

## Defluoridation of groundwater using brick powder as an adsorbent

Asheesh Kumar Yadav\*, C.P. Kaushik, Anil Kumar Haritash, Ankur Kansal, Neetu Rani

*Department of Environmental Science and Engineering, Guru Jambheshwar University, Hisar 125001, India*

Received 11 May 2005; received in revised form 4 August 2005; accepted 9 August 2005

Available online 17 October 2005

### Abstract

Defluoridation of groundwater using brick powder as an adsorbent was studied in batch process. Different parameters of adsorption, viz. effect of pH, effect of dose and contact time were selected and optimized for the study. Feasible optimum conditions were applied to two groundwater samples of high fluoride concentration to study the suitability of adsorbent in field conditions. Comparison of adsorption by brick powder was made with adsorption by commercially available activated charcoal. In the optimum condition of pH and dose of adsorbents, the percentage defluoridation from synthetic sample, increased from 29.8 to 54.4% for brick powder and from 47.6 to 80.4% for commercially available activated charcoal with increasing the contact time starting from 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<sup>-1</sup> fluoride, respectively, under the optimized conditions. Presence of other ions in samples did not significantly affect the defluoridation efficiency of brick powder. The optimum pH range for brick powder was found to be 6.0–8.0 and adsorption equilibrium was found to be 60 min. These conditions make it very suitable for use in drinking water treatment. 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. The adsorption process was found to follow first order rate mechanism as well as Freundlich isotherm.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Defluoridation; Adsorption; Brick powder (BP); Commercially available activated charcoal (CAC)

### 1. Introduction

Widespread occurrence of fluoride above the prescribed limit in groundwater meant for human consumption has caused multidimensional health problems, most common being dental fluorosis and skeletal fluorosis. Fluoride is one of the most abundant constituents occurring in groundwater in India and creates a major problem in safe drinking water supply. Several methods of defluoridation of drinking water have been developed. However, in India, precipitation and adsorption are the most preferred. 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, e.g. activated alumina [1], coconut shell carbon [2], chemically

activated carbon [3], bone charcoal [4], natural zeolites [5], burnt clay [6] and other low-cost adsorbents.

The shortcomings of most of these 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 involved in the treatment. The most commonly adopted method in India, Nalgonda technique of community defluoridation, is based on precipitation process and is very efficient and cost effective. The major limitations of Nalgonda 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 soluble aluminium complex and practically, removes only a small portion of fluoride in the form of precipitate (18–33%). Therefore, this technique is erroneous [7]. Residual aluminium ranging from 2.01 to 6.86 mg l<sup>-1</sup> was also reported in Nalgonda technique [8], which is dangerous to human health as aluminium is a neurotoxin, concentration as low

\* Corresponding author. Present address: Centre for Rural Development and Technology, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India. Fax: +91 11 26515616.

E-mail address: ashyaduvanshi@yahoo.co.in (A.K. Yadav).

as  $0.08 \text{ mg l}^{-1}$  in drinking water has been reported to cause Alzheimer's disease [9–11] and has strong carcinogenic properties [12–15].

In the present study, an attempt has been made for defluoridation of drinking water using brick powder (BP) as a new, feasible, suitable and low-cost adsorbent.

## 2. Materials and methods

Bricks utilized as adsorbents were manufactured in a brick kiln, situated near Hisar, Haryana (India). These bricks were washed with distilled water, dried and ground to obtain fine powder. The brick powder was washed several times with distilled water till clear water was obtained and was dried in oven at  $105^\circ\text{C}$  for 12 h. The dried material was sieved to separate less than  $300 \mu\text{m}$  size of particles for the present study. The comparison of the BP was made with the commercially available activated charcoal (CAC) LR grade. The characteristics of BP and CAC used in the present study are given in Table 1. The BP does not require any impregnation or activation in preparation of adsorbent as well as its easy accessibility in rural area reduce its cost as compared to CAC.

The stock solution of  $100 \text{ mg l}^{-1}$  fluoride was prepared by dissolving 221 mg of anhydrous NaF in 1 l of distilled water. Test solution of  $5 \text{ mg l}^{-1} \text{ F}^-$  was prepared from fresh stock solution keeping in view that the maximum concentration of fluoride reported in groundwater of most of the fluoride-affected area is around  $5 \text{ mg l}^{-1}$ . All the experiments were carried out in 250 ml conical flasks with 100 ml test solution at room temperature ( $25 \pm 3^\circ\text{C}$ ). These flasks, along with test solution and adsorbent, were shaken in horizontal shaker to study the various control parameters. At the end of desired contact time, the conical flasks were removed from shaker and allowed to stand for 2 min for settling the adsorbent. Then, samples were filtered using Whatman no. 42 filter paper and filtrate was analyzed for residual fluoride concentration by SPADNS method, described in the Standard Methods of Examination of Water and Wastewater [16]. Batch study was conducted to determine the optimum conditions and to study the effect of pH, adsorbent dose and contact time on test solution. The effect of pH on fluoride was studied by adjusting the pH of test solution using 0.1N HCl or 0.1N NaOH on fixed quantity of adsorbent, while effect of adsorbent dose and contact time were studied by vary-

Table 1  
Characteristics of adsorbents

Characteristic	BP	CAC
Bulk density (g/cc)	1.02	0.46
Moisture (%)	7.0	5.0
Matter soluble in water (%)	1.12	1.5
Matter soluble in acid (%)	2.23	2.5
pH	6.14	7.16
Particle size ( $\mu\text{m}$ )	<300	<300

Table 2

Physico-chemical properties of groundwater samples before treatment

Parameters	Hussainpur	Thodwal
pH	8.33	7.75
EC	7.34	8.75
Turbidity	18.0	3.5
TDS	4697.0	5600.0
Total alkalinity	304.0	164.0
Total hardness	904.0	948.0
Chloride	532.0	384.0
Fluoride	3.14	1.21
Phosphate	3.30	5.52
Sulphate	148.2	50.51

All values are in  $\text{mg l}^{-1}$  except pH, EC in  $\text{mmho cm}^{-1}$  and turbidity in NTU.

ing dose and contact time, respectively. Optimum conditions were selected for further studies. Groundwater 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 BP under field conditions. The physico-chemical properties of groundwater samples were determined before batch study according to the standard methods (Table 2).

## 3. Results and discussion

### 3.1. Effect of pH

The effect of pH on removal of fluoride was studied in the pH range of 4.0–9.0 and results are shown in Fig. 1. pH played a major role in fluoride adsorption on BP. Maximum adsorption of fluoride was found to be 51.0–56.8% in pH range between 6.0 and 8.0. Percentage removal fell sharply as pH decreased below 6.0 and above 8.0. The lower adsorption efficiency of fluoride in acidic medium might be due to the formation of weakly ionized hydrofluoric acid, which reduces availability of free fluoride for adsorption. In alkaline conditions, lower adsorption may be due to the competition of  $\text{OH}^-$  ions with  $\text{F}^-$  ions for adsorption because of similarity in  $\text{F}^-$  and  $\text{OH}^-$  in charge and ionic radius. The obtained results for maximum adsorption were similar, as reported for fluoride removal by rare earth oxides as adsorbent [17].

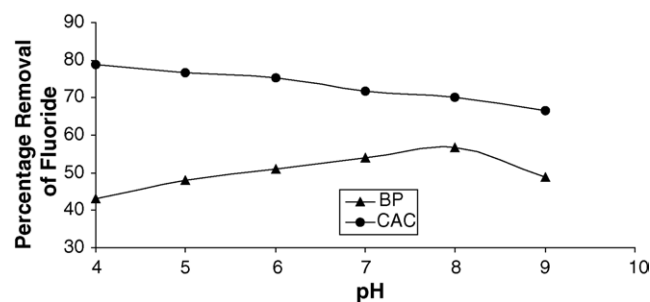


Fig. 1. Effect of pH on fluoride removal. Contact time and initial fluoride concentration are 60 min,  $5.0 \text{ mg l}^{-1}$  for both BP and CAC. Adsorbent doses are  $1.0 \text{ g}/100 \text{ ml}$  for BP and  $0.6 \text{ g}/100 \text{ ml}$  for CAC.

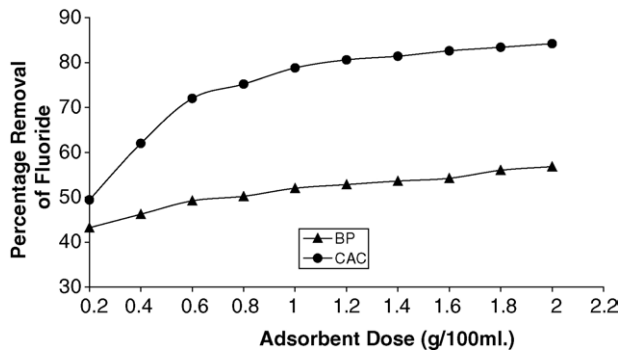
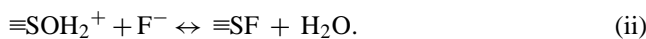


Fig. 2. Effect of adsorbent dose on fluoride removal. pH 8.0 for BP and 4.0 for CAC, contact time and initial fluoride concentration are 60 min,  $5.0 \text{ mg l}^{-1}$  for both adsorbents.

Typically, BP 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:



In case of CAC, adsorption of fluoride decreased with increase in pH. The results obtained in this study were found to be similar as reported in literature (for activated alumina) [18].

### 3.2. Effect of dose

The effect of adsorbent dosage on adsorption of fluoride at pH 8.0 for BP and 4.0 for CAC and contact time 60 min for both adsorbents was studied. The results are presented as percentage removal of fluoride versus adsorbent dosage in Fig. 2. The removal of fluoride increased from 43.2 to 56.8% for 0.2–2.0 g/100 ml dosage of BP and 49.4–84.2% for 0.2–2.0 g/100 ml dosage of CAC. However, it can be seen from Fig. 2 that after dosage of 0.6 g/100 ml in case of BP and 1 g/100 ml in case of CAC, there was no significant change in percentage removal of fluoride. It was due to the overlapping of active sites at higher dosage, thus, reducing the net surface area [19]. So, these amounts of doses were used for further study.

### 3.3. Effect of contact time

Fig. 3 shows the progression of adsorption reaction, the percentage removal of fluoride by BP and CAC after different contact times. As contact time was increased, initially, percentage removal also increased, but after some time, it gradually approached an almost 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 the present case, the equilibrium time was obtained at 60 min for BP and CAC. The changes in

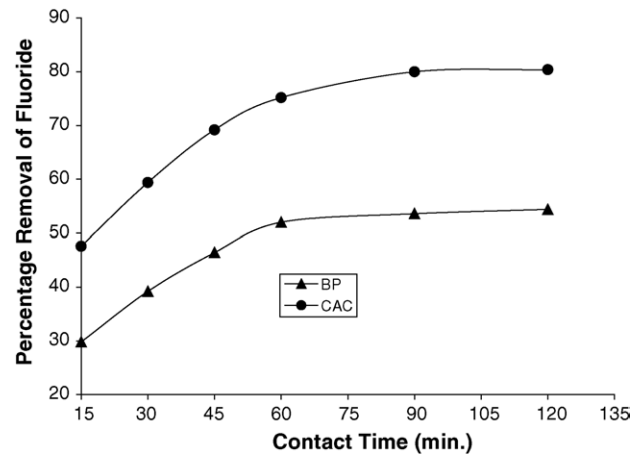


Fig. 3. Effect of contact time on fluoride removal. pH 8.0 for BP and 4.0 for CAC, adsorbent doses 0.6 and 1.0 g/100 ml for BP and CAC, respectively.

the rate of removal might be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high. Later, the fluoride uptake rate by adsorbent had decreased significantly, due to the decrease in number of adsorption sites. 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.

### 3.4. Adsorption isotherms

The adsorption data were fitted to linearly transformed Freundlich isotherms. The linearized Freundlich equation is given as:

$$\log \left( \frac{x}{m} \right) = \log K_f + \frac{1}{n} \log C_e \quad (\text{iii})$$

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  $K_f$  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. In the present study, values of  $K_f$  and  $n$  were found to be 41.56 and 0.135 for BP and 3.27 and 0.67 for CAC. The isotherm fitted well for both adsorbents with a correlation coefficient ( $R^2$ ) greater than 0.97.

### 3.5. Adsorption kinetics

The rate constant  $k_{ad}$  for sorption of fluoride, for both the adsorbents was studied by applying Lagergren rate equation:

$$\log (q_e - q) = \log q_e - k_{ad} \frac{t}{2.303} \quad (\text{iv})$$

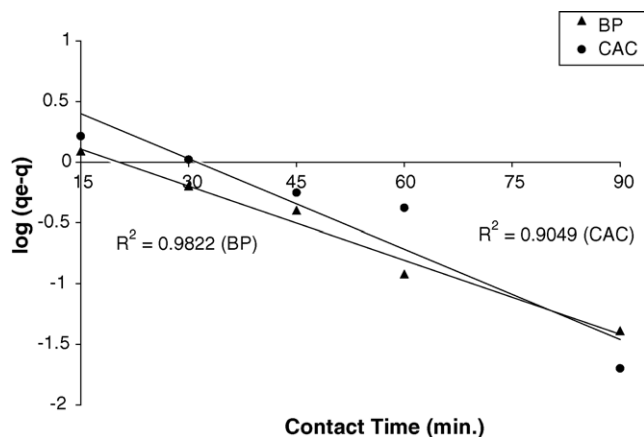


Fig. 4. Lagergren plots for adsorption of fluoride.

where  $q_e$  and  $q$  (both in mg/g) are the amounts of fluoride adsorbed at equilibrium and at time  $t$ , respectively. Straight-line plots of  $\log(q_e - q)$  versus  $t$  at different times indicate the validity of Lagergren rate equation (Fig. 4). In our study, adsorption data did not fit in the Lagergren equation partially. This is supported by the values of regression coefficient ( $R^2$ ) 0.9822 and 0.9049 for BP and CAC, respectively. The values of  $k_{ad}$  at room temperature were calculated from the slope of linear portion of plot and were found to be  $2.03 \times 10^{-2}$  and  $2.47 \times 10^{-2} \text{ min}^{-1}$  for BP and CAC, respectively. As in Fig. 4, linearity of the plots indicates the applicability of the first-order kinetics equation for the system under experimental conditions.

### 3.6. Intra-particle 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. Since the particles were vigorously agitated during the experiment, it is reasonable to assume that the mass transfer from the bulk liquid to the particle external surface did not limit the rate. One might, then, postulate that the rate-limiting step might be film or intra-particle diffusion. That is why, in this study, possibility of existence of intra-particle diffusion was tested by plotting the graph between amount of fluoride adsorbed and square root of time (Fig. 5). The double nature of these plots may be explained as: the initial curve portions are attributed to boundary layer diffusion effect, while the final linear portions are due to intra-particle diffusion effect [20]. The rate constant for intra-particle diffusion coefficient  $K_p$ , for both of the adsorbents was determined from slopes of linear portion of the respective plots. The values for  $K_p$  are  $3.77 \times 10^{-2} \text{ mg g}^{-1} \text{ min}^{-0.5}$  for BP and  $1.36 \times 10^{-2} \text{ mg g}^{-1} \text{ min}^{-0.5}$  for CAC. The extrapolations of liner 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 compar-

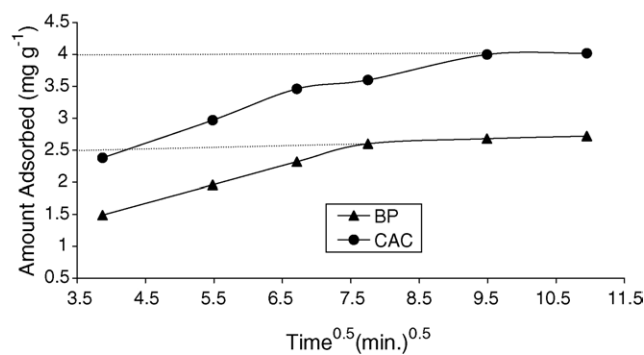


Fig. 5. Plots of amount of fluoride adsorbed vs. time for intra-particle diffusion of fluoride.

ison to CAC. This could be due to the increase in escaping tendency of fluoride ions from BP and hence 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 is complex and, both, the surface adsorption as well as intra-particle diffusion contribute to the rate-determining step [21,22].

## 4. Conclusions

In the present study, a new adsorbent BP was studied for removal of fluoride from synthetic as well as from two groundwater samples of different fluoride concentrations. The conclusions drawn from the above study are given below:

- (1) Adsorption of fluoride on BP from aqueous solution was found to be first order reaction and mechanism of fluoride removal on adsorbent was found to be complex. The surface adsorption as well as intra-particle diffusion contributes to the rate-determining step. Defluoridation capacity of BP 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 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 BP is selective adsorbent for fluoride. Comparisons of BP and CAC reveal that BP is economical adsorbent for removal of fluoride due to greater and easy abundance as compared to CAC, and it can work on natural pH while CAC can work on acidic pH.

## Acknowledgement

One of the authors, A.K.Y. is grateful to CSIR, New Delhi, for awarding senior research fellowship.

## References

- [1] S. Kumar, Studies on desorption of fluoride from activated alumina, *Indian J. Environ. Protect.* 16 (1995) 50–53.
- [2] A.J. Arulanantham, T. Ram Krishna, N. Balasubramaniam, Studies on fluoride removal by coconut shell carbon, *Indian J. Environ. Health* 13 (1992) 531–536.
- [3] K. Muthukumar, N. Balasubramaniam, T.V. Ramkrishna, Removal of fluoride by chemically activated carbon, *Indian J. Environ. Protect.* 12 (1995) 514–517.
- [4] D.J. Killedar, D.S. Bhargava, Effect of stirring rate and temperature on fluoride removal by fishbone charcoal, *Indian J. Environ. Health* 35 (1993) 81–87.
- [5] P.K. Shrivastava, A. Deshmukh, Defluoridation of water with natural zeolite, *J. Inst. Public Health Eng. (India)* 14 (1994) 11–14.
- [6] G. Karthikeyan, M.N. Andal, S.G. Sundar, Defluoridation property of burnt clay, *J. IWWA* 31 (1999) 291.
- [7] B.V. Apparao, S. Meenakshi, G. Karthikayan, Nalgonda technique of defluoridation of water, *Indian J. Environ. Protect.* 10 (1990) 292–298.
- [8] S.K. Gupta, A process for defluoridation of water by a filter bed using indigenous material, *Indian J. Environ. Sci.* 1 (1997) 149–156.
- [9] A.M. Davison, Water supply aluminium concentration: dialysis dementia and effect of reverse osmosis water treatment, *Lancet* 9 (1982) 785–787.
- [10] D.R. Crapper, S.S. Krishnan, A.J. Dalton, Brain aluminum distribution in Alzheimer's disease and experimental neurofibrillary degeneration, *Science* 180 (1973) 511–513.
- [11] R.G. Miller, F.C. Kopfler, K.C. Kelty, J.A. Stobler, N.S. Ulmer, The occurrence of aluminum in drinking water, *J. AWWA* 76 (1984) 84–91.
- [12] C.N. Martyn, D.J.P. Barker, C. Osmond, E.C. Harris, J.A. Edvardson, R.F. Lacey, Geographical relation between Alzheimer's disease and aluminium in drinking water, *Lancet* 1 (1989) 59–62.
- [13] K.L. Dearfield, C.O. Abernathy, S. Ottley, J.H. Brantner, P.F. Hayes, Acrylamide its metabolism, developmental and reproductive effects, genotoxicity and carcinogenicity, *Mutat. Res.* 195 (1964) 45–77.
- [14] D.D. Mccollister, E. Oyen, V.K. Rowe, Toxicology of acrylamide, *Toxicol. Appl. Pharmacol.* 6 (1964) 172–181.
- [15] J. Mallevialle, A. Bruchet, F. Fiessinger, How safe are organic polymers in water treatment, *J. AWWA* 76 (1984) 431–436.
- [16] Standard methods for the examination of water and wastewater. APHA, AWWA, WEF, APHA, AWWA, WEF, Washington, DC, 1995.
- [17] A.M. Raichur, M.J. Basu, Adsorption of fluoride onto mixed rare earth oxides, *Sep. Purif. Technol.* 24 (2001) 121–127.
- [18] E.A. Savinelli, A.P. Black, Defluoridation of water with activated alumina, *J. Am. Water Works Assoc.* 50 (1958) 33–44.
- [19] D.J. Killedar, D.S. Bhargava, Feasibility of fluoride adsorption on fishbone charcoal, *J. Inst. Eng. (India), Environ. Eng. Div.* 70 (1990) 47–49.
- [20] G. McKay, M.S. Otterburn, A.G. Sweeny, The removal of color from effluent using various adsorbents. Part III. Silica: rate processes, *Water Res.* 14 (1980) 15–20.
- [21] C. Namasivayam, R.T. Yamuna, Waste biogas residue slurry as an adsorbent for the removal of Pb(II) from aqueous solution and radiator manufacturing solution and radiator manufacturing industry wastewater, *Environ. Pollut.* 52 (1995) 125–131.
- [22] M. Mahramanlioglu, I. Kizilcikli, I.O. Bicer, Adsorption of fluoride from aqueous solution by acid treated spent bleaching earth, *J. Fluorine Chem.* 115 (2002) 41–47.