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Defluoridation of Drinking Water using Brick Powder as an Adsorbent

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Kinetics study in batch process to understand the feasibility and effectiveness of adsorbents brick powder were applied on aqueous samples prepared in laboratory and groundwater samples of higher fluoride concentration collected from two villages, namely Hussainpur and Thodwal of Haryana, India. Different parameters, for instance, effect of pH, effect of dose and contact time of adsorbent were studied and optimized. For the optimum condition *i.e.*, pH (6-8) and dose of adsorbents (0.6-1.0 g/100 mL), the percentage of defluoridation from aqueous (synthetic) sample, was found to be increase from 29.8 to 54.4 % for brick powder and 47.6-80.4 % for chemically activated carbon (CAC) with the increase in contact time of 15 to 120 min. Fluoride removal was found to be 48.73 and 56.4 % from goundwater samples having 3.14 and 1.21 mg/L fluoiride, respectively under the optimized conditions. Defluoridation capacity of brick powder can be explained on the basis of the chemical interaction of fluoride with the metal oxides under suitable pH conditions.

Key Words: Defluoridation, Drinking water, Adsorption, Brick powder, Chemically activated charcoal.

INTRODUCTION

Widespread occurrence of fluoride, above the prescribed limit, in groundwater consumed by human beings has caused multi-dimensional health problems. Most common of these are dental fluorosis and skeletal fluorosis. Fluoride is one of the most abundant constituent occuring in groundwater in India and creates a major problem for safe ground water supply. Fluoride exists fairly abundantly in the earth's crust and can enter groundwater by natural process; especially soil at the food of mountains is particularly likely to be high in fluoride from the weathering and leaching of bedrock with high fluoride content. Fluorine is so highly reactive that it is never encountered in its elemental gaseous state except in some industrial processes.

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An optimum concentration can reduce the incidence of dental caries. Low levels of fluoride are required for humans as it has beneficial effects on tooth and bone structures. However ingestion of excessive fluorides, mainly through drinking water causes dental and skeletal fluorosis. Long-term ingestion of excessive fluoride has a chronic effect on the kidneys as well. The optimum level suggested by WHO[1] is 0.7 mg/L from infancy to 16 years. According to the WHO, the maximum acceptable concentration of fluoride ions in drinking water is 1.5 mg/L to prevent tooth and bone problems[1].

Concentration of fluoride below 1.5 ppm is helpful in prevention of tooth decay and such level of fluoride also assists in the development of perfect bone structure in human and animals. However, a dose of fluoride above 1.5 ppm increases the severity of tooth mottling and induces the prevalence of osteoporosis and collapsed vertebrae[2]. Fluorosis, resulting from excessive consumption of fluoride, has no treatment and is considered to be deadly disease.

It is considered that probable source of high fluoride in Indian waters is that during weathering and circulation of water in rocks and soils, fluorine is leached out and dissolved in ground water. Tile fluoride content of ground water varies greatly depending on the type of rocks from which they originate. Among the various minerals responsible for high concentration of fluoride, the Fluor-apatite $3Ca^{3-}(PO^{4-})^{2-}$, CaF_2 and fluorite, CaF^{2-} is important. However, the most important being the fluorite, CaF^{2-} and the leaching of fluoride from the metamorphic rocks hornblende gneiss of proterozoic age[3].

Concerned with the magnitude of health problems due to excess concentration of fluoride in drinking water several methods of defluoridation of drinking water have been developed. The ion-exchange, adsorption and precipitation are the usual means of defluoridation. However, in India precipitation and adsorption methods are most preferred. The adsorption method involves the contact of the fluoride containing water with a suitable adsorbent.

Precipitation process is based on the addition of chemicals and removal of insoluble compounds as precipitates. In adsorption method, different types of adsorbents are being used for defluoridation and other minerals dyes and heavey metals *e.g.*, activated alumina[4], coconut shell carbon[5], bagasse[6], chemically activated carbon[7], bone charcoal[8], natural zeolites, hydroxyapatite[9], burn clay[10], clay pots and crushed clay pots[11], membrane technologies *i.e.*, donnan dialysis[12] and other low cost bioadsorbents like saw dust[13], used tea leaves, cows dung[14] have been found to be highly effective, cheap and eco-friendly.

The shortcomings of most of the preferred methods are high operational and maintenance costs, low fluoride removal capacity, lack of selectivity for fluoride, undesirable aftereffects on water quality, generation of large amount of sludge and complicated procedure. The most common available method in India, Nalgonda Technique of community defluoridation, is based on precipitation process and is very efficient and cost effective. The main limitation of Nalgonda technique are daily addition of chemicals, large amount of sludge production, least effective with water having high total dissolve solids and high hardness. Besides it converts a large portion of ionic fluoride (67-87 %) into soluble aluminium complex and practically removes only a small portion of fluoride in the form of precipitate (18-33 %). Therefore, this technique is erroneous[15]. Residual aluminium ranges from 2.01-6.86 mg/L was also reported in Nalgonda technique[16], which is dangerous to human health as aluminium is a neurotoxin and concentration as low as 0.08 mg/L in drinking water has been reported to cause Alzheimer's disease[17] and has strong carcinogenic properties[18,19]. Adsorption methods are effective on both terms *i.e.*, fluoride removal and cost for removal. Hence the need to find locally available defluoridation media for less expensive and technically feasible in rural communities in India and of easy use at both household and small community level is desirable.

In present study, an attempt has been made for defluoridation of drinking water by using brick powder as a new feasible, suitable, effective and low cost adsorbent.

EXPERIMENTAL

Bricks utilized as adsorbents were manufactured in a brick kiln, situated near Hisar, Haryana (India). The brick powder was washed several times with distilled water till clear water was obtained and dried in oven at 105 ºC for 12 h. The dried material was sieved to obtain particles, of size less than 300 μm, for the present study. The comparison of the brick powder was made with the LR grade chemically activated carbon (CAC). The characteristics of brick powder and CAC used in the present study are given in Table-1.

TABLE-1
CHARACTERISTICS OF ADSORBENTS USED FOR DEFLUORIDATION

Characteristics	Brick powder	Chemically activated carbon
Bulk density (g/cc)	1.02	0.46
Moisture (%)	7.00	5.00
Matter soluble in water (%)	1.12	1.50
Matter soluble in acid (%)	2.23	2.50
pH	6.14	7.16
Particle size (μm)	< 300	< 300

The stock solution of 100 mg/L fluoride was prepared by dissolving 221 mg of anhydrous NaF in 1 L of distilled water and test solution of 5 mg/L. F^- was prepared from fresh stock fluoride solution by appropriate dilution. All studies were carried out in 250 mL conical flask with 100 mL test solution at room temperature (25 ± 30 ºC). The adsorbent suspensions were equilibrated by shaking in horizontal shaker for different time intervals ranging from 15 to 120 min and various control parameters like pH, adsorbent dose, initial concentration of fluoride in samples, *etc*. At the end of the shaking period, the suspension were centrifuged and filtered using Whatmann filter paper no. 42 and residual fluoride concentration was determined in the supernatant liquid by SPADNS method[20]. Batch study was conducted to determine the optimum conditions and study the effect of pH, adsorbent dose and contact time on test solutions. The effect of pH on fluoride was studied by adjusting the pH of test solution using 0.1 HCl or 0.1 N NaOH on fixed quantity of adsorbent, while effect of adsorbent lose and contact time were studied by varying dose and contact time, respectively. Optimum conditions were selected for further studies. Drinking water samples collected from two villages namely Hussainpur and Thodwal, Haryana were studied for defluoridation under the feasible optimized conditions to check the suitability of the brick powder adsorbent under field conditions. The physico-chemical properties of drinking water samples were determined before batch study according to standard method of APHA[21] (Table-2).

TABLE-2
PHYSICO-CHEMICAL CHARACTERISTICS OF DRINKING WATER SAMPLES BEFORE TREATMENT

Parameters	Thodwal, Haryana	Hussainpur, Haryana
pH	7.75	8.33
EC	8.75	7.34
Turbidity	3.5	18.0
TDS	5600	4697
Total alkalinity	164	304
Total hardness	948	904
Chloride	3848	532
Fluoride	1.21	3.14
Phosphate	5.52	3.30
Sulphate	50.51	148.2

All values are in mg/L except EC in mho/cm, turbidity in NTU and pH.

RESULTS AND DISCUSSION

Effect of pH of samples on removal of fluoride: The removal of fluoride using brick powder was studied in the pH range of 4.0 to 9.0 and the results are shown in Fig. 1. Maximum adsorption of fluoride was found to be 51.0-56.8 % in pH range 6.0 to 8.0. Percentage fluoride removal falls sharply with decreases in pH (*i.e.*, below 6.0) and increase above pH 8.0. The lower adsorption efficiency of fluoride in acidic medium might be due to formation of weakly ionized hydrofluoric acid, which reduces availability of free fluoride for adsorption. In alkaline condition, lower adsorption may be due to competition of OH^- ions with F^- ions for adsorption because of similarity in charge these carry and in their ionic radius. The similar results were obtained for maximum adsorption of fluoride removal by rare earth oxides as adsorbent[22].

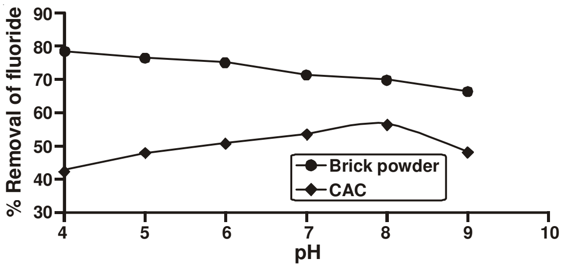

Fig. 1. Effect of pH on fluoride removal

As studied in laboratory, typically the brick powder is a mixture of oxides of silicon, aluminium, iron, calcium, magnesium, *etc*. In the presence of water these species can be hydroxylated. The specific adsorption reaction can be explained by two step mechanism as follows:

$$\equiv \text{S-OH} + \text{H} \longleftrightarrow \text{S-OH}_2^+ \tag{1}$$

$$\equiv \text{S-OH}_2^+ + \text{F} \longleftrightarrow \text{S-F} + \text{H}_2\text{O} \tag{2}$$

In case of CAC, adsorption of fluoride decrease with the increase in pH. The results obtained in this study were found to be similar as reported in literature for activated alumina[23].

Effect of adsorbent dose on removal of fluoride: The effect of adsorbent dosage on adsorption of fluoride was studied at pH 8 and 4 for brick powder and CAC, respectively for a contact time of 60 min. The results are presented as percentage removal of fluoride *vs.* adsorbent dosage in Fig. 2. The removal of fluoride was increased from 43.2 to 56.8 % and 49.4 to 84.2 % for 0.2 to 2.0 g/100 mL dosage of brick powder and CAC, respectively. However, it can be observed in Fig. 2 that after a dose of 0.6 g/100 mL in case of brick powder and 1 g/100 mL in case of CAC, there is no significant change in percentage removal of fluoride. This indicates that at these doses equilibrium is reached, which is due to overlapping of the active sites at higher dosage, thus reducing the net surface area[24]. So these amounts of dosage have been used in further studies.

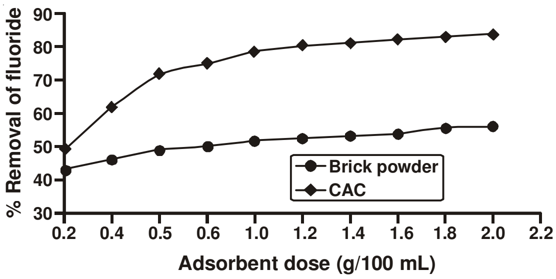

Fig. 2. Effect of adsorbent dose on fluoride removal

Effect of contact time with adsorbent on removal of fluoride: The progress of adsorption reaction and the percentage removal of fluoride by brick powder and CAC after different contact times (15 to 120 min) are graphically prsented in Fig. 3. From figure, it can be observed that with the increase in contact time, initially percentage removal also increased, after some time it gradually approached a more or less constant value, denoting attainment of equilibrium. It was assumed that the equilibrium time is that at which curves appear nearly asymptotic to the time axis. In present case, 60 min contact period have been considered as the equilibrium time for brick powder and CAC, respectively. These changes in the rate of the removal might be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high. Afterwards, the fluoride uptake rate by adsorbent had decreased significantly, due to decrease of adsorption sites. A decreased removal rate, particularly towards the end of experiment, indicates the possible monolayer of fluoride ions on the outer surface, pores of both the adsorbents and pore diffusion onto inner surface of adsorbent particles through the film due to continuous shaking maintained during the experiment. Similar effects have been observed by Raghuvanshi *et al.*[6], in their study on dyes removal.

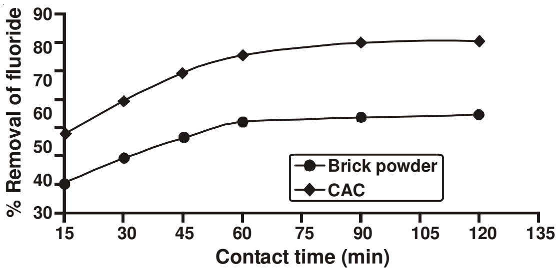

Fig. 3. Effect of contact time on fluoride removal

Adsorption kinetics of fluoride removal: The rate constant k_{ad} for sorption of fluoride using both of the adsorbents were studied by applying Lagergren rate equation:

$$\log (q_e - q) = \log q_e - k_{ad}\, t/2.303 \tag{3}$$

where q_e and q (both in mg/g) are the amount of fluoride adsorbed at equilibrium, at any time (t), respectively. Straight-line plots of log (q_e-q) *vs.* t at different time indicate the validity of Lagergren rate equation (Fig. 4). In present case, adsorption data partically not fitted in the Lagergren equation. This is supported by the values of regression coefficient (R^2) 0.9822 and 0.9049 for brick powder and CAC, respectively. The values of k_{ad} at room temperature were calculated from the slop of linear partion of plot and were found to be 2.03×10^{-2}/min and 2.47×10^{-2}/min for brick powder and CAC, respectively. As can be observed from Fig. 4, linearity of plots indicates the applicabiity of the first-order kinetics equation for the system under experimental conditions.

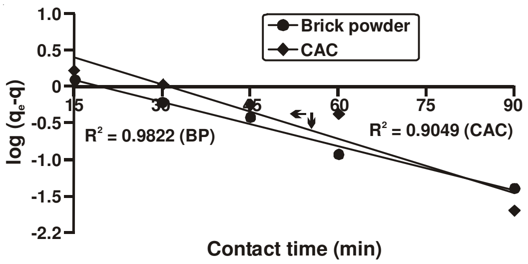

Fig. 4. Lagergren plots for adsorption of fluoride

Intraparticle diffusion study: In adsorption studies, it is necessary to determine the rate limiting step. Therefore, the results obtained from the experiments were used to study the rate-limiting step in the adsorption process. Since the particles were vigorously agitated during the experiment, it is probably reasonable to assume that the mass transfer from the bulk liquid to the particle external surface does not limit the rate. One might then postulate that the rate limiting step may be film or intraparticle diffusion. That is why, in this study the possibilities of existence of intraparticle diffusion were used tested by plotting the graph between amount of fluoride adsorbed and square root of time (Fig. 5). The dual nature of this plots may be explained as, the initial curve portions are attributed to boundary layer diffusion effect, while the final linear portion are due to intraparticle diffusion effect[25]. The rate constant for intraparticle diffusion coefficient K_p, for both of the adsorbent was determined from slopes of linear portion of the respective plots. The values for K_p are 3.77×10^{-2} mg/g/min^{½} for brick powder and 1.36×10^{-2} mg/g/min^{½} for CAC.

The extrapolations of linear portion of plots back to y-axis provide intercepts, which are proportional to the extent of boundary layer thickness. As evident from Fig. 5, film thickness is less for BP in comparison to CAC.

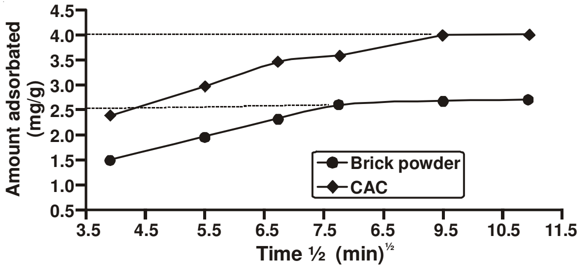

Fig. 5. Intraparticle diffusion of fluoride (amount of fluoride adsorbed *vs.* time^{½})

This may be due to the increase in escaping tendency of fluoride ions for brick powder than CAC so reducing the film thickness. The linear portions of the curves do not pass the origin in Fig. 5. This indicates that mechanism of fluoride removal on adsorbents are complex and both, the surface adsorption as well as intraparticle diffusion contribute to the rate determining step[26].

Conclusion

In the present study, a new adsorbent brick powder was studied for removal of fluoride from synthetic as well as from two drinking water samples of different fluoride concentrations. The main conclusions that can be drawn from the above study are given below: (1) Adsorption of fluoride on brick powder from aqueous solution was found to be first order reaction, mechanism of fluoride removal on adsorbent was found to be complex, both the surface adsorption as well as intraparticle diffusion contributes to the rate determining step. Defluoridation capacity of brick powder can be explained on the basis of the chemical interaction of fluoride with the metal oxides under suitable pH conditions. (2) The optimum pH was found to be in the range of 6.0-8.0 for maximum adsorption of fluoride, which makes it very suitable for use in drinking water treatment especially in rural areas. (3) Presence of others ions in groundwater did not significantly affect the defluoridation process thereby indicating that brick powder is selective adsorbent for fluoride. Comparisons of brick powder and CAC revealed that brick powder is economical adsorbent for removal of fluoride due to greater and easy abundance as compare to CAC and it can work on natural pH while CAC work on acidic pH. (4) High concentration of fluoride may also cause harm to the ecosystem and vegetation, if used for irrigation.

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