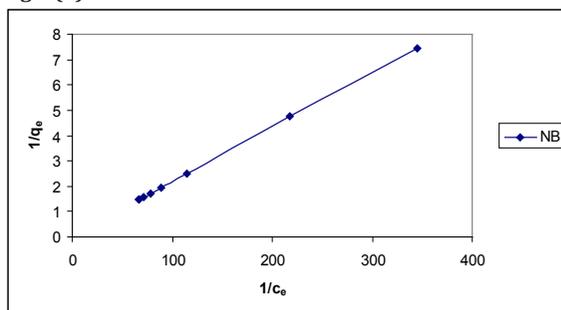


Fig. 7(e)

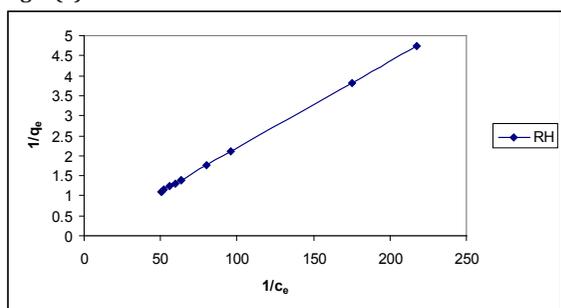


Fig. 7(f)

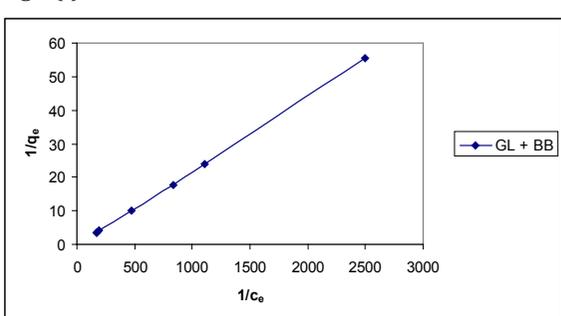
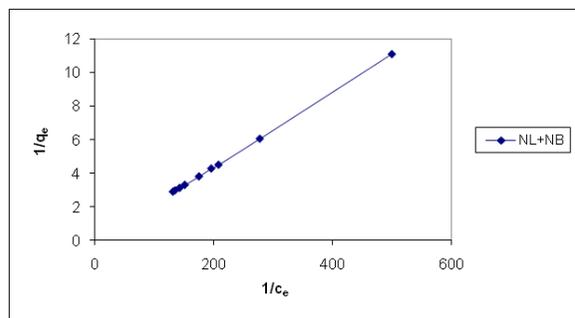


Fig. 7(g)



Conclusion

The adsorbents used in the present study have proved to be very efficient and economical for removing fluoride from water. The substrate raw materials employed are widely available and inexpensive. The fluoride removal capacity of these adsorbents is appreciably high. Thus it can be concluded that these alternative adsorbents seem to offer a very cheap and useful products for effective removal of fluoride from water. It is also clear from the above data that mixed adsorbents give more effective and satisfactory results as compared to the single one.

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