A lab-to-land transition success story

Radiation technology for purification of Arsenic contaminated water

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Abstract

Arsenic pollution in drinking water has evolved into a critical environmental hazard in several parts of India, such as Chhattisgarh, West Bengal, Uttar Pradesh, Bihar and the northeastern region. To mitigate this problem, Radiation Technology was employed as a facile, environment friendly tool for tailoring a novel, functionalized cellulose based cationic bio-adsorbent system via radiation induced grafting process. The optimized adsorbent system was demonstrated to efficiently remove Arsenic from aqueous streams, in both batch and continuous flow mode operations. Arsenic contaminated groundwater samples collected from different affected areas were successfully treated to reduce contamination level below the WHO permissible limits of 10 ppb in drinking water. A portable water treatment setup was designed, fabricated and employed for field trials at affected areas. Post upscalation from bench to pilot scale and field trials, the technology has been successfully transferred to private licensees for point of use and point of entry water treatment applications. We have followed the concept of Technology Readiness Levels (TRLs), a method used to quantify the technical maturity of a technology throughout research, development and deployment phases.

Keywords: Arsenic, Technology Readiness Levels (TRLs), Water purification, PMAETC-*g*-Cellulose adsorbent, Radiation grafting

Introduction

Ensuring safe drinking water as an indispensable part of everyday life has been one of the foremost priorities of every country in the world. Consumption of unsafe drinking water leads to various infectious diseases, often causing fatalities. One of the major toxic water pollutants globally and a well-known carcinogen is Arsenic. Prolonged consumption of arsenic contaminated water leads to diseases such as cancer of the skin, bladder, kidney, lungs, and dermatological disorders namely, skin lesions (e.g. hyperpigmentation, hyperkeratosis), formation of rough patches on palms and soles, which are collectively termed as Arsenicosis. The World Health Organization (WHO) and the U.S. Environmental Protection Agency (USEPA) have recommended the Arsenic Maximum Contaminant Level (MCL) for public drinking water supplies to be less than 0.010 mg/L(10 ppb). In 2012, it was reported that over 200 million people worldwide are exposed to contaminated drinking water with Arsenic concentrations above 50 ppb[1]. Considering its vast population and the significant number of people that rely heavily on groundwater sources to fulfill their daily requirements, India ranks as one of the most vulnerable countries in terms of Arsenic exposure. Parts of states like West Bengal, Uttar Pradesh, Bihar, Chhattisgarh, Jharkhand, Assam, Manipur and regions mainly in the Ganga-Meghna-Brahmaputra plains have reported Arsenic levels in groundwater way above MCL values. It has been observed that drinking and cooking water along with water-soil-crop-food-transfer is the major exposure pathway for Arsenic to infiltrate the human food chain. With such a crisis looming over large sections of India's populace, the need of the hour is to provide a feasible, efficient and cost effective solution for mitigation of Arsenic contamination, both at the domestic and community levels, to evade an imminent health crisis. Conventional technologies that have been adapted over the years include use of ion exchange resins, activated charcoal, coagulation/co-precipitation, Reverse Osmosis, ultrafiltration, etc.[2-4]. But most of these methods suffer from limitations in terms of reusability, secondary waste/sludge generation, ease of operation, production process feasibility or economic viability.

The most prevalent forms of Arsenic in water are Arsenite and Arsenate. It exists in Arsenite (As(III)) form under anoxic reducing conditions, whereas Arsenate (As(V)) is prevalent in aerobic oxidizing environments, such as surface waters.[5] Moreover, the ionic forms of As(III) and As(V) depend on pH: As(V) persists in its oxyanionic forms ($H_2AsO_4^-$, $HAsO_4^{2-}$) at pH>3, while As(III) exists in its anionic form at pH>9. Hence, most of the proposed methods such as ion-exchange, adsorption, coagulation, co-precipitation, etc., display superior efficiency in removal of As(V) compared to As(III). The solution to this issue lies in pre-oxidation treatment for converting As(III) to the more easily extractable As(V) form using oxidants such as chlorine, permanganate, ozone and manganese-oxide-based solid media.[6] Therefore, it is recommended to analyze the target water quality in terms of As concentration, speciation, pH and other contaminants, in order to design an effective arsenic removal system best suited to the prevalent conditions.

Radiation Technology has been employed for the first time, to the best of our knowledge, as a facile tool for tailoring robust, recyclable functionalized cellulose

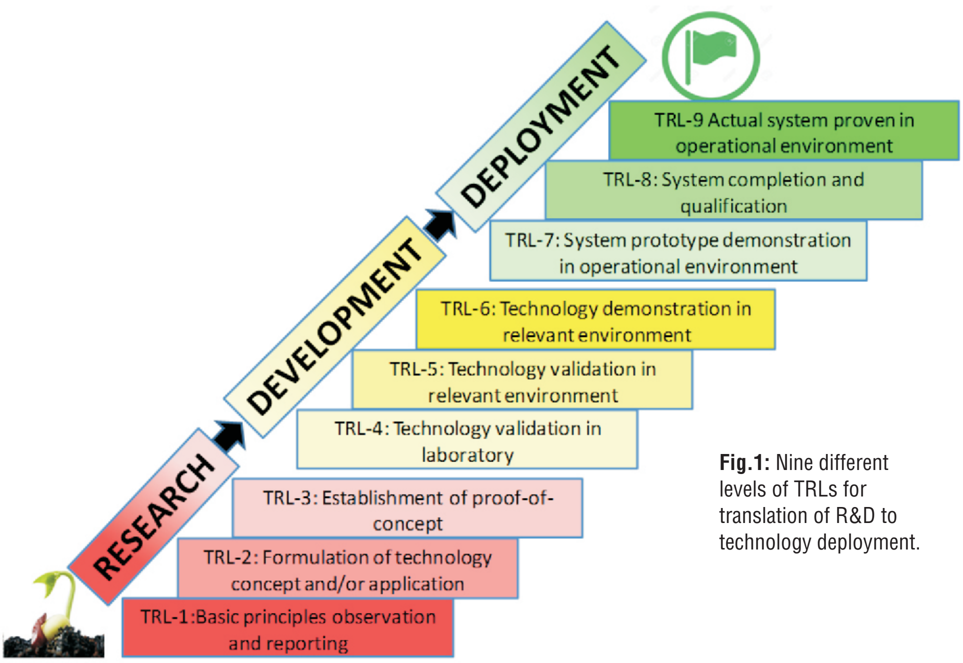

Fig.1: Nine different levels of TRLs for translation of R&D to technology deployment.

based efficient ionic bio-adsorbent for Arsenic removal from water. Post successful field trials, the scope of the work was subsequently expanded to conceptualize and materialize a unique water treatment technology for Arsenic remediation at both domestic and community levels. Throughout the evolution of this technology, we have adhered to the sequential standards demarcated under the concept of Technology Readiness Levels (TRLs), a method used to quantify the technical maturity of a technology throughout its research, development and deployment phase progression. Originally developed by NASA in the 1970s for space exploration technologies, the European Union (EU), further normalized the NASA readiness-level definitions[7], allowing for easier translation to multiple industry sectors, as presented in Fig. 1. In our scenario, the adoption of this concept has facilitated a streamlined approach towards attaining the set goals in a time bound and perspicuous manner.

Radiation induced grafting process

A single step, green synthesis of cationic cotton cellulose based adsorbent (PMAETC-*g*-cellulose) was carried out via mutual-irradiation grafting of Poly methaacryloloxyethyltrimethylammonium chloride (PMAETC), which contains a quaternary ammonium group, on to cellulose backbone using ^{60}Co-gamma radiation source[8]. The schematic of chemical modification of cellulose backbone using radiation induced graft polymerization process is illustrated in Fig. 2. Briefly, cellulose samples of predetermined weights were immersed into an optimized monomer aqueous solution in stoppered glass reactors, which were irradiated in the ^{60}Co gamma chamber (GC5000) under optimized grafting parameters. Samples were thoroughly washed to a constant weight using a soxhlet extraction assembly. This is to ensure that there is no leach out of any physically entrapped species including PMAETC homopolymer during the actual adsorption process. The grafted adsorbents were then characterized by extent of grafting, estimated gravimetrically as grafting yield (%), using the following relation (1):

$$\text{Grafting yield (\%)} = \frac{W_f - W_i}{W_i} \text{ X } 100 \qquad \textbf{(1)}$$

where, W_i and W_f are the weights of dry cellulose samples before and after grafting.

Basic principle and formulation of technology concept (TRL-1 & TRL-2)

The cationic groups present on radiation grafted PMAETC-g-cellulose fibrils attract the oppositely charged pollutant species present in water, followed by adsorption on the available high surface area of the cellulose adsorbent fibrils. The ionic pollutant species are removed from water through a combination of ionic interaction and adsorption processes. When the grafted polymer comes in contact with the aqueous medium, the grafted PMAETC chains form brush like structures, which offer 3D spaces for the

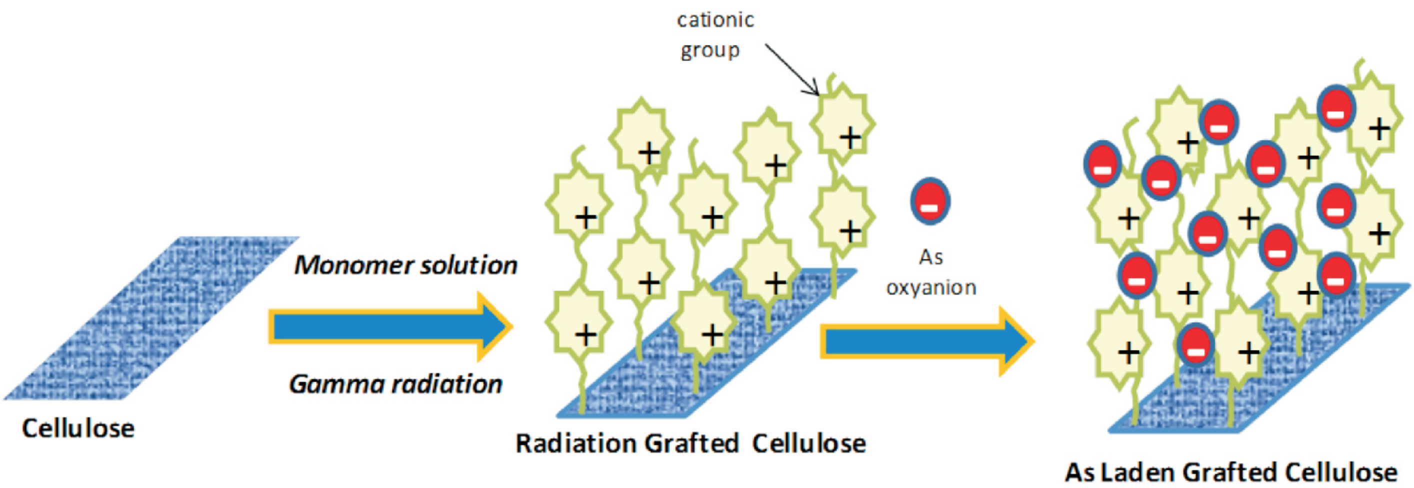

Fig.2: Schematic of radiation induced graft polymerization process and removal of Arsenic from water.

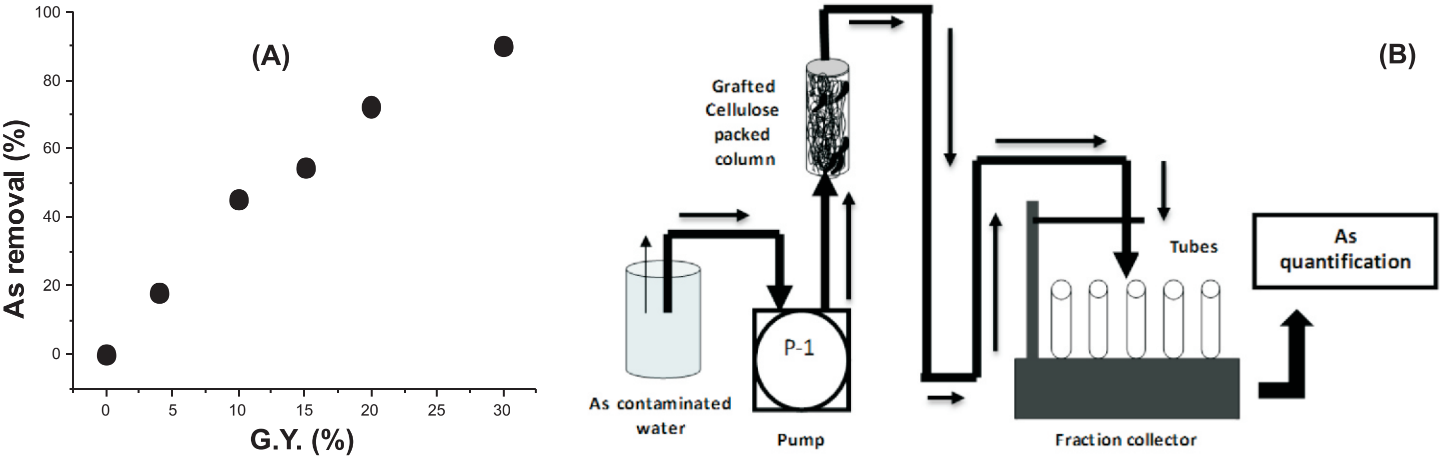

Fig.3: (A) Batch process adsorption: Arsenic removal (%) as a function of grafting yield ([As]=2.5 ppm, Adsorbent weight=10 mg, Volume=150 mL) (B) Schematic of laboratory scale fixed bed column adsorption process

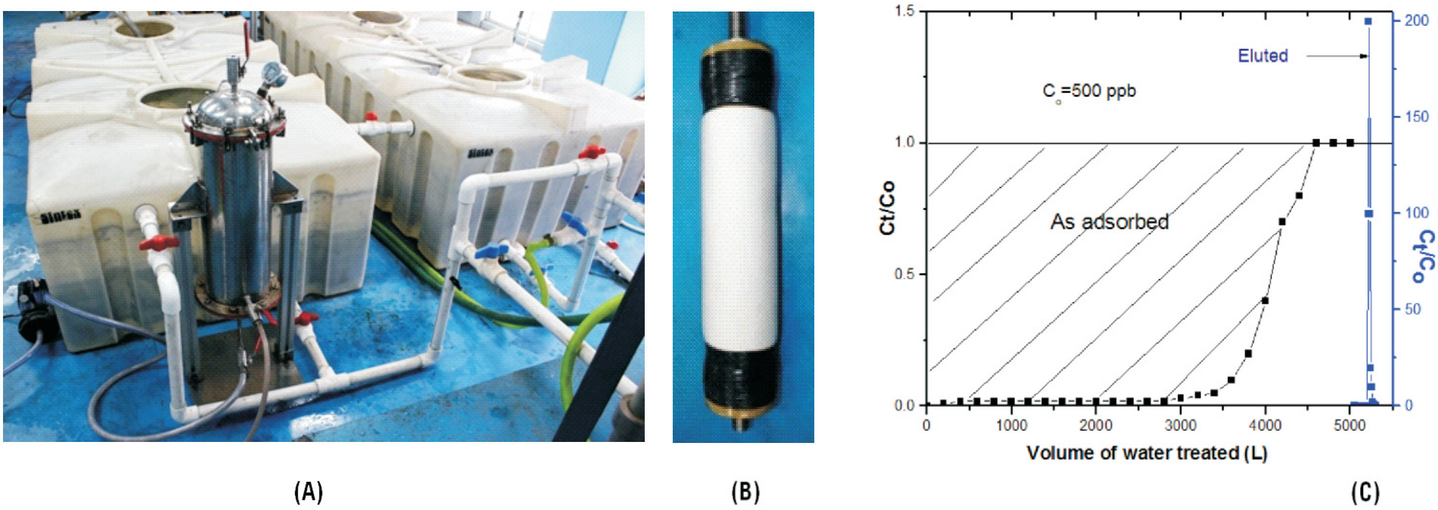

Fig.4: (A) Pilot scale study using a portable water purifier (B) Adsorbent cartridge (C) Breakthrough curve for Arsenic contaminated water ([As]=500 ppb, pH=6.5, TDS=100 ppm).

pollutant species, yielding high capacity and fast uptake kinetics (Fig. 2). The Arsenic contaminated water is pre-oxidized using sodium hypochlorite, which not only converts Arsenic (III) to Arsenic (V) but also disinfects the drinking water. The radiation grafted cellulosic adsorbent based technology is intended to remove Arsenic from water and render it safe for drinking purposes by reducing the feed concentration of over 500 ppb to less than 10 ppb, which is much lower than the limit set for Asian countries including India, i.e. 50 ppb.

The novelty of the process lies in its reusability post regeneration of the adsorbent cartridge using an optimized aqueous eluent solution, as well as in the antibacterial property of the PMAETC-*g*-Cellulose adsorbent[8]. The developed cellulose fabric based adsorbent carries brush like grafted chains containing pendent cationic groups, which can pick up negatively charged moieties. Exchange affinity is a function of net surface charge on the moieties. So the Arsenic oxyanions may have competition with other anionic species with higher surface charge (e.g., Sulphate, phosphate ions, etc.) present in the water at reasonably high concentrations. Therefore, prior to application, the water samples need to be tested to ensure that the system is conducive to removal of Arsenic (from 500 ppb to less than 10 ppb) without any significant interference from other competing species.

Establishment of proof of concept and technology validation in laboratory (TRL-3 & TRL-4)

In order to establish the proof of concept, radiation grafted bio-adsorbent was tested for removal of Arsenic from water in laboratory based batch and fixed bed column processes. For batch process studies, PMAETC-*g*-cellulose sample of a predetermined weight was equilibrated with known concentration of aqueous Arsenic (V) solution. The system was kept on stirring for ~24 hours under room temperature conditions.

The residual Arsenic (V) concentration in the solution was determined using ICP-OES (ULTIMA 2, HORIBA Scientific). The Arsenic removal (%) was found to increase almost linearly with the increase in grafting yield (Fig. 3A), which also indicated that the adsorption sites of the grafted adsorbent are readily available for the adsorbate moieties due to brush like structure of grafted chains. For regeneration and reusability of the adsorbent, an optimized aqueous eluent solution (high ionic strength aqueous solution) was used for desorption of Arsenic from the Arsenic laden adsorbent.

(A)

(B)

(C)

Fig.5: (A) Domestic Arsenic water purifier (B) Portable Arsenic water purifier for onsite field trials (C) Community level Arsenic water purifier.

For column process studies, a known weight (~1.0 g) of PMAETC-*g*-Cellulose adsorbent was packed in a cylindrical glass column (7.5 cm^3 bed volume) and an aqueous solution of Arsenic (V) passed through the fixed bed packed column under controlled flow rate using a peristaltic pump. Effluent fractions were collected at regular time intervals using a fraction collector system (Fig. 3B). Once the column gets fully saturated, the feed line was switched to the aqueous eluent solution to desorb the Arsenic from the adsorbent and regenerate it. The breakthrough curve for the complete adsorption-desorption cycle was established for multiple cycles.

A setup (Fig. 4A) was designed and fabricated for carrying out pilot scale trials and large scale technology validation at laboratory. The set up comprised of the adsorbent material (~1.0kg) wrapped as a multilayered cartridge around a perforated SS rod to collect the clean water (Fig. 4B). Arsenic contaminated water was pumped into the cartridge housing at a flow rate of 60 L/h^{-1} and the treated water collected at regular time intervals to monitor the Arsenic concentration. Over 3000L of Arsenic contaminated tap water with [As]=500 ppb (pH~6.5 to 7.5, TDS=100ppm) was successfully cleaned to safe drinking level (Arsenic <10ppb) in a single cycle. The recyclability/ regeneration of the system was also established in multiple adsorption-desorption cycles carried out by eluting the adsorbed Arsenic using the optimized eluent solution. Fig. 4C presents the breakthrough curve for complete adsorption-desorption cycle.

Technology validation in relevant environment (TRL-5)

To further validate the technology in relevant environment and on actual samples, several ground water samples were collected from affected areas of Chhattisgarh, analysed and treated using the radiation grafted cellulose adsorbent based process. The water samples were found to be severely contaminated with Arsenic, with concentration levels in the range of 200-700 ppb (pH~ 6.5 to 7.5, TDS ~100-500ppm). These samples were successfully treated in batch as well as continuous process to generate clean water with safe drinking water limits of Arsenic ([As]<10 ppb).

Technology and system prototype demonstration in relevant and operational environment (TRL-6 & TRL-7)

Depending on the scale of water treatment required, three different types of water purification prototype systems have been designed and fabricated.

a. *Gravity driven domestic level Arsenic water purifier: Suitable for small volumes of water for household drinking water purpose (Fig. 5A)*

b. *Portable Arsenic water purifier: Suitable for field trials of the technology at user sites (Fig. 5B)*

c. *Community level water purifier: Appropriate for treating large volumes of drinking water at the community level (Fig. 5C).*

A portable Arsenic water purification setup was deployed in affected villages near Raipur, Chhattisgarh and successfully demonstrated for treatment of real Arsenic contaminated bore well water samples ([As]=100 ppb to 700 ppb) (Fig. 6). For further system prototype demonstration in operational environment, the developed community level prototype treatment setup was also employed and validated for purification of Arsenic contaminated water samples. The total Arsenic concentrations in the water samples were estimated before and after treatment using Arsenic field testing kit (Merck MQuantTM 1.17927) and observed to be <10 ppb in all treated samples at site.

Technology transfer (Attaining TRL-8 and TRL-9)

To accomplish TRL-8 for system completion and qualification and TRL-9 for proving the actual system in operational environment, the technology "Cellulose

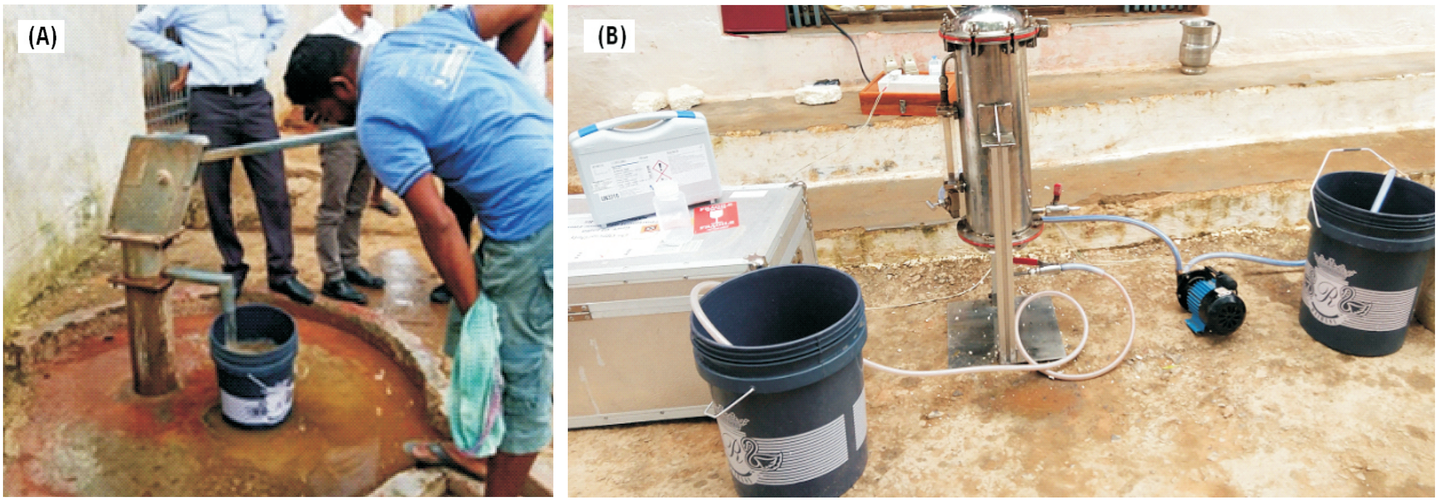

Fig.6: Field trials at an affected village near Raipur, Chhattisgarh (A) Arsenic contaminated water collected from hand pump, (B) Portable Arsenic water purifier being tested at site.

based water purifier for arsenic removal (WT21RTDD)" has been made available for transfer through TTCD, BARC. The technology has already been transferred to three licensees till date. Based on the prototype setups, the purification systems for real use in operational environment are being produced by the licensees with the requisite technical support and guidance from BARC.

Conclusion

Radiation Technology was demonstrated to be an effective tool in designing a low cost, robust and recyclable cellulosic adsorbent for Arsenic removal from water. On the basis of preliminary investigations, a prototype water treatment setup was conceptualized, designed and tested at affected sites in and around Raipur for rapid and efficient Arsenic removal from groundwater to achieve Arsenic concentration <10 ppb (WHO permissible MCL). Technology Readiness Levels (TRLs) method was followed to quantify the technical maturity of the technology. The technology has been successfully transferred to three licensees in a concerted effort towards disseminating this technical knowhow for the benefit of the people residing in regions afflicted with high Arsenic groundwater contamination.

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