

SORAS - a simple arsenic removal process

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Bangladesh in need of simple arsenic removal methods

The serious threat to the health of millions of people through consumption of arsenic-rich groundwater in Bangladesh calls for immediate action on various levels. One of these actions is the development of a low-cost and simple arsenic removal method available to every household. The development of alternative water sources and/or the installation of larger arsenic removal units will take more time due to logistic and financial constraints. Currently existing small-scale arsenic removal procedures require chemicals that are either not easily available and/or affect water taste and odour.

Solar oxidation and removal of arsenic (SORAS) is a simple method that uses irradiation of water with sunlight in PET- or other UV-A transparent bottles to reduce arsenic levels in drinking water. The SORAS method is based on photochemical oxidation of As(III) followed by precipitation or filtration of As(V) adsorbed on Fe(III)oxides as shown in Fig. 1. Groundwater in Bangladesh naturally contains Fe(II) and Fe(III) and therefore, SORAS could reduce arsenic contents and would be available to everyone at virtually no cost. It could be a water treatment method used at household level to treat small quantities of drinking water.

SORAS Laboratory Tests

Introduction

SORAS removes arsenic in a two-step procedure. In the first step, As(III), which only weakly adsorbs to iron(hydr)oxides, is oxidized to the strongly adsorbing As(V). In the second step, Fe(III)(hydr)oxides formed from naturally present iron are allowed to settle to the bottom of the container with the adsorbed As(V) and the clear water is decanted. Instead of adding chemical oxidants such as chlorine or permanganate, reactive oxidants are produced photochemically with sunlight.

In 1997, a patent was issued for an As-removal procedure using the addition of Fe(II,III), followed by exposure to UV or solar light (Khoe, Emett et al. 1997). This procedure was initially developed to treat acidic mining effluents. Efforts to enhance As(III) photooxidation at higher pH are being made, e.g. by adding S(VI) (Khoe, Zaw et al. 1999). The goals of our studies was: 1) to work without addition of Fe(II,III) salts when the naturally present iron is above 5mg/L, 2) to increase the efficiency of the As(III) photooxidation at pH 7-8 with locally available materials and 3) to conduct the treatment in closed and easily available PET bottles. To enhance the photooxidation, we tested natural compounds that are able to complex Fe(III) at pH 7-8 and thus increase the production of oxidants. We have

observed in previous studies that citrate kept Fe(III)-photochemistry efficient at neutral pH (Hug, Laubscher et al. 1997). Citrate occurs as citric acid in lemons or limes. Closed PET bottles have several advantages over open containers: no contamination by airborne pathogens, minimal loss of CO₂ (which leads to an increase of the pH value), precipitation of iron(hydr)oxides and decantation of the supernatant water is easily possible in vertically placed bottles. PET bottles have been successfully used for solar disinfection (SODIS) (Wegelin and Sommer 1998); they are locally available and reusable for several months.

Photo-oxidation and removal of As

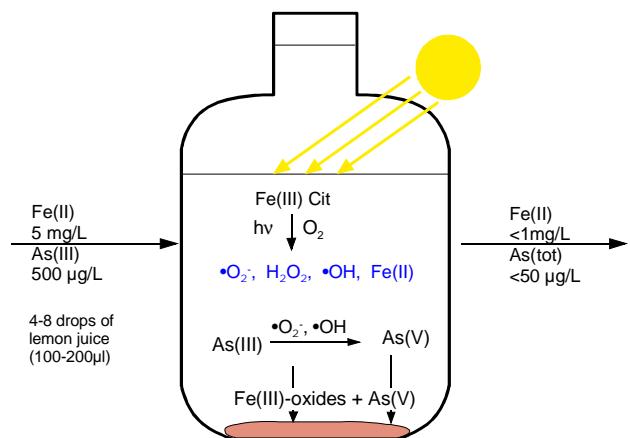


Fig. 1 Basic principle of SORAS with illumination, photochemical formation of the reactive oxidants for the oxidation of As(III) to As(V) and precipitation of iron(III)(hydr)oxides with adsorbed As(V).

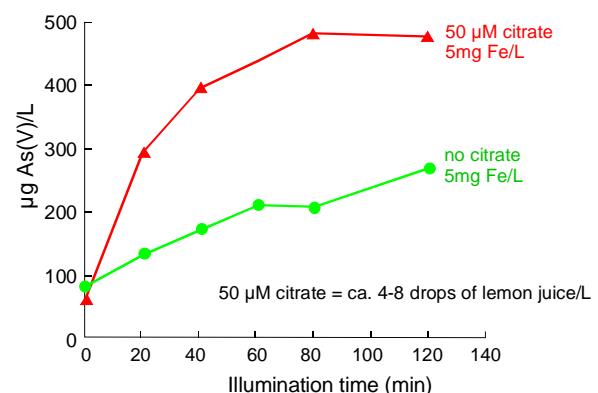


Fig. 2 Formation of As(V) from initially 500 µg/L As(III) during illumination of tap water with 5mg/L iron (initially Fe(II)), with and without citrate. Photooxidation of As(III) to As(V) in the presence of citrate is much faster.

Laboratory Experiments

Preparation of As-contaminated water

To simulate arsenic and iron-containing well water in Bangladesh, we spiked laboratory tap water with As(III) and Fe(II). The pH and the concentrations of calcium and bicarbonate in the tap water were similar to the well water in Bangladesh, as shown in Table 1. After addition of 500 µg/L As(III) and 5mg/L Fe(II) (from acidic stock solutions) to aerated tap water, the water resembled tubewell water immediately after pumping and aeration of the water by vigorous shaking of the bottle. Both the tubewell water and the spiked tap water were initially clear and colourless and then turned brown and turbid within 5-20 min, due to oxidation of Fe(II) to Fe(III) and formation of Fe(III)(hydr)oxide colloids. The rate of Fe(II) oxidation is strongly pH-dependent. Fe(II) is oxidised within 15-30 min at pH 7.0 and within 9-15s at pH 8.0 (Stumm and Lee 1961), (Millero, Sotolongo et al. 1987).

| | Bangladesh | Switzerland |
|--|------------|-------------|
| initial pH | pH 7.0-7.2 | pH 7.0-7.3 |
| Ca and Mg (as CaCO ₃) mg/L | 250-460 | 200-300 |
| HCO ₃ ⁻ mg/L | 305-561 | 244-366 |
| Fe(tot) mg/L | 0.41-19 | 0.056, 2, 5 |
| As(III) µg/L | 6-720 | 500 |
| As(tot) µg/L | 61-1240 | 500 |

Table 1 Composition of well water in Bangladesh and enriched tap water in Switzerland

Addition of citrate

Among different fruit juices or fruit pulps, lemon juice was found to be the most effective in enhancing the photochemical oxidation of As(III). Only small amounts of lemon juice have to be added, so that the pH of the water (which is buffered by the presence of bicarbonate) is not changed. In the laboratory, citrate was added 1-3 min after addition of Fe(II) to the tap water, either in the form of trisodium citrate to a total concentration of 50µM or in the form of 100-200 µl (4-8drops) of lemon juice per litre of water, equivalent to 40-80µM citrate.

UV-A Illumination

330ml or 1.5L PET bottles filled to 90% with water were illuminated either with sunlight or with UV-A light from Philips TL20W/05 (actinic blue) lamps, which emit light between 300 and 400nm. The light intensity of the lamps was measured with a ferrioxalate actinometer and was $90 \pm 15 \text{ W/m}^2$. The light intensity of solar light between 300nm and 400nm was $80 \pm 20 \text{ W/m}^2$ in Bangladesh and $60 \pm 20 \text{ W/m}^2$ in Switzerland. Illumination times were 3h with the UV-A lamps and 4-5h with sunlight.

Precipitation of Fe(III)(hydr)oxides and decantation or filtration

After illumination of the bottles, the Fe(III)(hydr)oxides

with the adsorbed As(V) were allowed to precipitate and settle by letting the bottles stand upright overnight. The clear water above the brown precipitates was either carefully decanted or filtered through fine cloth. A rest of about 100 ml with the precipitates was discarded. Addition of citrate and illumination lead to a much faster formation of precipitates and settling than illumination without citrate.

As(III) and As(tot) analysis

As(III) and total As were measured with a Perkin Elmer 5000 Atomic Absorption Spectroscopy (AAS) equipped with a batch MHS-20 mercury/hydride generator. As(III) was selectively detected by hydride generation in a pH5 citrate buffer and total As by hydride generation with 2.5M HCl. As(III) was measured in the water with the Fe(III)(hydr)oxides in suspension, while As(tot) was measured in the clear water after precipitation of the Fe(III)(hydr)oxides. In field experiments, As(tot) was measured with a new portable instrument, the Arsenator 510 (<http://www.arsenator.com>). The Arsenator was tested in the laboratory and results concurred with AAS measurements within the range of $\pm 20\%$.

Results

The basic principle of SORAS is shown in Fig. 1. Photolysis of Fe(III)citrate complexes leads to the formation of reactive oxidants, such as hydroxyl radicals ($\cdot\text{OH}$), superoxide anion radicals ($\cdot\text{O}_2^-$) and hydrogen-peroxide (H_2O_2). Fig. 2 shows that citrate accelerates the photochemical oxidation of As(III) to As(V). (Illumination with UV-A light). In addition to the acceleration of As(III) oxidation, citrate leads to a faster and more complete precipitation of the Fe(III)(hydro)oxides after illumination.

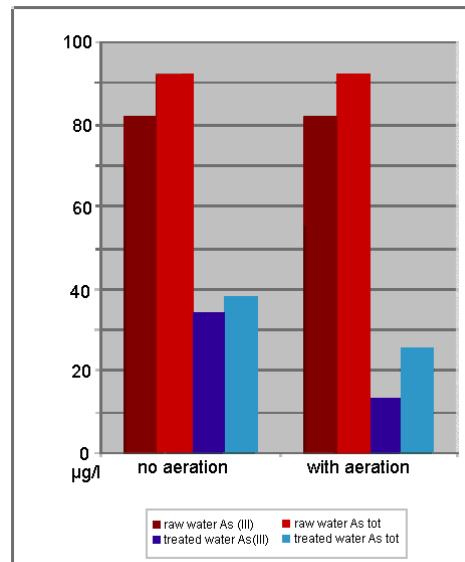


Fig. 3 Arsenic removal by SORAS without and with aeration of the pumped water.

With citrate, 80-90% of the total arsenic could be removed. A limited number of experiments were conducted with water containing silicate and phosphate. With 2mg/L phosphate and 50mg/L H₄SiO₄ (typical in some wells in Bangladesh) the overall removal efficiency was somewhat lower, but still between 80-85%.

SORAS Field Tests

Three series of field tests carried out in Bangladesh to confirm the laboratory results, further developed the arsenic removal method and studied its acceptance by the target population. The first phase of the tests were run with 7 wells during the end of the dry season (April - June '99), the second with 5 wells at the end of the wet season (October - December '99) and the third one with 2 wells in the dry period (March '00). In all experiments 1.5-litre PET bottles were used and arsenic concentrations analysed by a field test kit (Arsenator 510) and partly cross-checked in the laboratory (AAS). Chemical parameters (e.g. Fe, Mn, pH, O₂, COD, hardness, alkalinity, nitrate, phosphate) were recorded with field kits and in the laboratory.

The Arsenator proved to be a reliable field kit to determine arsenic concentrations < 200 µg/L. Furthermore, the field tests carried out during different climatic periods and fluctuating groundwater tables revealed that the arsenic concentration varies with time. The respective level at the end of the wet season can, in some cases, be nearly twice as high than at the end of the dry season. Most of the arsenic found in the groundwater is in its reduced form; i.e. As(III).

The arsenic removal efficiency depends to a great part on the iron concentration, which should not be smaller than 3 mg/l, and on the dissolved oxygen concentration. The low oxygen content of the pumped water generally varies between 1 - 2 mg/l. Due to the oxidation of the dissolved iron, the colour of the initially clear water changes to red within a period of 30 - 120 minutes. Shaking of the partly (approx. 4/5) filled bottles with groundwater for about 30 sec increases the dissolved oxygen concentration to 6 - 7 mg/l. The almost oxygen-saturated water accelerates the oxidation of the dissolved iron and is, therefore, important to increase the efficiency of the SORAS process as shown in Fig. 3. The arsenic removal efficiency depends on the relation of the iron and arsenic concentration and varied between 56 and 88% for the raw water of the tested wells.

As studied by laboratory tests, photochemical oxidation of As(III) and Fe(II) is accelerated and more complete in the presence of citrate forming Fe(III)-complexing compounds. In the field, citrate is replaced by lemon juice. Different types of lemon such as the juicy "Kagoji" and "Kakja" are available in Bangladesh throughout the year except for a 2-month period (February - March). The different experiments revealed that approx. 3 - 10 drops of lemon juice per litre of water should be added immediately after filling the bottle with pumped groundwater. A too high concentration of lemon juice reduces the efficiency of SORAS, as it is the case when the dosage is not carried out immediately after pumping. Finally, adding more lemon juice during irradiation neither hinders nor improves the final arsenic removal efficiency.

The photooxidation process is driven by solar radiation and, hence, irradiation duration and intensity are rather important parameters. The experiments proved that the longer the irradiation and higher the UV-A radiation intensity, the more efficient is the SORAS process. Best results were obtained by irradiating the water throughout the day under a clear sky.

Fe(III)-(hydr)oxide particles are produced during the irradiation period. The oxidised As(V) is absorbed on these particles which have now to be separated from the water in a second treatment step. Flocculation of the Fe(III)-(hydr)oxide particles already occurs during the irradiation phase. The experiments revealed that the greater the iron content in the water, the sooner flocculation occurs (first flocs after 90 min for 8.35 mg Fe/l as compared to 195 min for 4.65 mg Fe/l). After the irradiation phase, the plastic bottles have to be turned from horizontal into vertical position to allow an efficient separation of the flocs. Slight shaking of the bottles does not enhance flocculation and, therefore, the bottles should rather be left stationary during the solid separation phase, which is normally completed after a few hours. Finally, the settled Fe(III)-(hydr)oxide particles with the adsorbed As(V) have to be separated from the water either by decantation or filtration through a piece of cloth.

In summary, the application procedure developed by SORAS field tests comprises the following steps:

1. fill 4/5 of the plastic bottle with pumped groundwater
2. add approx. 6 drops of fresh lemon juice per litre of water
3. shake the bottle vigorously for approx. 30 seconds
4. expose the plastic bottle in horizontal position to sunlight for a full day
5. turn the bottle in vertical position and let the solids settle overnight
6. decant the water carefully the next day or filter it through a piece of cloth

The field tests in Bangladesh revealed a lower removal efficiency than the one observed in the laboratory. The reason could be the fact that Bangladesh's groundwater shows a large variability in water constituents. Constituents such as silicate, natural DOC, phosphate etc., might have a significant influence on As(III) oxidation and on subsequent removal by adsorption and precipitation. The arsenic removal efficiency of the SORAS method is between 45 - 78% and averages 67%. Concerning the Bangladesh guideline value of 50 µg/L arsenic in drinking water, SORAS can treat raw water containing an arsenic concentration below 100 - 150 µg/L provided that sufficient iron and UV-A intensity are available. As shown in Fig. 4, addition of potassium permanganate (if necessary together with aluminium sulphate), attains a higher arsenic removal efficiency, approx. 80% and 90%, respectively. Hence, SORAS(+) would allow treatment of raw water containing a higher arsenic concentration.

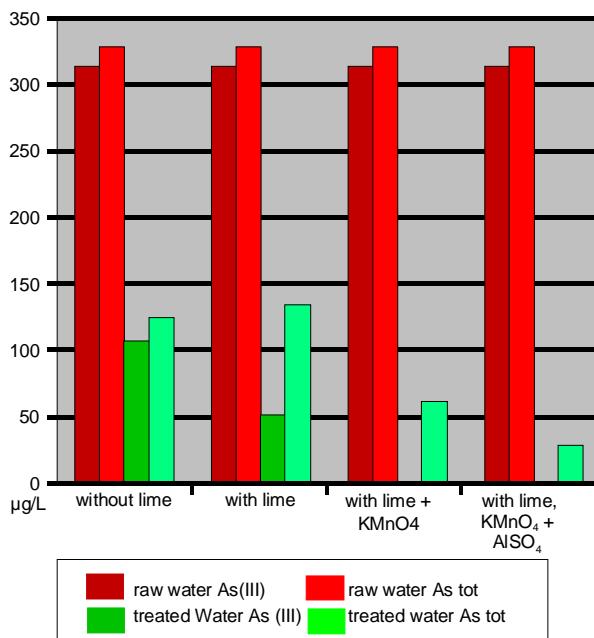


Fig. 4 Arsenic removal by SORAS without and with the addition of chemicals.

Preliminary field tests carried out with four families revealed that the people are primarily interested in removing the iron. Unlike arsenic, a high iron concentration in the water can be seen, tasted and smelt. The SORAS-treated water is clear and "light". The people like the taste and they say that food cooked with this treated water keeps its natural colour and freshness, e.g. cooked rice and vegetables are no longer of a red-brown colour. People living in arsenic-affected areas seem to be willing to use the SORAS treatment method. However, lemons are not always available and the cleaning of bottles is somewhat cumbersome. Potassium permanganate could be used during periods of low sunlight radiation or non-availability of lemons and coating of the inner walls of the bottles by iron particles which can be avoided by not completely filling the plastic bottle.

SORAS Perspectives

SORAS is a simple arsenic removal process applied at household level with locally available resources. However, the arsenic removal efficiency is limited to approx. 50 - 70 % and hence, raw water up to 100 - 150 µg/L can be treated with this low-cost method. Arsenic affected people are desperately waiting for water treatment options which have to be developed and promoted by the different actors of the Bangladesh Arsenic Mitigation Water Supply Project (BAMWSP). SORAS is such an option, at least it is a useful interim measure until better options are available. Faced with the choice between drinking water that contains 150 and more µg/L of poisonous arsenic, or after treatment by SORAS, water that contains half or a quarter of that amount, who would not opt for the latter? Furthermore, SORAS also removes the iron and improves the taste of the water to which people attribute a high interest.

The SORAS method is now ready to be applied within a certain range of arsenic concentration. It has to be carefully introduced in arsenic-affected villages by demonstration projects in which the users are adequately trained and the socio-cultural acceptance of SORAS assessed. In case of successful application, the supply problem of robust plastic bottles in adequate numbers will then have to be studied in order to embark on large-scale programmes required to solve the arsenic problem in Bangladesh and in other parts of the world.

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