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Defluoridation of Groundwater in Agra City Using Low Cost Adsorbents

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Fluoride is known to contaminate groundwater reserves globally. A high fluoride content in groundwater has been reported from North and South American countries, India, China, Sri Lanka, West Indies, Spain, Holland, Italy, Norway & Mexico (Latha et al. 1999; MRD, 1993; Skjelkvale 1999). In India, its occurrence in the upper aquifer system is endemic in many places of Uttar Pradesh, Andhra Pradesh, Bihar, Gujrat, Rajasthan, Punjab, Hariyana, Tamil Nadu, Karnataka and Kerala.

Agra city (latitude 27°10'N and longitude 78°5'E) lies 200 km south of Delhi and is situated on the right bank of the Yamuna river between Mathura and Surajpur, two sites of great antiquity. Agra city is also known as the Taj city because of its Tajmahal, one of the seven wonders of the world. It is 169 m above sea level and has population of 1.5 million, so groundwater is extensively used for drinking though it is very hard and has excess fluoride at most places. Many Agrites complain pain and stiffness in joints. Several cases of dental and skeletal fluorosis alongwith secondary neurological complications, digestive and nervous disorders have been reported.

High profile of fluoride in shallow zone groundwater is mainly due to geochemical disposition in the vicinity of the groundwater extraction structures. Glass, electroplating, aluminium, steel and fertilizer industries also contribute fluoride to the aquatic environment through their effluents.

Excess fluoride, wherever present in groundwater in India, is mainly in the concentration range of 1.5 to 6.5 mg L^{-1} against its critical limit of 1.5 mg L^{-1} in drinking water (BIS, 1991; WHO 1994). The levels above this pose serious health hazards to humans and plants. High oral intake of fluoride results in physiological disorders, skeletal and dental fluorosis, thyroxine changes and kidney damage (Latha et al., 1999; Cao et al., 1996). Fluoride accumulates in bones and teeth as fluorapatite and causes bone to become brittle (Cauley et al., 1995; Fratzl, 1994; Grynpas.,l990). Loss of weight, anorexia, anemia, wasting and cachexia are common symptoms of chronic fluorosis. Excess fluoride also causes respiratory failure, fall in blood pressure and paralysis. Fluoride ions inhibit a variety of enzymes often by forming complexes with Mg^{2+} ions or by forming fluorophosfate complexes with Mg^{2+} ions. High fluoride inflicts several

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physiological and biochemical disorders in plants (Li et al., 1999) such as it inhibits germination, reduces. photosynthetic ability, alters membrane permeability, causes ultrastructural malformations like injury in leaf tips and margins, reduces productivity and biomass.

This paper reports the results of the determination of fluoride concentration in 130 groundwater samples from Agra city whose residents mostly rely on groundwater for their potable water source. It also presents the outcome of studies on defluoridation of this groundwater using activated charcoal prepared from wheat husk and flyash obtained from a thermal power plant.

MATERIALS AND METHODS

Groundwater samples were collected between 5 to 25 April 1999 at 130 locations in Agra city. The collection was done in 1-litre precleaned plastic bottles between 6-10 a.m. The fluoride concentration was determined in the samples the same day within 4 hours using Orion 920A *p*H/ISE Meter after calibrating the ion selective electrode (ISE) for fluoride with two standards (limit of detection = 0 to 7 mgL^{-1}). Then the samples were classified as A, B, C, D & E, with fluoride concentration ranges O-l, 1-2, 2-3, 3-4 and 4-5 mg L^{-1} respectively.

Activated charcoal (AC) was prepared from wheat husk as follows: The husk was treated with hot distilled water and dried at 100°C. Then 100 g of the product so obtained was treated with 100 ml of conc. H_2SO_4 and was carbonized at 150°C for 12 hours. The adsorbent was dried and ground to increase the surface area. The particle size of 100 mesh ASTM was determined with standard test sieves.

Alum treated flyash (ATF) was prepared as follows: Flyash was obtained from Harduaganj Thermal Power Station (HTPS), NTPC Aligarh. It was soaked in 1% NaOH, washed with distilled water and then dried at 115 ± 5°C in an oven for half an hour. The dried matter was mixed with 2% $Al_2(SO_4)_3$ solution and allowed to stand for half an hour. The white precipitate of $Al(OH)_3$ so appeared was dissolved by adding 1:1 HCI till a clear solution was obtained (*p*H 3.5). The solution was left overnight. The flyash was then separated, washed until free from Al^{3+} and dried at 115 ± 5°C for 6 hours. This is referred here as ATF.

All the chemicals used were AR grade. Stock fluoride solution was prepared by dissolving 100 mg of anhydrous NaF in 500 ml of double distilled water. Batch sorption tests with AC or ATF of 100 ml groundwater sample were carried out in stoppered 250-ml Erlenmeyer flasks and rotated at 150 rpm in a rotatory shaker. At the end of the desired contact time, flasks were removed and allowed to settle for 5 minutes. The samples were filtered using gravimetric filter paper (Whatman 42) filter before analysis.

Table 1. Concentration of fluoride in groundwater of Agra City.

Area	No. of Analyzed	Mean Concn of F^- (mg L^{-1})	Std. Deviation	Type*
Left Bank of Yamuna				
1. Ram Bagh	12	1.5	1.2	B
2. Trans Yamuna	7	2.5	1.2	C
Right Bank of Yamuna				
3. Water Works	7	1.5	0.4	B
4. Balkeshwar Colony	7	1.5	0.4	B
5. Kamala Nagar	5	2.0	0.0	B
6. Balenganj	4	0.8	0.1	A
7. Tajganj	9	0.9	0.1	A
8. Daresi	6	4.2	0.2	E
9. Agra Fort	3	3.1	0.0	D
10. Shahjahan Park	2	4.1	0.1	E
11. Peepal Mandi	4	2.9	0.1	C
12. Surya Nagar	2	2.0	0.0	B
Along with Byepass				
13. New Agra	4	2.9	0.1	C
14. Dayalbagh	3	2.5	0.4	C
15. Transport Nagar	7	2.8	0.3	C
Along with M.G. Road				
16. Nehru Nagar	3	2.0	0.0	B
17. Sanjay Place	4	1.8	0.2	B
18. B.M. Khan	8	2.2	0.2	C
19. Gokulpura	3	3.0	0.0	D
20. Nai Ki mandi	5	3.5	0.3	D
21. Raja ki mandi	10	2.0	0.0	B
Miscellaneous				
22. Wazir Pura	9	3.7	0.3	D
23. Shahganj	3	1.6	0.2	B
24. Khandari	3	1.8	0.2	B

**Type indicates type of groundwater samples with fluoride concentration ranges A=0-1, B=1-2, C=2-3, D=3-4 and E=4-5 mg L^{-1}*

Table 2. Defluoridation of groundwater of Agra city at pH 6.8 and 25°C in 24 hours.

Type* of Groundwater	Initial F^- Concn. (mg L^{-1})	Adsorbent	Sorbent dose (g/100ml)	Final F^- concn. (mgL^{-1})	Percent Removal (%)
A	0.5	AC	2.5	0.03	94.0
B	1.5	AC	2.5	0.12	92.0
C	2.5	AC	2.5	0.24	90.4
D	3.5	AC	2.5	0.39	88.9
E	4.5	AC	2.5	0.60	86.6
A	0.5	ATF	3.5	0.15	70.0
B	1.5	ATF	3.5	0.49	67.3
C	2.5	ATF	3.5	0.81	67.6
D	3.5	ATF	3.5	1.25	64.2
E	4.5	ATF	3.5	1.67	62.9

**Type indicates type of groundwater samples with fluoride concentration ranges A=0-1, B=1-2, C=2-3, D=3-4 and E=4-5 mg L^{-1}*

Table 3. Effect of adsorbent dose on the defluoridation at pH 6.8 and 25°C in 24 hours.

Initial F^- Concn (mg L^{-1})	Adsorbent	Adsorbent Dose (g/100 ml)	Final F^- concn. (mgL^{-1})	Percent Adsorption
1.5	AC	1	0.57	62.0
1.5	AC	2	0.14	90.7
1.5	AC	3	0.12	92.0
1.5	AC	5	0.09	94.0
1.5	ATF	1	0.82	45.3
1.5	ATF	2	0.70	53.3
1.5	ATF	3	0.48	68.0
1.5	ATF	5	0.45	70.0

RESULTS AND DISCUSSION

The concentration of F^- in groundwater of Agra city ranged 0.8-4.9 mg L^{-1} with mean values as 2.1 mg L^{-1} which is more than the limit prescribed by various agencies like USEPA, WHO, BIS & ICMR.

Table 1 lists the fluoride concentration analyzed in the study of fluoride in groundwater of Agra city. Most of 130 groundwater wells from where samples were taken were found with excess fluoride. and defluoridation of Agra groundwater was attempted.

Table 2 presents fluoride uptake by both sorbents AC & ATF as a function of initial fluoride concentration in different types (A, B, C, D & E) of groundwater samples. It is obvious that percentage removal of fluoride decreases as the initial fluoride concentration increases.

For example, 0.5 mg L^{-1} fluoride is defluoridised by 93.4% whereas 4.5 mg L^{-1} fluoride by 86.7%. Table 2 also indicates that AC is a much better adsorbent than ATF. For AC, the percentage removal was 92.3% for 1.5 initial fluoride concentration whereas ATF gave hardly 67.5% under similar conditions at higher dose of 3.5 g/ 100 ml than that of AC 2 g/100 ml.

Table 3 shows the effect of adsorbent dose on the defluoridation. As the sorbent dose was increased, percentage fluoride removal also increased. For AC, percentage defluoridation was 62.1% at a dose of 1 g/100ml whereas it became 90.7% at 2 g/100 ml. Further increase in dose did not bring a drastic rise in percentage. Thus 2 g AC/100 ml of groundwater can be taken as an optimum dose for the treatment of Agra city groundwater. Similarly, 3 g ATF/100 ml is the minimum dose required for 68.6% removal. The AC & ATF spent to defluoridate water are being regenerated using calcium chloride and sodium di hydrogen phosphate with pH adjusted to about 3.

These results show the presence of high fluoride content in groundwaterwells of Agra city. Several physical and chemical defluoridation methods have been designed to treat high fluoride water. Ion exchange and chemical treatments (Christoffersen et al., 1991) are cost intensive and biological defluoridation of drinking water cannot be a good alternative. Therefore, fluoride contaminated drinking groundwater of Agra city can be treated in homes (Phantumvanit 1998) using self made activated charcoal columns. Fluoride can be tested in influent and effluent samples with a water analysis kit prepared by Central Pollution Control Board (CPCB), Delhi. The kit is cheap and uses acidzirconyl-SPANDS reagent (APHA 1995) to develop colour that is matched manually with the provided colour chart.

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REFERENCES

APHA (1995) Standard Methods for the Examination of Water and Wastewater, 19th ed., APHA-AWWA-WPCF, Washington DC.

BIS (1991) Drinking Water Specification 1st revision, Bureau of Indian Standards, IS 10500.

Cao J, Bai X, Zhao Y, Liu J, Zhou D, Fang S, Jia M, Wu J, (1996) The relationship of fluorosis and brick tea drinking in Chinese tibentans. Eviron Health Prespect 104: 1340-1343.

Cauley JA, Murphy PA, Riley TJ, Buhari AM, (1995) Efffect of fluorinated drinking water on bone mass and fractures the study osteoporotic fractures. J Bone Min Res 10 : 1076-1086.

Christoffersen J, Christoffersen MR, Larsen R, Moller IJ, (1991) Regeneration by surface-coating of bonechar used for defluoridation of water. Water Res 25:2, 227-229.

Fratzl P, Roschger P, Eschberger J, Abendroth B, Klaushofer K, (1994) Abnormal bone mineralization after fluoride treatment of osteoporsis. asmall - angle X-ray scattering study. J Bone Min Res 9: 1541-1549.

Grynpas MD, (1990) Fluoride effects on bone crystals. J Bone Min Res 5: 169-175.

Latha SS, Ambika SR, Prasad SJ, (1999) Fluoride contamination status of groundwater in Karnataka. Curr Sci 76:6, 730-734.

Li HB, Xu XR, (1999) Sepration and determination of fluoride in plant samples. Talanta 48 : 57-62.

MRD (Ministry of Rural Development) (1993) Govt of India Prevention and control of fluorosis in India - Health aspects, RGNDWN report No. 1 25-32.

Phantumvanit P, Songpaisan Y, Moller IJ, (1998) A defluoridator for individual households. Wld Hlth Forum 9: 555-558.

Skjelkvale BL, (1994) Factors influencing fluoride concentrations in Norwegian lakes. Wat Air Soil Pollut Netherlands. 77: 151-167.

WHO (World Health Organization) (1994) Expert committee on oral health status and fluoride use, fluoride and oral health, Geneva.