



Investigation on Sorption of Fluoride in Water Using Rice Husk as an Adsorbent

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ABSTRACT

The batch adsorption studies were undertaken to assess the suitability of inexpensive adsorbent prepared from agricultural waste, rice husk. The adsorbent was prepared by chemical impregnation method followed by physical activation. Static studies have aimed for investigation of fluoride removal efficiency under the varying conditions of the major parameters of adsorption, viz. pH, dose of adsorbent, rate of stirring, contact time and initial adsorbate concentration, and optimized by batch procedure in the mixture of known concentration of fluoride solution. The optimum sorbent dose was found to be 10g/L by varying the dose of adsorbent from 0 to 16g/L; equilibrium was achieved in 120 min for the optimum pH. It has been observed that the optimum adsorption takes place at lower pH by varying pH from 2, 4, 6, 8, 10. Maximum fluoride removal was observed to be 75% at optimum conditions. Freundlich as well as Langmuir isotherms were plotted and constants of isotherms were determined.

INTRODUCTION

Fluorine, the most electro-negative of all compounds, has not only notable chemical properties but also physiological properties of great importance to human health and well being. The chemical activity of the fluoride ion makes it physiologically more active than any other elemental ion. Small amount of it is found in seawater, bone, teeth and in groundwater mainly as fluoride ion. With low concentration of fluoride ion, enzymatic processes may be either inhibited or stimulated, and interactions with other organic and inorganic body components may occur that are of great importance to humans.

Fluoride has dual significance. If its content is less, it may result in problems like dental caries. World Health Organization recommended it in the range of 0.1-0.5 ppm. The standard of United States of America is 0.6-1.5 ppm. Thus, the requirement of fluorine varies among countries and depends on the geography and the age of people involved. An intake of more than 6 mg of fluoride per day results in fluorosis. The occurrence of high fluoride concentration beyond permissible limit in groundwater is a problem faced by many countries notably India, Sri Lanka, Pakistan, China and parts of East Africa. Fluoride epidemic has been reported in as many as 19 states of India and Union Territories. India is among 23 nations in the world, where the fluoride contaminated groundwater is creating the health problems. The state of art report of UNICEF confirms the fluoride problem in 177 districts of 20 states of India.

Several methods suggested from time to time for removing excess fluorides from water are adsorption, ion exchange, precipitation and membrane separation. Nalgonda technique, developed by NEERI, is commonly preferred at all levels because of its low price and ease of handling. Adsorption

is the process considered to be efficient to defluoridate water. Researches were carried out on different adsorbents, viz., activated carbon, processed bone char powder, activated bauxite, fly ash, granular calcite, alum, lime, etc. (Choi & Chen 1979, Bhargava & Killedar 1993, 1998a, 1998b). Some of the researchers also tried for the adsorbent prepared from the natural materials such as dry powder of hollyoke, neem bark powder, activated cotton jute carbon and leaf powder adsorbents (Jamode et al. 2004a, b).

The different methods so far tried for removal of excess fluoride from water can be broadly classified in to four categories. a) adsorptive methods, b) ion exchange methods, c) precipitation methods, d) miscellaneous methods. Some defluoridation techniques developed to control fluoride in water are reverse osmosis, adsorption method using sunflower plant, bagasse ash, burnt bone powder, etc. as adsorbents. However due to high cost, lower efficiency or non-applicability on mass scale, these techniques are not much in use. The present paper deals with the investigation of removal efficiency of fluoride by activated rice husk as an adsorbent.

MATERIALS AND METHODS

Fluoride stock solution was prepared by dissolving 221 mg anhydrous sodium fluoride in 1000 mL distilled water. Fluoride standard solution was prepared by diluting 100 mL stock solution to 1000 mL distilled water. This 1 mL solution has 0.1 mg of fluoride.

Equipment: Fluoride ion was estimated by fluoride ion meter as per standard methods. Batch adsorption studies were made using jar test apparatus (Scientific Corporation, India) equipped with stirring paddles with provision for controlling mixing speed.

Material development: Rice husk was partially carbonized in laboratory oven at 250°C to 300°C for 4 to 5 hours. The partially carbonized material was then completely carbonized in muffle furnace at temperature 500°C to 600°C. The material from muffle furnace was cooled to room temperature. Material was then repeatedly washed with hot boiling water so as to open the pores of carbon. Completely carbonized rice husk was further treated by acid treatment.

Acid treatment: Rice husk biomass, mixed with 1N HNO₃ (nitric acid) in 1:1 ratio, was taken in a 1000 mL conical flask. The mixture then optionally moulded and heated to 600°C to 700°C in muffle furnace. Treated biomass was washed with distilled water. Washing was done until maximum colour was removed and clear water obtained.

RESULTS AND DISCUSSION

In order to apply the adsorption technique successfully, innovation of cheap, nontoxic and easily available adsorbents are necessary. Bioadsorbent prepared from agricultural waste, rice husk, meet these requirements. Successful applicability and extent of adsorption depend on the knowledge of optimum conditions such as the effect of major parameters like pH, contact time, dose of adsorbent, effect of initial concentration of fluoride ion and effect of stirring rate. Adsorption studies were performed by batch technique to obtain the equilibrium data and rate of adsorption. Experiments were carried out by taking suitable adsorbent dose with 50mL of solution containing known concentration of fluoride ion. Initially, the stirring rate maintained was 30 rpm. Samples containing fluoride ions were maintained at a desired pH by adding 0.5N HNO₃ or 0.1M NaOH. All the experiments were conducted at room temperature (29±0.5°C).

Effect of pH: The pH has a very significant role on adsorption of fluoride as it affects the solubility

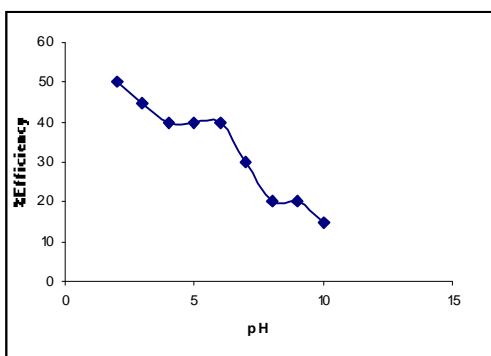


Fig. 1: Effect of pH on % removal of fluoride ion. (Adsorbent dose: 2g/L, Volume: 50 mL, initial adsorbate concentration: 5mg/L, contact time: 60 min, stirring rate: 30 rpm).

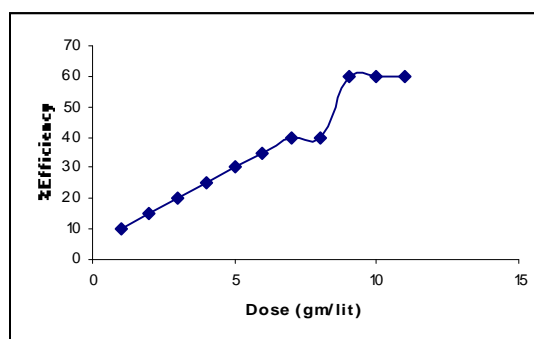


Fig. 2: Effect of adsorbent dose on % removal of fluoride ion. (pH: 2, Volume: 50 mL, initial adsorbate concentration: 5mg/L, contact time: 60 min, stirring rate: 30 rpm)

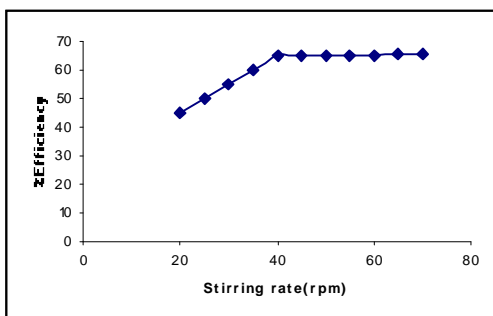


Fig. 3: Effect of stirring rate on % removal of fluoride ion. (Adsorbent dose: 10g /L, volume: 50 mL, initial adsorbate concentration: 5mg/L, contact time: 60 min, pH: 2)

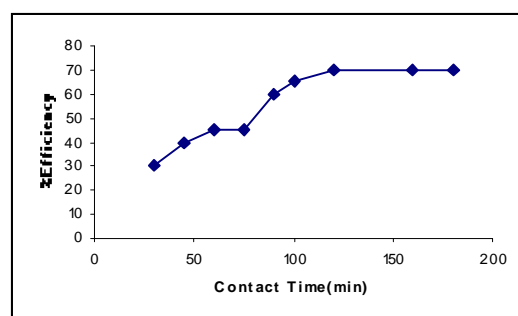


Fig. 4: Effect of contact time on % removal of fluoride ion. (Adsorbent dose: 10g/L, volume: 50 mL, initial adsorbate concentration: 5mg/L, stirring rate: 40 rpm, pH: 2)

of fluoride ion to a great extent. The role of hydrogen ion was studied by taking 50 mL of solution having initial concentration 5 mg/L with dose of adsorbent 2 gm/L by keeping contact time of 60 minutes, pH in the range of 2 to 10, and the stirring rate at 30 rpm.

It was observed that percentage of fluoride removal decreases as the pH of the solution increases (Fig 1). The maximum fluoride removal efficiency was observed 50% at pH 2, which decreases up to 15% as the pH of the solution increases. Hence, the pH of 2 was maintained for the further studies.

This may be due to neutralization of the negative charges at the surface of biosorbent by greater hydrogen concentration at lower pH values. This reduces the hindrance to diffusion of negatively charged fluoride ions on to the increased active surface of treated biosorbent. Jamode et al. (2004b) observed the similar results using treated leaf biosorbents.

Effect of adsorbent dose: The effect of adsorbent dose on the removal of fluoride ion was studied by keeping fluoride ion concentration constant at 5mg/L. The response of the adsorbent dose on the removal of fluoride shows that an increase in the adsorption occurs with the corresponding increase in the dose of adsorbent. The increase in the removal efficiency with the simultaneous increase in adsorbent dose is due to increase in the surface area, and hence more active sites available for adsorp-

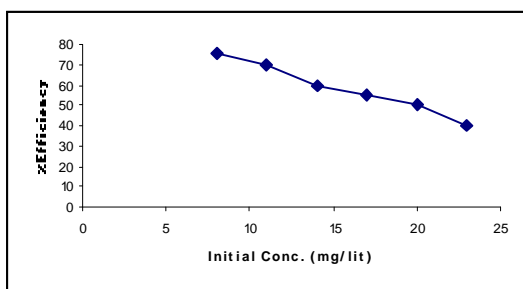


Fig. 5: Effect of initial concentration on % removal of fluoride ion. (Adsorbent dose: 10g/L, volume: 50 mL, stirring rate: 40 rpm, pH: 2, contact time: 120 min)

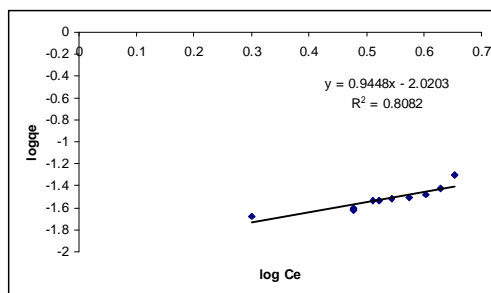


Fig. 6: Linear model for Freundlich isotherm.

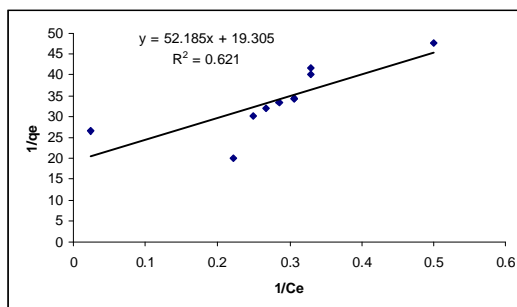


Fig. 7: Linear model for Langmuir isotherm.

tion of fluoride. The adsorbent dose was varied in the range of 1 g/L to 12 g/L by maintaining optimum pH 2, contact time 60 minutes with a stirring rate of 30 rpm. The result shows that the maximum dose of adsorbent was 10 g/L giving a maximum of 60% fluoride ion removal efficiency (Fig. 2). Further increase in the dose of adsorbent does not show any considerable improvement, hence, for further study the optimum dose was considered as 10g/L.

Effect of stirring rate: Studies were conducted to find the effect of stirring rate on the fluoride removal efficiency. For this, the stirring rate was varied between 20 and 75 rpm at the optimum values of pH and dose of adsorbent, with a contact time of 1 hour and initial concentration of 5 mg/L. The influence of rate of stirring on the extent of adsorption is shown in Fig. 3. It reveals that the fluoride removal is a function of stirring rate. At a given time fluoride removal increases with the rate of stirring (Dongre & Tembhurkar 2006, Bhargava & Killedar 1993). The removal was 45% at 20 rpm and attains 65% at the stirring rate of 40 rpm. The percentage adsorption is less at lower stirring rate and increases with the stirring rate up to 40 rpm, and thereafter remains more or less constant. The reason for the increase in the efficiency may be due to increase in the contact between adsorbate and adsorbent at higher speed. Further increase in the rpm beyond 40 does not show any increase in the adsorption, hence, 40 rpm was considered the optimum stirring rate.

Effect of contact time: Studies on effect of contact time on the fluoride removal efficiency was carried by varying it from 30 to 180 minutes keeping pH of 2, dose of adsorbent 10 g/L, and initial concentration of fluoride of solution of 5mg/L. Rate of stirring was maintained to its optimum value of 40 rpm.

Table 1: Calculation of Langmuir isotherms.

Dose (g)	Ce (mg/L)	qe (mg/mg)	1/Ce	1/Qe
1	4.5	0.05	0.222	20
2	4.25	0.0375	0.0235	26.66
3	4.0	0.033	0.25	30.30
4	3.75	0.03125	0.267	32
5	3.5	0.03	0.285	33.33
6	3.25	0.0291	0.307	34.36
7	3.25	0.0291	0.307	34.36
8	3	0.025	0.33	40
9	3	0.024	0.33	41.66
10	2	0.021	0.5	47.619

Table 2: Calculation of Freundlich isotherms.

Dose (g)	Ce (mg/L)	qe (mg/mg)	logCe	logqe
1	4.5	0.05	0.653	-1.3020
2	4.25	0.0375	0.6286	-1.4259
3	4.0	0.033	0.6020	-1.4814
4	3.75	0.03125	0.5740	-1.5051
5	3.5	0.03	0.544	-1.5228
6	3.25	0.0291	0.522	-1.536
7	3.25	0.0291	0.511	-1.536
8	3	0.025	0.477	-1.60
9	3	0.024	0.477	-1.6197
10	2	0.021	0.3010	1.6777

Fig. 4 shows the progression of adsorption reaction and percentage removal of fluoride for different contact times. It is found that removal of fluoride ions increases with increase in contact time to some extent, but further increase in the contact time does not increase the uptake due to deposition of fluoride ion on the vacant sites of adsorbent. Preliminary investigation shows that the rate of adsorption is quite high and most of adsorption takes place within first half hour. Typically, 60% of adsorption occurs during the 90 minutes and it increases up to 120 minutes and remains constant thereafter. For further optimization of other parameters, this contact time was considered as the equilibrium time. The changes in the extent of adsorption might be due to the fact that initially all the adsorbent sites were open and the solute concentration was high. Later the fluoride uptake by the adsorbent decreased significantly due to decrease in the active sites. It indicates that the possible monolayer of fluoride ions on the outer surface is formed, pores of the adsorbent are blocked and pore diffusion onto inner surface of adsorbent particles through the film due to continuous mixing maintained during the experiment is restricted (Dongre & Tembhurkar 2006, Yadav et al. 2005).

Effect of initial fluoride ion concentration: The effect of initial concentration on adsorption capacity of the biosorbent was studied for optimized conditions of all other parameters by keeping pH, contact time, rate of stirring, dose of adsorbent and contact time at their optimum values of 2, 40 min, 3.5 g/L, 120 min respectively by varying the initial concentration from 5 mg/L to 23 mg/L.

As shown in Fig. 5, results indicate that the percentage of removal of fluoride ion decreased as the initial concentration of fluoride ion in solution increases. The percent removal efficiency was ob-

served 75% at initial fluoride concentration of 5 mg/L and it goes on decreasing up to 40% at initial fluoride ion concentration of 23 mg/L. This is due to the capacity of adsorbent materials get exhausted sharply with the increase in the initial fluoride ion concentration.

Sorption mechanism: Adsorption of the solute involves the establishment of equilibrium between the amount adsorbed on the surface and the concentration of substance in solution. The variation of extent of adsorption with concentration of solute has been correlated by the Freundlich and Langmuir adsorption isotherms.

Freundlich isotherms: The isotherm provides the detailed idea about the effectiveness of the adsorbent and the maximum amount of adsorbate will get adsorbed by the adsorbent. The Freundlich equation is basically empirical but it is often useful as a means for data description. The general form of Freundlich isotherm is given in the following equation:

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

The linearized form of Freundlich isotherm is given by the following equation.

$$\text{Log}(q_e) = \text{log } K_f + 1/n \text{ log } C_e$$

Where, $\text{Log}(q_e)$ is the amount of fluoride ions adsorbed per unit weight of adsorbent (mg/g). C_e is the equilibrium concentration in solution (mg/L). K_f and $1/n$ are the Freundlich constants.

As shown in Fig. 6, Freundlich isotherm was plotted with $\text{log } q_e$ vs. $\text{log } C_e$. From the graph, the value of K_f is 1.9932 and $1/n = 0.908$, and thus, Freundlich isotherm is-

$$q_e = 1.9932 C_e^{0.908}$$

A smaller value of $1/n$ points out a better adsorption mechanism and formation of relatively stronger bond between adsorbate and adsorbent.

If $1/n < 1$, bond energies with surface density, if $1/n > 1$, bond decreases with surface density and if $1/n = 1$ all surface sites are open in order to generate the equilibrium data C_e (mg/L). The different adsorbent doses are applied to confirm the applicability of Freundlich isotherm

Langmuir isotherm: Langmuir isotherm is based on the assumption that point of valance exists on the surface of the adsorbent and that each of these site is capable of adsorbing one molecule. It is assumed that the adsorption sites have equal affinities for molecules of adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site. The Langmuir equation is commonly written as:

$$q_e = q_0 b C_e / (1 + b C_e)$$

Where, q_e is the amount adsorbed (mg/g) and C_e is equilibrium concentration of adsorbate (mg/L), q_0 and b are Langmuir constants related to capacity and energy of adsorption respectively. Thus, from Fig. 7, the Langmuir equation for defluoridation using rice husk biosorbent becomes:

$$q_e = 0.019 C_e / (1 + 0.3759 C_e)$$

CONCLUSION

Based on these studies, it is concluded that the biosorbent prepared from rice husk has shown promising results for the removal of fluoride. The uptake of fluoride is possible in the range of pH 2 to 10, adsorption reached maximum at lower water pH of 2. Hence, it is preferable to carry out defluoridation at lower value of pH. From the present study, it is observed that fluoride removal for adsorbent increases with time attaining equilibrium within 1 to 1.5 hours.

The percentage of fluoride removal was found to be function of adsorbent dose and contact time at a given initial solute concentration. It increased with time and adsorbent dose, but declines with higher initial solute concentration with time and adsorbent dose. The present study on defluoridation using biosorbent prepared from rice husk follows Freundlich as well as Langmuir adsorption isotherms.

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