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DEFLUORIDATION OF CONTAMINATED WATER EMPLOYING BRICK POWDER AS AN ADSORBENT

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ABSTRACT

Kinetics study in batch process to understand the feasibility and effectiveness of adsorbants brick powder were applied on aqueous sample prepared in laboratory and groundwater samples of higher fluoride concentration collected from two villages, namely Reenu and Mardatoo of Rajasthan, India. Different parameters for instance, effect of pH, effect of dose and contact time of adsorbed were studied and optimized. For the optimum condition i.e. pH (6-8) and dose of adsorbents (0.6-1.0 g/100ml), the percentage of defluoridation from aqueous (synthetic) sample, was found to be increased 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 groundwater samples having 3.14 and 1.21 mg/l fluoride, 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.

KEYWORDS: Defluoridation; Groundwater; Adsorption; Brick Powder; Chemically Activated Charcoal: Lagergren rate equation

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 occurring in groundwater in India and creates a major problem for safe groundwater supply. Fluoride exists fairly abundantly in the earth's crust and enter groundwater natural process; especially soil at the food of mountains is particularly likely to be high in fluoride from the weathering and leaching of bed rock with high fluoride content. Fluorine is so highly reactive that it is never encountered in its elemental gaseous state except in some industrial processes. 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 structures. However, ingestion of excessive fluorides, mainly through drinking water causes dental, skeletal and non skeletal fluorosis. Long term ingestion of excessive fluoride has a chronic effect on the kidneys as well, the optimum level suggested by WHO is 0.7, ppm from infancy to 16 years. According to the WHO, the maximum acceptable concentration of fluoride ions in drinking water is 1.5ppm, to prevent tooth problems.

Concentration of fluoride below 1.5ppm is helpful in prevention of tooth decay and such level of fluoride also assists in the development of perfect bone structure in humans and animals. However, a dose of fluoride above 1.5ppm increases the severity of tooth mottling and induces the prevalence of osteoporosis and collapsed vertebrae. Fluorosis, resulting from excessive consumption of fluoride, has no treatment and is considered to be crippling disease. It is considered that probable source of high fluoride in Indian waters is that during weatherg and circulation of water in rocks and soils, fluorine is leached out and dissolved in groundwater. Tile fluoride content of groundwater 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 $Ca_3(PO_4)_2.CaF_2$ and CaF_2 is important. However, the most important being the fluorite, CaF_2 and the leaching of fluoride from the metamorphic rocks hornblende gness of proteozoic age, Shanker (1987).

Concerned with the magnitude of health problems due to excess concentration of fluoride in drinking water several method of defluoridation of drinking water have been developed. The ion-exchange, adsorption, reverse osmosis 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 containg water with a suitable adsorbant. Precipitation process is based on the adition 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 heavy metals e.g. activated alumina (Kumar, 1995), coconut shell carbon (Arulaanantham, 1989), bagasse (Raghuvanshi *et al*., 2004), chemically activated carbon (Muthukumaran *et al.,* 1995), bone charcoal (Killedar and Bhargava, 1993), natural zeolites, hydroxyapatite (Choi and Kenneth, 1979), burn clay (Karthikeyan *et al*., 1999), and crushed clay pots (Hauge *et al*., 1994), electrodialysis (Hichour et al., 2000) and othe low cost bioadsorbants like saw dust (Raghuvanshi *et al*., 2002), used tea leaves, cow dung (Raghuvanshi, 2001) have been found to be highly effective, cheap and eco-friendly.

The shortcomings of most of the methods are high operational and maintenance costs, low fluoride removal capacity, lack of selectivity for fluoride, undesirable after effects 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 limitations of this technique are daily addition of chemicals, large amount of sludge production, least effective with water having high total dissolved solids and high hardness. Besides it converts a large portion of ionic fluoride (67-87%) into insoluble aluminium complex and practically removes only a small portion of fluoride in the form of precipitate (18-33%). Therefore, this technique is erroneous (Apparao et. al., 1990) residual aluminium ranges from 2.01-6.86ppm was reported in Nalgonda technique (Gupta, 1997), which is dangerous to human health as aluminium is a neurotoxin and concentration as low as 0.08ppm in drinking water has been reported to cause Alzhemer's disease (Davison, 1982) and has strong carcinoproperties (Crapper *et al*., 1973; Dearfield *et al*., 1964). 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 level is desirable. In present study, an attempt has been made for defluoridation of drinking water by employing brick powder as a new feasible, effective and low cost adsorbant.

EXPERIMENTAL ANALYSIS

Bricks utilized as adsorbent were manufactured in brick kiln situated near Ghaziabad, UP (India). The brick powder was washed several times with distilled water till clear water was obtained and dried in oven at 105°C 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 brick powder and CAC used in the present study

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 ppm fluoride was prepared by dissolving 221 mg of anhydrous NaF in 1 L of distilled water. and test solution of 5 mg/L fluoride was prepared from fresh stock solution by appropriate dilution. All studies were carried out in 250 ml conical flask with 100 ml test solution at room temperature. The absorbent suspensions were equilibrated by shaking in horizontal shaker for different time interval ranging from 15 to 120 min and various control parameters like pH, adsobent 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 SPANDS method (APHA,1995). 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 0.1N HCl or 0.1M 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 Reenu and Mardatoo of Rajasthan, India were studied for defluoridation under the feasible optimized conditions to check the suitability of the brick powder adsobent under field conditions. The physico-chemical properties of drinking water samples were determined before batch study according to standard method of APHA, 1992 as depicted in Table-2.

TABLE-2. Physicochemical characteristics of drinking water samples before treatment

Parameters	Reenu	Mardatoo
EC	8.75	9.00
Turbidity	9.75	7.00
TDS	3200	2300
Total alkalinity	132	280
Total hardness	1500	1100
Chloride	50.0	10.10
Fluoride	3.1	3.00
Phosphate	55.00	34.2
Sulphate	56.9	18.9

All values are in ppm (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 to 9 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.

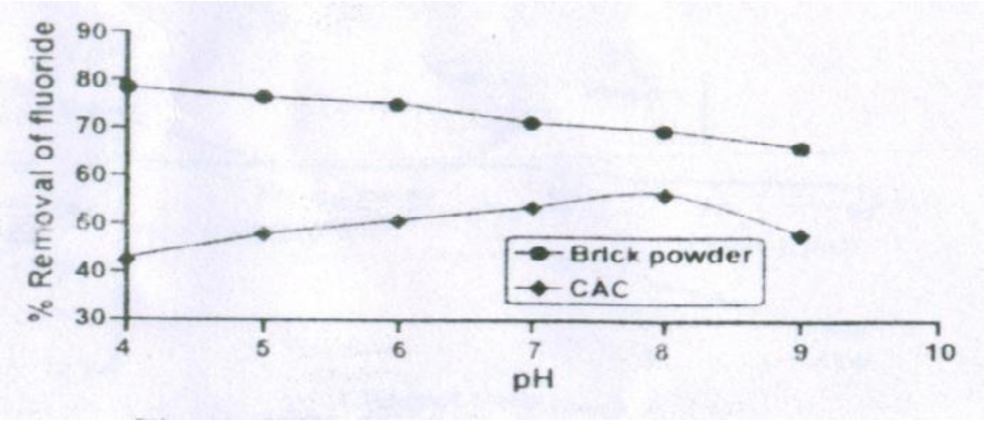

FIGURE 1. Effect of pH on fluoride removal

Percentage fluoride removal falls sharply with decrease in pH (i.e. below 6.0) and increase above pH 8.0. The lower absorption efficiency of fluoride in acidic medium might be due to formation of weakly ionised hydrofluoric acid, which reduces availability of free fluoride for absorption. In alkaline medium, lower adsorption may be due to competition of OH ions with fluoride ions for absorption because of similarity in charge these carry and in their ionic radius. The similar results wee obtained for maximum absorption of fluoride removal by rare earth oxides as adsorbent (Raichur and Basu, 2001). As studied in laboratory, typically the brick powder is a mixture of oxides of silicon (Si), aluminium (Al), iron (Fe), calcium (Ca), magnesium (Mg), etc. in the presence of water these species can be dydroxylated. The specific adsorption reaction can be explained by two step mechanism as follows:

$$S - OH + H \longleftrightarrow S - OH_2$$

$$S - OH_2 + F \longleftrightarrow S - F + H_2O$$

In case of CAC, adsorption of fluoride decrese with the increase in pH. The result obtained in this study were found to be similar as reported in litrature for activated alumina (Savinelli and Black, 1958).

Effect of adsorbent dose on removal of fluoride: The effect of adsorbant 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.

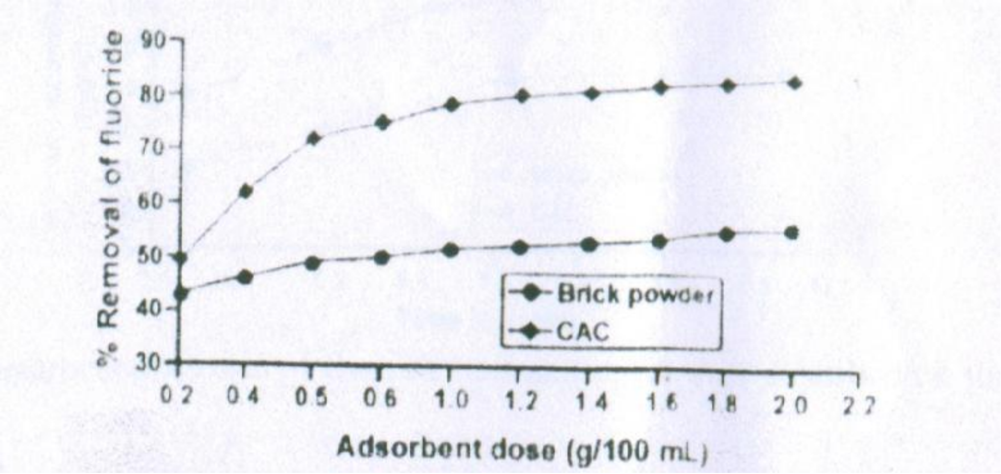

FIGURE 2. Effect of adsorbent dose on fluoride removal

The removal of fluoride was increased from 43.2 to 56.8% and 49.4 to 84.2 % for 0.2 to 2.0g/100mL dosage of brick powder and CAC, respectively. However, it can be observed in fig.2 that after a dose of 0.6g/100 mL in case of brick powder and 1 g/100mL 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 (Killedar and Bhargava, 1990). So these amounts of dosage have been used in further studies.

Effect of contact time with adsobent 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 presented in fig. 3.

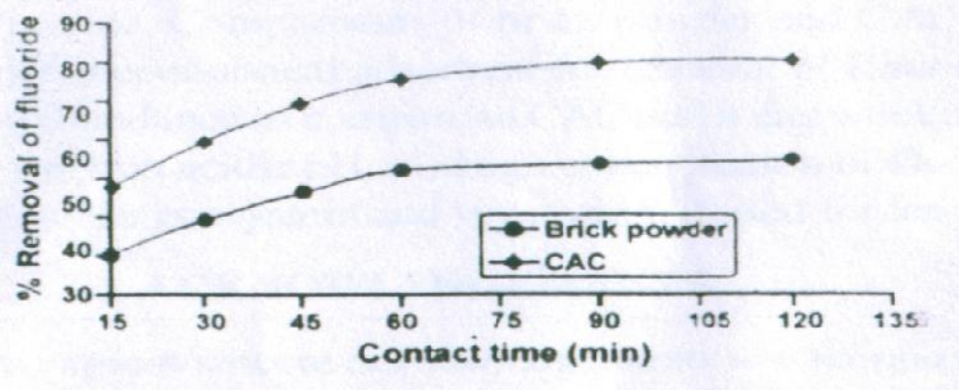

FIGURE 3. Effect of contact time on fluoride removal

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 axix. 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 night be due to the fact that initially all adsobent sites were vacant and the solute concentration gradient was high. Afterwards, the fluoride uptake rate by adsobent had decreases significantly, due to decrease of adsorption sites. A decreased removal rate, particularly towards the end of experiment, indicated the possible monolayer of fluoride ions on the outer surface, pores of both the adsorbents and pore diffusion onto surface of adsorbent particles through the film due to continuous shaking maintained during the experiment. Similar effects have been observed by Raghuvanshi *et al.,* 2008 in their study on dyes removal

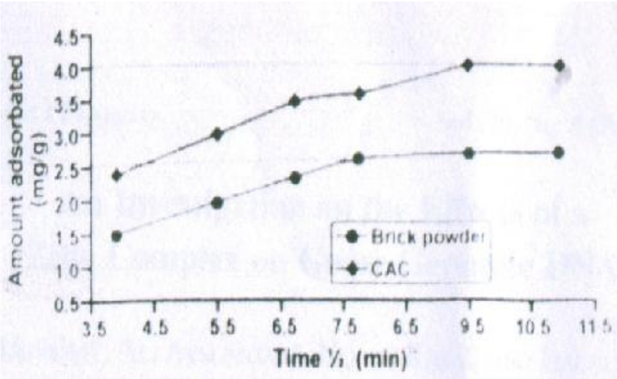

FIGURE 4. Lagergren plots for adsorption of fluoride

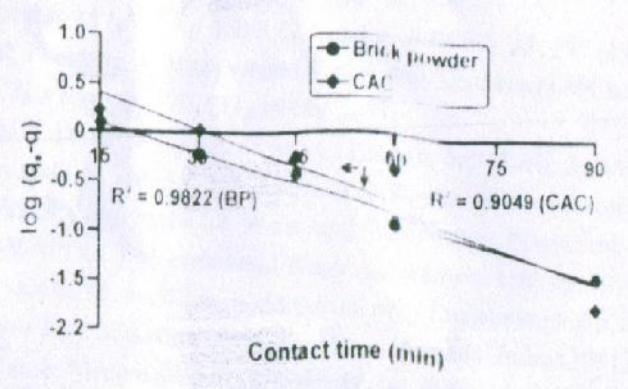

FIGURE 5 Intraparticle diffusion of fluoride (amount of fluoride absorbed *vs* time)

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

$$\text{Log}\ (q_c - q) = \log q_c - \text{kad}\ t/2,303$$

Where q_c and q (both in mg/g) are the amount of fluoride adsorbed at equilibrium, at any time (t), respectively. Straight line plot of log (q_c-q) *vs t at* different time indicate the alidity of Lagergren rate equation (Fig.4). in present case, adsorption data practically not fitted in in the Lagergren equation. This is supported by the value of regression coeficient (R) 0.9822 and 0.9049 for brick powder and CAC respectively. The vaue od k_{ad} at room temperature were calculated from the slop of linear portion of plot and were found to be 2.03 x 10^2/min for brick powder and the applicability of the first order kinetics under experimental conditions.

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 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 the 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 plot may be explained as, the initial curve portions are attributed to the boundary layer diffusion effect, while the final linear portion are due to intraparticle diffusion effect (McKay, 1980). 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 value for K_p are 3.77 x 10^2 mg/min$^{1/2}$ for brick powder and 1,36 x 10^2 mf/min$^{1/2}$ for CAC.

The extrapolations of linear portion of plots back to y-axis provide intercepts, which are proportional to the extent of boundry layer thickness. As evident from fig. 5, film thickness is less for brick powder in comparison to CAC. 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 (Mahramanlioglu, *et al*., 2002).

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 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 other ions in groundwater did not significantly affect the defluoridation process thereby indicating that brick powder is selective adsorbent for fluoride. Comparions of brick powder and CAC revealed that brick powder is economocal adsorbent for removal of fluoride due to greater and easy abundance as compare ti 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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