

Approaches for removal of arsenic from groundwater of northeastern India

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High concentration of arsenic (As) in groundwater in the northeastern states of India has become a major cause of concern in recent years. As in groundwater has been detected in some parts of Assam, Tripura, Manipur, Nagaland and Arunachal Pradesh. Recognizing the problem of As poisoning, simple and cheap methods to produce As-free water in rural areas is an urgent need. This article deals with As-free water production and may be recommended according to National Standard for use in rural areas of the northeastern region. The article also explains the removal of As from water using wood charcoal and sand, by chemical treatment, by sedimentation method, by coagulation process or by removing the layer floating on As-bearing water. Using this method more than 90% removal of As can be achieved. Therefore, it is a possible option for use in rural areas.

Keywords: Arsenic removal, groundwater, rural areas.

THE reliability of groundwater sources for irrigated agriculture in India has promoted high crop yields among small and marginal farmers (having less than 2 ha of land), who account for about 29% of the total agricultural area cultivated. Nearly 38.1% of the net area irrigated by wells belongs to small and marginal farmers, who have nearly 35% of the tube-wells fitted with electrical pump sets¹. Nearly one million irrigation wells are added annually in the vast stretches of west and northwest India and the southern peninsula, where groundwater withdrawal exceeds annual recharge. In the northeastern state of Assam, the government during the 9th Five-year Plan period has provided around one lakh shallow tube-wells to meet the irrigation requirement and increase the cropping intensity. The apparent success of the first phase of installation of shallow tube-wells state-wise prompted the government to launch the second phase in the 10th Five-year Plan. Similarly, groundwater is also being tapped for drinking, cooking and bathing purposes by sinking shallow and sometimes deep tube-wells to obviate the diseases caused by pathogenic organisms brought into surface water bodies due to organic contamination. Due to the withdrawal of excessive amounts of groundwater, problems of increased

iron, fluoride and arsenic (As) contamination have been reported in different parts of India²⁻⁴.

Arsenic in aquatic environment is predominant in places with high geothermal activities. As has acquired an unparalleled reputation as poison, with arsenic trioxide contributing a convenient agent for homicide⁵. A recent study on cancer risks from As in drinking water indicates that it could cause liver, lung and kidney/bladder cancer besides skin cancer⁶. The most important remedial measure is prevention of further exposure by providing safe drinking water. Yet no proven technologies for the removal of As at water-collection points, such as wells are available. Hence, simple technologies for removal of As from tube-well water are needed. From this point of view, several approaches have been highlighted in this article to remove As from tube-well water used for household activities.

Distribution of arsenic in groundwater in northeastern states

The presence of As in groundwater in West Bengal is the most serious health hazard India has ever faced. A recent study shows many areas within the northeastern states with As concentration greater than 0.05 mg/l, implying that millions of people are at serious risk of As poisoning⁴. According to a report, the concentration of As generally varies from 0.02 to 0.9 mg/l (exceeding the WHO standard of 0.01 mg/l and Bureau of Indian Standard (BIS) of 0.05 mg/l). While As and iron pose individual problems in the aqueous environment, their association in groundwater has the potential of providing a simple means of removing As by co-precipitation and adsorption. About 95% of the area of the northeastern region contains dissolved iron in excess of 2 mg/l, and the iron concentration is as high as 15 mg/l in many areas⁴.

The present study undertaken by the author revealed the presence of As in groundwater as an environmental hazard, following analysis of more than 4000 water samples from 2000 wells and other drinking-water sources during the monsoon and non-monsoon seasons of 2003-04 in the eight states of northeast India. Some of the affected districts of Assam and Tripura⁴ are close to the affected districts of Bangladesh, where As concentration is above 300 µg/l. In this part of India, the rural population is dependent on tube-well water for drinking as well as for

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irrigation. Most of the tube-wells are shallow. As contamination in groundwater in the region and the occurrence of melanosis, keratosis and cancers in future are serious environmental health concerns.

As has been detected in 21 of the 24 districts of Assam and three districts in the plains of Tripura, six districts in Arunachal Pradesh, one district in Manipur and two districts in Nagaland⁴. The existence of contamination has been well established in the old Brahmaputra Plain of Bangladesh^{7,8}. Field surveys found it also occurred extensively in groundwater of the Upper Brahmaputra Plain in Assam^{4,9}. Among groundwater samples from 137 hand-pumped tube-wells in different parts of Assam, 43% indicated As concentration above 10 µg/l and 26% above 50 µg/l. Maximum concentration of 490 µg/l was detected in the region⁹. According to the study, maximum As content was observed in Jorhat (Titabor, Dhakgorah, Selenghat and Moriani blocks), Dhemaji (Sissiborgoan and Dhemaji blocks), Golaghat district (Podumani block) and Lakhimpur (Boginodi and Lakhimpur blocks), Assam; West Tripura (Jirania block), Dhalai (Salema block) and North Tripura (Dharmanagar block) districts, Tripura; Thuobal (Kakching block), Manipur and Dibang valley (Midland), Arunachal Pradesh⁴. Groundwater in these blocks belonging to the five states is contaminated with As. In Manipur, As was found only in Kakching block of Thoubal district, where As concentration was as high as 798–986 mg/l. In Arunachal Pradesh, six districts were contaminated with As and maximum As concentration (618 µg/l) was found in part of the Midland block, Dibang valley district. These six districts of Arunachal Pradesh are situated near the border area of Assam. In Tripura, parts of West Tripura, North Tripura and Dhalai districts had As concentration in the range 65–444 µg/l. In Nagaland, seven areas in Mokochung district and five areas in Mon district showed the presence of As in groundwater. These two districts are situated near Jorhat district, Assam. Traces of As were also found in the plains of Wokha and Zunheboto districts, Nagaland⁴.

In the floodplain areas of Assam, viz. Barpeta, Dhemaji, Dhubari, Darrang and Golaghat, As content was between 100 and 200 µg/l. In the remaining 11 districts of Assam where As was detected, the range was 50–100 µg/l. Only three districts, namely Karbi Anglong, NC Hills and Morigaon (floodplain) were found free from As contamination⁴.

Very high concentration of As was found in four districts, viz. Jorhat, Lakhimpur, Nalbari and Nagaon. In Jorhat district, 80 samples were collected and 21% of the samples were found contaminated with As in the range 228–657 µg/l. In Lakhimpur district, 76 samples were analysed and 21.2% were contaminated with a range 210–550 µg/l. In Nalbari district, 19% samples (total 72 samples) contained As in the range 234–422 µg/l. In Nagaon district, 76 samples were collected and 13% were found contaminated with As⁴. The range of As concentra-

tion in Nagaon was between 217 and 601 µg/l. A survey report of two districts in Assam, i.e. Dhemaji and Karimganj indicated As contamination in groundwater. So far 241 hand tube-wells have been analysed for As in these two districts; 42.3 and 19.1% have concentration above 10 and 50 µg/l respectively⁹. From these two districts, 27 villages have been identified where As in groundwater is above 50 µg/l. Recently, the Public Health Engineering Department (PHED) in association with UNICEF collected groundwater samples in the districts of Assam situated near Brahmaputra River and, found the presence of As above BIS permissible limits in the places spread over in 15 districts.

In Tripura, distribution of As in groundwater varied from 1.38 to 191.91 µg/l in West Tripura (27.19%), 4.49 to 444.48 µg/l in Dhalai (36.12%), and 3.23 to 215.0 µg/l in North Tripura (24.47%). Maximum As in drinking water was found in Jirania and Bishalgarh blocks, West Tripura; Salema and Kamalpur blocks, Dhalai and Dharmanagar, Kailasahar, Kanchanpur and Jampui blocks, North Tripura. Only South Tripura was found to be free from arsenic contamination⁴. In Thoubal district of Manipur, about 25% of the collected samples had As in the range 798–986 µg/l.

The concentration of As was relatively high in shallow tube-wells compared to deep tube-wells and ring-wells. A study on identification of arsenicosis and other related disease of As is yet to commence. Hence there is no report of arsenicosis from any of the areas in the region till date. Hydro-geochemical information of Assam suggests that elevated As concentration in groundwater is governed by the presence of organic matter in the sediments and reduced alluvial aquifers with high iron, low sulphate and nitrate concentrations⁴.

The sediment in the northern region contains a high percentage of clay and organic compounds¹⁰, which may retain and release As in the groundwater aquifers. A study¹¹ on As in carbonaceous matter in Arunachal Pradesh, Assam, Nagaland and Meghalaya, indicated that the mean As concentration of samples from the four regions was 95.1 mg/kg. It is believed that the weathering of sulphide associated with carbonaceous matter may have produced As-rich iron oxyhydroxides, which in turn released As (after reduction) to the existing sedimentary environment^{2,12}. Results indicated increased As enrichment from east to west in Northeast India. The distribution of arsenic in northeastern India is presented in Figure 1.

Arsenic chemistry and its removal

As occurs in waters in several different forms depending upon the pH and redox potential (Eh) of water¹³. Arsenate (As^{5+}) and arsenite (As^{3+}) are the primary forms of As found in natural waters¹³. The thermodynamically stable forms are As^{5+} in oxygenated surface water and As^{3+} in

reducing groundwater. Both forms can occur together in both environments due to the slow oxidation and reduction kinetics¹⁴.

Many technologies have been developed for the removal of As. All the technologies for As removal rely on a few basic chemical processes. Oxidation/reduction reactions reduce (add electrons to) or oxidize (remove electrons from) chemicals, altering their chemical form. These reactions do not remove As from solution, but are often used to optimize other processes. Precipitation causing dissolved As to form a low-solubility solid mineral, such as calcium arsenate. This solid can then be removed through sedimentation and filtration. When coagulants are added and form flocs, other dissolved compounds such as As can become insoluble and form solids. This is known as co-precipitation. The solids formed may remain suspended, and require removal through solid/liquid separation processes, typically coagulation and filtration. In adsorption and ion exchange, various solid materials, including iron and aluminum hydroxide flocs have a strong affinity for dissolved As. As is strongly attracted to sorption sites on the surfaces of these solids, and is effectively removed from solution. Ion exchange can be considered as a special form of adsorption. Other forms of adsorption involve stronger bonds, and are less easily reversed. Precipitation, co-precipitation, adsorption and ion exchange all transfer the contaminant from the dissolved to a solid phase. In some cases the solid is large and fixed (e.g. grains of ion exchange resin), and no solid/liquid separation is required. If the solids are formed *in situ* (through precipitation or coagulation), they must be separated from the water. Gravity settling (also called sedimentation) can accomplish some of this, but filtration is more effective. Most commonly, sand filters are used for this purpose. A study with just As-containing water showed that sedimentation could only remove 8.7% As after 24 h settling time¹⁵.

The study is restricted to As and provides no insight into the potential influence of iron and the removal efficiency.

From several studies, it is already known that coagulation-precipitation is an effective and most frequently applied technique in As removal^{14–19}. In this technique, addition of coagulant facilitates the conversion of soluble As species into insoluble products through co-precipitation and adsorption. Adsorption of As on preformed $\text{Fe}(\text{OH})_3$ has also been shown to be an effective method for removing As^{19,20}. However As removal during coagulation with FeCl_3 is more efficient than As adsorption onto preformed hydrous ferric oxide²¹. It is suggested that where As removal depends on iron precipitation, the settling time must exert a major influence on the removal process. Depending on the initial iron concentration in the raw water, a study indicated that a 1 h design period was 'inadequate to complete iron precipitation'²². Some simple household As-removal systems have also been developed based on traditional-sand filtration water purification along with wood charcoal or rusted iron nails as an adsorption medium. These As-removal filters have been used in As-affected areas of Bangladesh and Nepal.

Most of the established technologies for As removal make use of several of these processes, either at the same time or in sequence. Many laboratories, organizations and institutions in different parts of the world have looked into the development of As-removal devices based on such processes. All of the removal technologies have the added benefit of removing other undesirable compounds along with As—depending on the technology, bacteria, turbidity, colour, odour, hardness, phosphate, fluoride, nitrate, iron, manganese and other metals can be removed¹⁶.

Arsenic removal using wood charcoal and sand

A simple As-removal system has been developed in Bangladesh, based on a traditional sand-filtration water-purification system. In this method, As-contaminated water was allowed to pass through successive layers of sand and wood charcoal at different flow rates (Table 1). The method was demonstrated in a study in which three pitchers (11 l each) were placed one above another vertically in a bamboo-tripod²³. The top pitcher contained coarse sand, the second pitcher wood charcoal and fine sand, and the third served as storage. Weight of the layers of charcoal (size of pieces: 1–1.5 cm) was varied (606, 754 and 457 g), while weight of the layer of fine sand was 4480 g. The small orifice at the bottom of the second pitcher was covered with a screen (cloth filter) to prevent sand from leaking out. As-rich groundwater was poured into the top pitcher, which trickled through small holes into the second and third pitchers. The flow rates of water supplied for the experiment was in the range of 720 ml to 20.16 l/h.

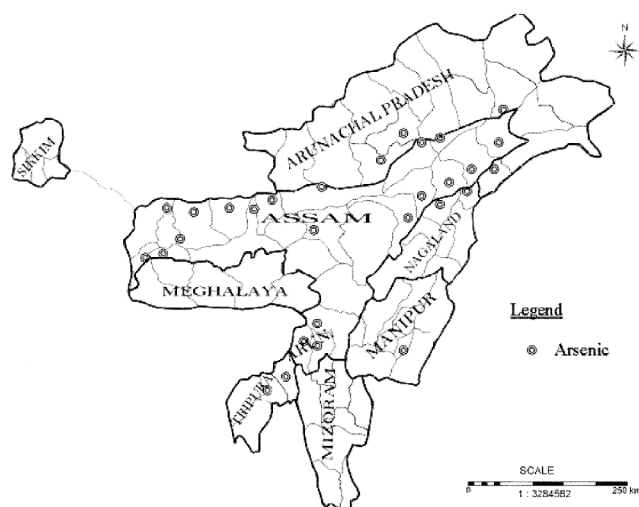


Figure 1. Distribution of arsenic in groundwater of northeastern India.

Table 1. Arsenic removal from contaminated water by charcoal method at different flow rates

Flow rate (ml/min)	Initial arsenite content (mg/l)	After filtration (mg/l) (Sand 4480 g + charcoal)			Per cent removal (Sand 4480 g + charcoal)		
		Coal			Coal		
		606 g	754 g	757 g	606 g	754 g	757 g
12	0.46	0.004	0.012	0.006	99	97	99
30	0.46	0.007	0.014	0.006	98	97	99
40	0.46	0.007	0.02	0.006	98	96	99
54	0.46	0.013	0.027	0.011	97	94	98
126	0.46	0.015	0.047	0.014	97	92	97
137	0.46	0.026	0.052	0.019	94	89	96
148	0.46	0.028	0.067	0.02	94	85	96
150	0.46	0.034	0.066	0.024	93	86	95
192	0.46	0.038	0.098	0.032	92	79	93
260	0.46	0.05	0.017	0.04	89	63	91
265	0.46	0.054	0.22	0.048	88	53	90
336	0.46	0.25	0.28	0.16	46	39	65

The experiment showed that the three-pitcher filter can remove As present in groundwater in a wide range of concentrations. Arsenite proportions in groundwater ranged from 39% to near total (99%). Table 1 shows percentage of As removal from As-bearing water at different flow rates. It was found that removal of As was higher with lower flow rates through the layer of charcoal. With the successive layers containing 4480 g of fine sand and 606 g of coal, about 99 to 97% removal of As was observed with flow rates varying from 12 to 54 ml/min (720 ml to 3.24 l/h) respectively. Similar results were found when 754 and 757 g of charcoal were used with the 4480 g of fine sand respectively. The different flow rates of contaminated water indicate different saturation conditions and absorption capacities of the materials used for As removal. Information on saturation curve was not presented in the experiment. However, the results indicate that materials used in this system have a limited capability of absorption when saturation condition was increased by increasing the water flow rate above 3.24 l/h.

Field-testing of two hundred similar pitcher filter units in As affected areas of Bangladesh confirmed that after one week of operation, 90% of the filters produced water in which no As could be detected using field kits, and 7% produced water with significantly reduced but detectable arsenic levels²⁴. Iron levels were also dramatically reduced, in some cases from over 1 mg/l to below 0.1 mg/l. After four months of operation, the filters were still performing efficiently (S. B. Rasul *et al.*, unpublished).

This system shows great promise in that it is highly effective, inexpensive, easy to operate, and similar to traditional water-treatment methods. A significant drawback of the three-pitcher filter is that treated water can easily become contaminated with faecal bacteria, either during transport of water from the well, or storage in the households. Bacteria may also be present in the medium, if it is

not sterilized. Field tests showed that slight contamination occurred before filtration, but that bacterial counts increased dramatically during filtration and storage (S. B. Rasul *et al.*, unpublished)²⁴. It may be possible to reduce the risk of bacterial contamination by sterilizing the medium before filter-construction.

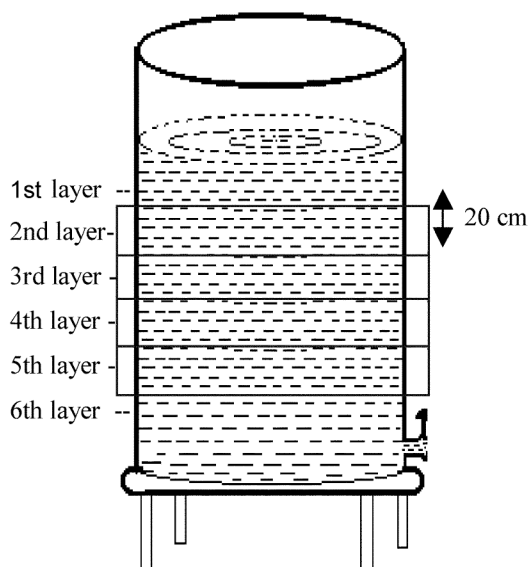
Arsenic removal using sedimentation method

Passive sedimentation received considerable attention because of the rural people's habit of drinking stored water from pitchers. Oxidation of water during collection and subsequent storage in households may cause a reduction in As concentration in stored water. As reduction by plain sedimentation appears to be dependent on water quality, particularly the presence of precipitating iron in water.

In an experiment using the sedimentation method²³, As-contaminated water was kept in a tank (capacity 3000 l). At every 72 h, As level in the water was tested at five different layers of water in the tank. Each layer was assumed to be 20 cm thick and the sixth layer at the bottom acted as sedimentation trap (Figure 2). Sampling of water for As at different levels was done with the help of a glass pipette. During the experiment it was found that As contaminated water, when kept in a storage tank under room temperature, formed a thin layer at the top of its surface after a couple of days. This may occur due to formation of As compound in the presence of iron, when the water containing As came in contact with atmospheric oxygen, which is the most readily available oxidizing agent. Repeated removal of this thin layer from the top surface reduced the As content to safe level (0.05 ml As/l according to BIS). The dissolved oxygen in water oxidizes arsenite to less-mobile arsenate and the ferrous iron in the aquifer to ferric iron, resulting in a reduction of As content in water. Table 2 shows that concentration of As

Table 2. Reduction of arsenic level in water by sedimentation method

Duration (h)	Amount of arsenic (mg/l)					6th layer
	1st layer	2nd layer	3rd layer	4th layer	5th layer	
0	0.45	0.45	0.45	0.45	0.45	Sedimentation trap
72	0.05	0.10	0.20	0.30	0.30	
144	0.05	0.10	0.20	0.20	0.30	
216	0.05	0.03	0.04	0.20	0.30	
288	0.05	0.01	0.01 ⁺	0.02 ⁺	0.2 ⁺	

**Figure 2.** Different layers of water in a tank.

in storage water decreases after 72 h of storage time. After a period of 216 h (nine days), the second and third layers of water from the top surface attained safe level of As content. The third layer also showed safe level of As content after 288 h (12 days) of sedimentation period. The air oxidation of As is a slow process and it takes weeks for oxidation to occur²⁵. Another study²⁶ showed that more than 50% reduction in As content is possible by sedimentation of groundwater containing 380–480 mg/l CaCO_3 and 8–12 mg/l iron, but cannot reduce As concentration to the desired level of 0.05 mg/l.

Arsenic removal by coagulation process

Adsorption and co-precipitation using coagulants for sequencing As from drinking water has been studied by different workers and its economic feasibility established^{14,18,27}. Coagulation and filtration is the most common As-removal technology. By adding a coagulant such as alum, ferric chloride or ferric sulphate to contaminated water, much of the As can be removed. As removal is possible with either ferric or aluminum salts, with laboratories reporting over 99% removal under optimal condi-

tions¹⁸, and residual As concentrations of less than 1 $\mu\text{g/l}$. If As is present as arsenite, the water should be oxidized first using chlorine, permanganate, ozone or other oxidants. After adding the coagulant, the water should be stirred, allowed to settle and filtered for best results. Coagulation improves parameters such as turbidity and colour, and can reduce levels of organic matter, bacteria, iron, manganese, and fluoride, depending on operating conditions.

Alum and ferric salts dissolve upon addition to water; ferric salts dissolve and the ferric ion forms an amorphous solid with oxygen and hydroxyl groups. This is variously called amorphous iron oxyhydroxide, iron (oxy)hydroxide, hydrous ferric oxide (HFO) and ferrihydrite. These metal hydroxides form gelatinous flocs that bind to other flocs and settle out of solution, scavenging many dissolved and particulate materials in the process. HFO formed can remove approximately five times as much As from contaminated water¹⁴. If water is soft and of low alkalinity, it may be necessary to increase its alkalinity to ensure floc-formation.

Conventional coagulation process using alum (1% ferric alum grade-2, BIS specification) and poly aluminium chloride (1% PAC) as coagulant has been found effective for removal of As from groundwater²⁸. Floc-formation and settlement is relatively better with PAC in comparison with alum. Complete floc settlement can be observed within 15 min in case of coagulation with PAC, whereas it takes 20 min with alum (Tables 3 and 4). This was demonstrated in an experiment in which measured volumes (1000 ml) of the test water were coagulated and flocculated using the jar test apparatus in 1000 ml beakers. After simultaneous addition of coagulant in each beaker, the solution was stirred maintaining rapid mix at 90 ± 10 rpm for 1.0 min followed by slow mix at 40 ± 5 rpm for 14 min. At the end of the stirring period, the contents of the beakers were allowed to settle for 30 min. The supernatant was filtered and samples were prepared in 3M HCl solution. As concentration was determined in the filtered waters by the hydride generation – inductively coupled plasma atomic emission spectrometric (HG-ICP-AES) method²⁸.

Studies also indicate that the efficiency of removal of arsenate by coagulation with alum can be improved with increased dose of alum. Metal coagulants do not completely remove arsenite from groundwater as in the case of

Table 3. Performance of alum and PAC in arsenic removal

		Alum dose (mg/l)						PAC dose (mg/l)					
		0	30	40	50	60	70	0	10	15	20	25	30
Residual arsenic (µg/l)	105	77	70	59	30	BDL	BDL	105	80	63	23	15	BDL
	(-)	(26.7)	(33.3)	(43.8)	(71.4)	(>99)	(>99)	(-)	(23.8)	(40.0)	(78.1)	(85.7)	(>99)
	0	100	150	200	210	220	220	0	100	110	120	130	-
Residual arsenic (µg/l)	519	186	82	37	20	BDL	BDL	519	12	2	BDL	BDL	-
	(-)	(64.2)	(84.2)	(92.9)	(96.1)	(>99)	(>99)	(-)	(97.7)	(99.6)	(>99.6)	(>99.6)	-
	0	100	150	200	210	220	220	0	100	125	150	-	-
Residual arsenic (µg/l)	1189	465	245	106	53	BDL	BDL	1189	36	7	BDL	-	-
	(-)	(60.9)	(79.4)	(91.2)	(95.5)	(>99)	(>99)	(-)	(97.0)	(99.4)	(>99.4)	-	-

Figures in parentheses indicate percentage of arsenic corresponding to the dose.
BDL, Below Detectable Limit (<2 mg/l).

Table 4. Arsenic removal from groundwater

Total arsenic in test water (µg/l)	Dose required to obtain residual arsenic concentration (≤10 µg/l)	
	Alum (mg/l)	PAC (mg/l)
105	70	30
519	220	110
1189	250	125

arsenate removal. Hence, it is necessary to identify the oxidation state of As present in the waters before selecting the treatment method or to bringing about modifications in the operation of existing treatment facility. When groundwater contains As in the form of arsenite, pretreatment with chlorine followed by coagulation is recommended. Pretreatment with chlorine oxidizes arsenite to arsenate. Studies on As removal from groundwaters of West Bengal using ferric chloride as coagulant have been reported²⁹.

Coagulation with ferric salts works best at pH below 8. Alum has a narrower effective range, from pH 6 to 7. If pH is above 7, removal may be improved by adding acid to lower the pH. In general, higher the coagulant dosage, better the As removal. Typical doses are 5 to 30 mg/l ferric salts or 10 to 50 mg/l alum. If the source water has high levels of phosphate or silicate, coagulation may be less effective. However, sulphate, carbonate and chloride have little effect on removal rates.

Arsenic removal using lime-softening

Lime-softening is a similar process to coagulation with metal salts. Lime ($\text{Ca}(\text{OH})_2$) hydrolyses and combines with carbonic acid to form calcium carbonate, which acts as the sorbing agent for arsenic removal. This process is typically used only with hard water, and shifts the pH of treated water to markedly higher values, in the range of 10–12. In an experiment, calcium oxide (lime) was added at different doses (0.5 to 8.5 g in) to As-contaminated tube-well water (5 l each) and allowed to stay for several hours in a container (plastic bucket). Table 5 shows that

adding 0.1% (by weight) of lime to As-contaminated water, reduced As to safe level after a period of 10 h, while no As was detected²³ after a period of 16 h. However, no information was provided about the change in pH and other water-quality parameters.

Nearly 100% removal of arsenate is possible at pH 10.5 and higher using the lime-softening technique. Maximum arsenite removal was found³⁰ to be about 80% at pH 11.10. The main removal mechanism is sorption of As onto magnesium hydroxide solids that form during softening. As removal at lower pH can be greatly improved by the addition of low levels of iron, but when carbonate is present, this effect is less pronounced. Trace levels of phosphate were found³¹ to slightly reduce As removal, especially below pH 12.0. However, a study showed that arsenite levels could be reduced by over 90% using lime-softening supplemented with a powdered coal additive³². These studies theorize that arsenite is directly adsorbed, but another study suggests that the carbon could catalyse As oxidation¹⁶.

Disadvantages of lime-softening for arsenic removal are that large coagulant doses are required, of the order of 800–1200 mg/l, and consequently a large volume of sludge is produced. Also the operating pH is rather extreme, and strong acids would probably be needed to adjust the pH after treatment.

Use of natural inorganic gradient

Calcium and sodium montmorillonite, activated alumina (Al_2O_3), calcium carbonate (CaCO_3) and calcium oxychloride (CaOCl_2) are naturally occurring chemical compounds that are effective absorbents for removing As from groundwater.

A laboratory-based experiment was carried out in three stages and in each stage the amount of adsorbents and physico-chemical properties like EC, pH and As concentration in water were changed³³. For all three stages, the chromatographic column was prepared by taking 500 g clay (calcium/sodium montmorillonite) + 50 g Al_2O_3 (activated alumina) + 25 g CaCO_3 (fine powdered limestone) + 50 g of calcium oxychloride. The aqueous medium was

Table 5. Treatment of arsenic contaminated water with calcium oxide

Amount of water (ml)	Amount of CaO (gm)	Initial arsenic content (mg/l)	Arsenic concentration (mg/l)			Per cent removal		
			After			After		
			1 h	10 h	16 h	1 h	10 h	16 h
5000	0.5	0.45	0.45	0.400	0.40	0.0	11	11
5000	1.0	0.45	0.45	0.350	0.30	0.0	22	38
5000	2.0	0.45	0.40	0.250	0.15	0.0	44	67
5000	2.5	0.45	0.40	0.090	0.06	0.0	80	87
5000	3.0	0.45	0.35	0.070	0.05	22	84	89
5000	3.5	0.45	0.30	0.070	0.05	33	84	89
5000	4.0	0.45	0.30	0.050	0.03	33	88	93
5000	4.5	0.45	0.30	0.050	0.03	33	88	43
5000	5.0	0.45	0.25	0.035	Nil	44	92	100
5000	5.5	0.45	0.25	0.030	Nil	44	93	100
5000	6.0	0.45	0.25	0.020	Nil	44	96	100
5000	6.5	0.45	0.20	0.150	Nil	56	97	100
5000	7.0	0.45	0.20	0.010	Nil	56	98	100
5000	7.5	0.45	0.15	0.010	Nil	67	98	100
5000	8.0	0.45	0.10	0.010	Nil	78	98	100
5000	8.5	0.45	0.10	Nil	Nil	78	100	100

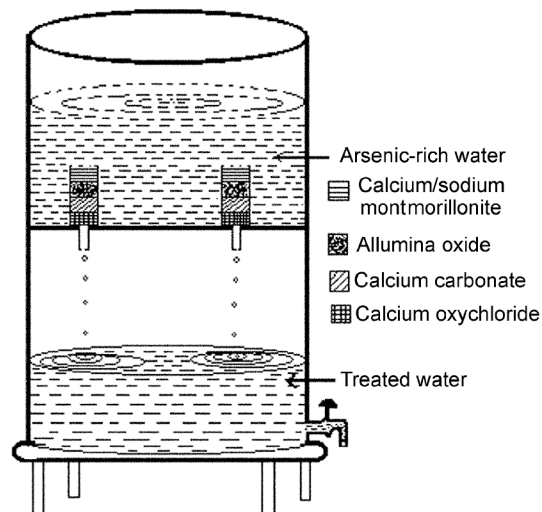
Table 6. Chemical components and aqueous ionic species used in the experimental study

Stage	Clay	Al ₂ O ₃ (g)	CaCO ₃ (g)	CaOCl ₂ (g)	pH	EC (μS/cm)	Arsenic (μg/l)
	(Ca/Na montmorillonite in g)						
1	500	50	25	25	7.3	1050	200
2	500	50	25	25	7.8	1500	400
3	500	50	25	25	8.2	1800	800

maintained at different pH levels (7.3, 7.8 and 8.2), EC (1050, 1500 and 1800 $\mu\text{S}/\text{cm}$) and arsenic concentration (200, 400 and 800 $\mu\text{g}/\text{l}$) at stages 1–3 (Table 6). The column and interaction solute fractions were collected at fixed intervals of 20, 40, 60, 80, 120, 180 and 240 min, and were analysed quantitatively for As concentration in drinking water. In stages 2 and 3, the chemical concentration of aqueous medium and compound used in the columns was varied. As-removal impacts at various initial concentration levels are presented in Table 7. It was observed that calcium/sodium montmorillonite, activated alumina, calcium carbonate and calcium oxychloride are effective coagulants and absorbents. They can remove As from water having low-to-moderate levels of concentration (<200 $\mu\text{g}/\text{l}$), neutral to mildly alkaline pH and low-to-moderate EC (1050 $\mu\text{S}/\text{cm}$). Based on this study, a simple and symmetric diagram was designed for removal of As from groundwater (Figure 3).

Household arsenic filter

The US-based Massachusetts Institute of Technology (MIT), in collaboration with a Nepal-based non-governmental Environment and Public Health Organization (ENPHO) has developed the KanchanTM arsenic filter under the Nepal Water Project, which not only removes carcinogenic chemicals like As but also pathogens, iron, turbidity and odour without using any chemicals³⁴.

**Figure 3.** Removal of arsenic using natural inorganic gradient.

The KanchanTM arsenic filter is comprised of two removal units: the As-removal unit and the pathogen removal unit. The As-removal unit consists of a plastic diffuser basin, iron nails and some brick chips. The pathogen removal unit consists of sand and gravel layers. The cross-section of the KanchanTM Arsenic Filter is shown in Figure 4. It works on a simple principle: when the nails are exposed to air and water, they rust quickly, producing

ferric hydroxide (iron rust) particles, which are an excellent adsorbent for As. When As-contaminated water is poured into the filter, the toxic element is rapidly adsorbed onto the surface of the ferric hydroxide particles. The As-loaded iron particles are then flushed into the sand layer below. The layer of fine sand traps the As-loaded iron particles in the top few centimetres, thus effectively removing As. The system works at optimal pH (6.5–8.5) and water flow rate between 10 and 30 l/h. It can remove both arsenite and arsenate without any chemical pre- or post-treatment. Field research by MIT and ENPHO showed that As removal using the filter was in the range 85–95%. Independent field studies of the KanchanTM arsenic filter in Nepal by the Tribhuvan University, Kathmandu University and United States Peace Corp also confirm the rate of arsenic removal³⁵.

Arsenic-removal devices at community level

There are various As-removal devices based on different technologies like ion-exchange, adsorption or co-precipitation, developed and tried by various laboratories, organizations, and institutions in different parts of the world. These devices, in case of adsorption, mostly use

Table 7. Change in arsenic concentration ($\mu\text{g/l}$) with time

Time (min)	Stage 1	Stage 2	Stage 3
0	200	400	800
20	185	395	800
40	175	320	710
60	160	280	625
80	140	190	575
120	50	120	415
180	50	118	405
240	50	118	400

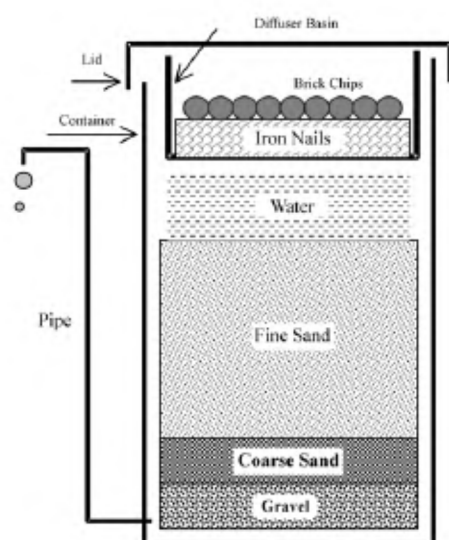


Figure 4. Kanchan arsenic filter developed under Nepal Water Project (MIT and ENPHO).

activated alumina or granular ferric hydroxide with or without add-ons or use ion-exchange approaches based on metal oxides, resins, etc. Some of the effective arsenic removal devices, currently available in the country are described here in brief:

AIHH&PH arsenic removal plant: The All India Institute of Hygiene & Public Health (AIHH&PH) designed an arsenic-removal plant (ARP) on the basis of maximum treatment rate of 1000 l/h. The principle of functioning of the ARP is oxidation–coagulation–flocculation–sedimentation–filtration. In the first chamber of the plant bleaching powder solution (oxidizing agent for conversion of As^{3+} to As^{5+}) and alum (30–60 mg/l) or ferric salts (20–40 mg/l) solution were added with pumped water, where they were thoroughly mixed in the presence of baffles. The chemical mixed water was then passed to the second chamber, i.e. non-mechanized clariflocculator, where at least 2 h detention time was allowed for precipitation of the flocs. The clear water (supernatant) was collected in the launder provided along the periphery of the clariflocculator. Water from the launder was then taken to the third chamber (filter chamber). The water was allowed to flow in an upward direction (up-flow) through graded gravel media (3–5 mm-sized gravel). The As-safe filtered water was finally collected through a tap provided in the filter chamber. During operation of the plant, the user must pump at least the same quantum of water that he/she wants to collect from the tap fitted in the third chamber. Intensive performance monitoring of the ARP highlighted that the removal efficiency of As as well as iron is 95 and 90% respectively, as claimed by AIHH&PH. The capacity of ARP is about 100 l/h. The drawback of this device is that it requires periodic sludge-removal and/or cleaning.

AdsorpAs® arsenic removal technology: This As-removal unit uses granular ferric hydroxide (GFH) as adsorbent, which can eliminate As (any concentration) from drinking water, bringing down its level to below permissible limits for potable use. GFH does not require to be regenerated. The spent GFH is claimed to be non-toxic and non-hazardous. Analysis conducted by the Federal Institute of Material Research and Testing and TUV-Umwelt has established that no leaching of As from the spent AdsorpAs® takes place under normal environmental conditions. The device is simple, easy to install, and operation of plant is user-friendly. No complicated dosing of chemical, pH adjustment or day-to-day monitoring of the system is required. The device requires periodic backwash.

Apyron technologies for arsenic removal: This device removes As by adsorption using manganese oxide and activated alumina. The manganese oxide converts As^{3+} to As^{5+} , which can then be adsorbed on activated alumina. Pure activated alumina cannot adsorb As^{3+} . The system

also removes iron and improves colour and taste of drinking water. The medium adsorbs As rapidly and can treat water at full flow from a tube-well hand pump. It typically provide As safe water to over 200 people for 6 to 8 months before the medium must be changed. It is claimed that the medium after use is non-toxic and can be disposed safely like ordinary sanitary waste.

Oxide (India) arsenic removal plant: Oxide (India) has also developed an As-removal plant using activated alumina. The capacity of the plant is 600–800 l/h. Periodic replacement of the medium and disposal of As-laden sludge are the main drawbacks of the system.

Ionochem: The As-treatment unit in the design comprises one iron-removal filter and one arsenic-removal filter. The device is designed to be operated manually and can be fitted with a hand tube-well along with pressure pump. Whenever the hand tube-well is pumped, raw water is pressurized by the pressure pump and water is then passed initially through iron-removal filter filled up with catalytic filtering media $\text{Fe}(\text{OH})_3$ and $\beta\text{-FeOOH}$. $\text{Fe}(\text{OH})_3$ reacts with sodium arsenate and $\text{Fe}(\text{OH})_2$ reacts with sodium arsenite. Due to chemisorption, As is bound with the material throughout and thus As (both arsenate and arsenite) is removed along with part of iron. The capacity of the device is about 600 l water/h. Regular backwashing of iron removal filter is necessary.

SFR arsenic and iron removal plant: This system has been designed by the School of Fundamental Research (SFR), Kolkata. It can be fitted to a hand pump which is connected through a check valve with a vertical PVC cylinder ($3'' \times 3''$) filled with a silicate matrix and an additional oxidizing element (proprietary item under patenting application) for removal of the major portion of iron before the water enters into the As-removal system. It is then connected with a 1" diameter flexible PVC delivery pipe leading to three vertically placed parallel PVC cylinders ($3'' \times 3''$), trigonal-shaped, filled with goethite compound specially deposited on activated alumina. After adsorption in three consecutive cylinders, the water is allowed to pass through the last cylinder and released through the flow metre. The medium used for adsorption of As in this system is aluminium silicate and ferric hydroxide. The device can provide 2000 l As-safe water per day for 6 to 8 months, before the medium is changed.

Critical analysis of chemical parameters³⁶ in respect of 19 devices available in the country was done by SFR at the Arsenic Technology Park during 2001–03 (two years). All the six devices mentioned above have shown consistent and good performance. These devices can remove As from the lower level (150–250 $\mu\text{g/l}$) to higher level (500–1000 $\mu\text{g/l}$) along with average iron content (5–10 mg/l) in raw water. Overall use and yield performance of all the units are good. It was observed that AIIH&PH and Apyron

tend to increase conductivity of water in the filtered stage. Hardness analysis showed that AIIH&PH and Ionochem tend to increase hardness.

It is generally observed that As^{5+} is better removed and hence in most of the As-removal devices, a primary oxidizing-interface for converting As^{3+} species to pentavalent status is ensured. Speciation studies show that while all the As^{3+} species present in the raw water get converted or removed through the medium interface, this is not essentially true for the removal or adsorption for As^{5+} . Whatever As remains after filtration is of As^{5+} species³⁶.

Conclusion

It was found that the pitcher filter unit can remove 90–98% As-bearing water when As bearing groundwater was passed through wood charcoal and sand. This technology is effective at household level in removing As, but the system may be quickly clogged as groundwater of the northeastern region contains excessive iron. Risk of bacterial contamination may also to be checked by sterilizing the medium before filter-construction.

The sedimentation method is chemical-free and simple, and is likely to be more acceptable, but the method is unable to reduce As content to safe limits when As content in groundwater is high. Other water-quality problems may also arise due to long storage time under room temperature.

The efficiency of the chemical process using lime/CaO should be largely independent of scale. High pH and large volume of waste generation are the major disadvantages of this technique. Though relatively inexpensive, it is more expensive than coagulation with iron salts or alum because of larger doses required, and waste-handling.

As-removal efficiency was excellent using activated alumina and some natural inorganic gradient. However, As capacity varies significantly, and is controlled by pH and influent As concentration and speciation. For neutral and acidic groundwaters of northeastern India, therefore, pH adjustment is necessary for effective As removal using inorganic gradients.

Coagulation with ferric salts works best at pH below 8. It was observed that pH of the water samples of different northeastern states is acidic to slightly alkaline: ranges from 6.0 to 8.3 in Arunachal Pradesh, 5.5 to 7.4 in Assam, 6.4 to 8.7 in Manipur, 4.0 to 8.0 in Meghalaya, 4.8 to 7.4 in Mizoram, 5.8 to 8.0 in Nagaland, 5.1 to 7.2 in Sikkim, and 4.3 to 8.3 in Tripura⁴. The water also has low levels of phosphate and hence coagulation and filtration would be more effective. In case of pH of water above 7, removal may be improved by adding acid to lower the pH.

Some of the innovative methods developed through Nepal Water Project, i.e. KanchanTM Arsenic filter may be helpful in prevention of arsenic contamination as the system works at optimal pH (6.5–8.5) without any chemical pre- or post-treatment.

Since As^{5+} species is less potent compared to As^{3+} , filtered water as obtained through As-removal devices is less liable to cause arsenicosis³⁶. Thus, As-removal devices are otherwise capable of providing As-free or low As (mostly as As^{5+}) water. These devices can filter As- and iron-contaminated water to a level below 50 $\mu\text{g/l}$, and may be effective for the rural community in the plain/valley areas of the region. However, community participation in maintenance and fund mobilization for the upkeep of the facilities at the time of replacement of the medium is essential. Proper cycle of backwashing and forward washing can ensure better longevity of chemical media.

Any of the methods mentioned above can be used to produce As-free water (below BIS permissible level of 50 $\mu\text{g/l}$) and it can be recommended for use in rural areas of the northeastern region.

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