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Application of natural citric acid sources and their role on arsenic removal from drinking water: A green chemistry approach

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HIGHLIGHTS

- ▶ Tomato and lime is reported for the first time to be the promoter of SORAS.
- ▶ As/Fe molar ratio is important for effective removal of arsenic from groundwater.
- ▶ The arsenic removal competence improved at specific citrate doses.
- ▶ Hydroxycinnamates in tomato enhances the generation of photocatalysts.
- ▶ Tomato is the most cost-effective and efficient to remove As than lemon and lime.

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ABSTRACT

Solar Oxidation and Removal of Arsenic (SORAS) is a low-cost non-hazardous technique for the removal of arsenic (As) from groundwater. In this study, we tested the efficiency of natural citric acid sources extracted from tomato, lemon and lime to promote SORAS for As removal at the household level. The experiment was conducted in the laboratory using both synthetic solutions and natural groundwater samples collected from As-polluted areas in West Bengal. The role of As/Fe molar ratios and citrate doses on As removal efficiency were checked in synthetic samples. The results demonstrate that tomato juice (as citric acid) was more efficient to remove As from both synthetic (percentage of removal: 78–98%) and natural groundwater (90–97%) samples compared to lemon (61–83% and 79–85%, respectively) and lime (39–69% and 63–70%, respectively) juices. The As/Fe molar ratio and the citrate dose showed an 'optimized central tendency' on As removal. Anti-oxidants, e.g. 'hydroxycinnamates', found in tomato, were shown to have a higher capacity to catalyze SORAS photochemical reactions compared to 'flavanones' found in lemon or lime. The application of this method has several advantages, such as eco- and user- friendliness and affordability at the household level compared to other low-cost techniques.

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1. Introduction

Groundwater is the main source of drinking water in most part of the Bengal Delta Plain (BDP), the world's largest deltaic alluvium. The easy accessibility of groundwater makes it a vital resource for the rural people living in this region. Currently,

groundwater is widely used for agricultural irrigation and crop production [1–4]. Though the aquifer is generally free from bacterial contamination, the large-scale exploitation of groundwater has resulted in severe water quality problems, the most threatening of which is the hydroarsenosis [5–12].

A number of technologies are currently available for the removal of As from groundwater. For example, iron and alum coagulation [13], lime softening [14], reverse osmosis [15], zero-valent iron and nano-particulate zero-valent iron [16,17], natural/synthetic metal oxides [18,19], iron doped activated carbons [20], granular TiO₂ adsorbent [21], hybrid materials [22] are some of the many proposed removal techniques. Among these, a few treatment technologies are efficient but expensive whereas some are cheaper

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but not efficient. The success of these technologies depends on several factors such as input water quality and composition, operation and maintenance, user awareness level and education. Nevertheless, treated surface water was recommended as an alternative option for the community drinking water supply to the affected population. However, this is a costly and time-consuming solution and requires distribution network for water supply. The field experience revealed that installation time for surface water treatment plant is ranged between 2 and 3 years [10]. Therefore, a method is required which should be readily available and affordable to poor, affected rural villagers and at the same time highly efficient to remove As from drinking water without producing hazardous wastes.

Solar Oxidation and Removal of Arsenic (SORAS) is a simple, cost effective and efficient technique for the removal of As from drinking water at the household level [23,24]. The method uses naturally available citric acid (as lemon juice) as the major complexing agent during irradiation with natural UV-A light (315–400 nm) to catalyze the photochemical oxidation. Similar to other oxidative removal methods, the dissolved As(III) is oxidized to As(V) in order to get adsorbed onto Fe-oxyhydroxide surfaces at circumneutral pH [25]. The citric acid from lemon generally maintains a larger fraction of Fe(III) in the dissolved phase at circumneutral pH. The dissolved Fe(III) then reacts with citrates producing superoxide ($O_2^{\bullet-}$) and some intermediate oxygen free radicals (like $OH^{\bullet}$). Then, through a cyclic photochemical reaction, equilibrium concentrations of these oxidizing species and Fe(II) are maintained. It has been postulated that a Fenton type reaction is possibly responsible for further oxidation of As(III) and Fe(II), producing As(V) with stronger adsorption affinity for Fe-oxyhydroxide surfaces formed in situ and thereby ensuing removal of As [23,24,26].

In this paper we reported for the first time (as per authors knowledge) the applicability and affordability of low-cost natural citrate sources from tomato and lime (locally known as 'kagzi lebu') in order to remove As from drinking water following SORAS technique developed by Hug et al. [23]. Initially, we have critically evaluated the effect of As/Fe molar ratios and citrate doses on the removal efficiency using synthetic test solutions to determine the optimal condition necessary for the SORAS photochemical reactions. The optimized condition was applied to treat a few As contaminated groundwater samples collected from Chakdaha Block, West Bengal, India. We have also compared the removal efficiencies posed by juices of tomato and lime with that of lemon for the recommendation of best available natural citrate sources to treat As contaminated groundwater.

2. Materials and methods

2.1. Preparation of synthetic test solutions

Synthetic test solutions were prepared in the laboratory in such a way that the solution represents the composition of groundwater (Table 1). The As concentration in the test solutions varied between 0.1 and 0.5 mg/L, while Fe concentrations varied between 2 and 6 mg/L (Fig. 1a). The test solutions were prepared by volumetric dilution procedure (micro-pipette, Merck) in acid clean, dry, pre-weighed volumetric flasks. Arsenic stock solution was prepared by dissolving 1.302 g of arsenic trioxide (As_2O_3 , Aldrich & Fluka) in high purity water (HPW, Millipore, 18 M Ω) containing 0.4 g of NaOH (Merck) and 20 mL of concentrated HCl (supra pure, Merck). The stock solution was diluted to 1 L with HPW to attain 1000 mg/L of As. The Fe stock solutions (1000 mg/L) were prepared by dissolving $FeSO_4 \cdot 7H_2O$ (Merck) in HPW. The reagents used were only of analytical grade.

Table 1
Physico-chemical characteristics and composition of major ions of synthetic solutions and groundwater (S-1 to S-3) samples.

Sample	Depth (m)	Temp. (°C)	pH	Eh (mV)	EC (μ S/cm)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	HCO ₃ ⁻ (mg/L)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	PO ₄ ³⁻ (mg/L)
Synthetic solutions	NA	NA	6.5–7.4	NA	680–1100	90–130	21–30	16–40	450–650	10–100	1.2–14	0.01–5.2
S-1	27	28.2	7.11	–130	991	124	27	35	512	88	6.8	2.8
S-2	24	28.9	7.08	–127	826	113	23	21	607	80	2.0	2.0
S-3	29	29.1	7.24	–105	739	109	27	24	457	48	9.6	3.7

NA, not available; BDL, below detection limit.

a)							
As (mg/L)	Fe (mg/L)	0.5	6	0.25	4	0.1	2
		1	0.5	2	0.5	3	0.5
		0.5	6	0.25	4	0.1	2
		4	0.75	5	0.75	6	0.75
Set No.	Citrate (mL/L)	0.5	6	0.25	4	0.1	2
		7	1	8	1	9	1

b)							
As (mg/L)	Fe (mg/L)	0.43	6.72	0.27	4.37	0.11	2.29
Sample ID	Citrate (mL/L)	S-1	0.75	S-2	0.75	S-3	0.75

Experimental set-up

Experimental condition

Fig. 1. Experimental set-up and condition for (a) treatment of synthetic solutions, and (b) treatment of groundwater samples exposed to natural solar radiation for the removal of arsenic. Blank samples containing distilled water were also run during each set of experiments without any added As and Fe concentrations.

2.2. Collection of groundwater samples

Groundwater samples for solar radiation experiments (Fig. 1b) were collected from the domestic hand-operated tube wells located in the rural villages of Chakdaha block, Nadia district (65 km north of Kolkata). The selection of tube wells was done based on the results of a previous survey on As contamination status of the region [27,28]. The groundwater samples were collected in plastic bottles. Prior to sampling, the tube wells were pumped for several minutes to flush the standing volume of water to get fresh water from the aquifer. Water samples were filtered (0.45 μm cellulose nitrate membrane filter) on-site and divided into two groups. The first group was acidified (HNO_3 0.2%, v/v) for the analysis of cations and As, while the second group was left un-acidified for anion analysis. Prior to sample collection, the groundwater samples were measured for pH, Eh, alkalinity, temperature and electrical conductivity at the well-head (Table 1). All the samples were stored under normal freezing condition at 4 °C until the analysis.

2.3. Solar radiation experiments with different citrate sources

Locally available lemon, tomato and lime were used as a citrate source for SORAS photochemical reaction. The raw fruit juices were extracted with the help of a grinder and then filtered through a pre-cleaned (with distilled water) domestic fine mesh tea-strainer. The citrate doses were set to 0.5, 0.75 and 1 mL/L. The reported citrate concentrations of lemon and lime were 48 and 45.8 g/L, respectively [29]. The citrate concentration in tomato usually ranges between 34 and 50 g/L [30]. Considering the above range of citric acid concentrations, the respective citrate level in case of lemon added to the experimental solutions were 0.024, 0.036 and 0.048 g/L. In case of lime the added citrate concentrations were 0.0229, 0.03435 and 0.0458 g/L. The added citrate concentrations as tomato juices were 0.017–0.025, 0.0255–0.0375 and 0.034–0.05 g/L.

One liter of synthetic solution containing range of As and Fe concentrations (set nos. 1–9, Fig. 1a) were transferred to transparent polyethylene-terphthalate (PET, volume 1.2 L) bottles. The solutions were then subjected to different doses of citric acids, i.e. juices from lemon, tomato and lime as mentioned above. The mixture was then shaken vigorously (~1–2 min) to ensure saturation of mixed liquid with the air. This provides sufficient oxygen to oxidize fraction of the dissolved Fe(II) into Fe(III). The experimental PET bottles were then tightly capped and exposed to sunlight for 4 h. The experiment

was conducted in March 2010 between 10 am and 2 pm. The PET bottles were set at 45° inclined position supported by a tin sheet on the wall of an open roof with free access to sunlight (Fig. 2a). During initial phase of the experiment, the visual inspection confirms precipitation of Fe(III)-oxyhydroxides (Fig. 2b). After complete irradiation (4 h), no significant visual change in color was observed (Fig. 2c). Samples were collected twice during the experiments (i.e. after 2 and 4 h) which were preserved with HNO_3 (0.2%, v/v) and stored in the refrigerator at 4 °C until analyzed for As and Fe concentrations. Blank samples (i.e. distilled water without any added As and Fe concentrations) were prepared and run during each experimental stage to ensure that the system returns to a clean condition and allow establishment of the baseline with respect to noise.

Groundwater samples (S-1, S-2 and S-3) were treated in the similar fashion (Fig. 1b). In groundwater samples, the solar radiation experiment was conducted with an optimal citrate dose of 0.75 mL/L which is based on the results of synthetic solutions. Separate control samples (i.e. groundwater with As concentrations below instrumental detection limit) were tested simultaneously alongside groundwater samples, without adding any citric acids.

2.4. Analytical procedures

The concentrations of Ca^{2+} , Mg^{2+} , Na^+ and As were measured using the acidified samples with a double focusing High Resolution Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS VG AXIOM, VG Elemental) in a clean room (sample dilution 1:1 with 1% HNO_3 of sub-boiled quality). The concentrations of Cl^- , SO_4^{2-} and PO_4^{3-} were measured using the unacidified samples with the help of an Ion Chromatograph (IC, DIONEX ICS 1000) with a separating column (DIONEX AS 4 SC). Electrical Conductivity (EC), pH, Eh, temperature were measured using WTW multimeters. Alkalinity (reported as HCO_3^-) was quantified in the unacidified samples by titration with 0.2 M H_2SO_4 following the standard protocols. The concentration of citric acid was measured following the method detailed in Ranganathan [31].

3. Results and discussion

3.1. Arsenic removal efficiency in synthetic test solutions

Arsenic removal efficiency showed differential behavior with different citrate sources during SORAS photochemical cycle. Overall, the citric acid from tomato juices showed the highest removal

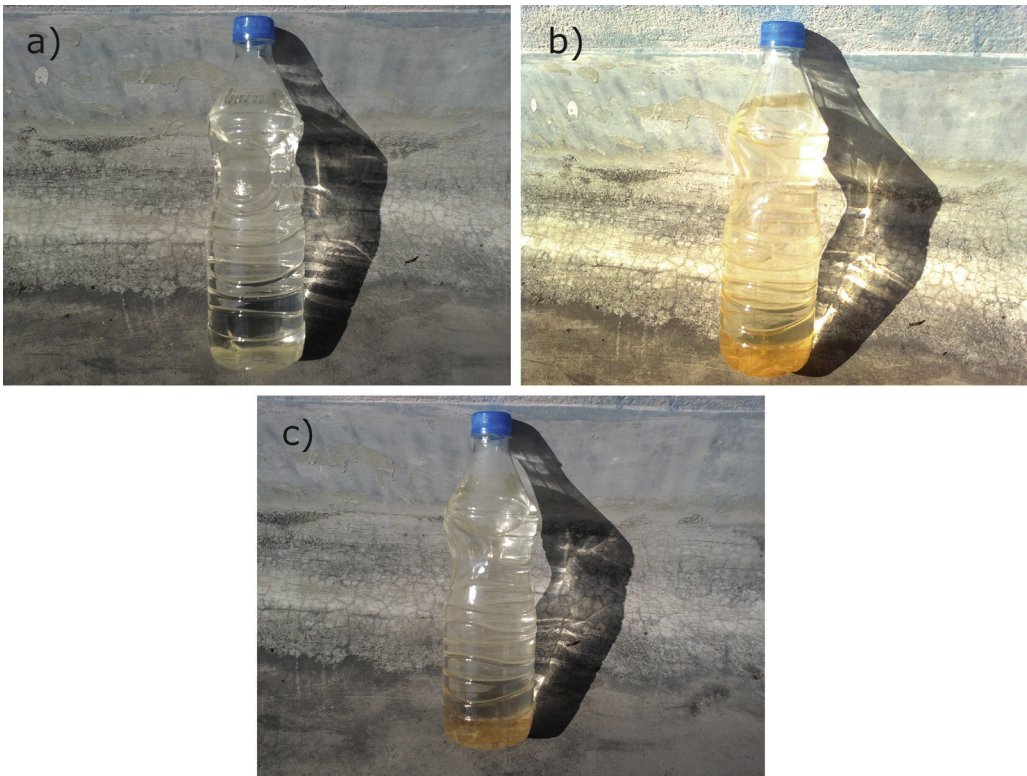


Fig. 2. Solar radiation experiment: (a) water samples in PET bottles before irradiation, (b) after 2 h of irradiation (brown coloration of Fe-oxyhydroxides), and (c) after 4 h of irradiation (precipitations of Fe-oxyhydroxide at the bottom of PET bottles).

efficiency (range: 78–98%, mean: 88%) compared to lemon (range: 61–83%, mean: 73%) and lime (range: 39–69%, mean: 50%) juices (Table 2a, Table 2b, Table 2c). This suggests tomato as the efficient natural citrate source for the removal of As from groundwater through solar irradiation. The removal rate was higher during the first half of the experiment compared to the last half (Table 2a,

Table 2b, Table 2c) which suggests fast adsorption of As onto Fe(III)-complexes. This is consistent with the findings of earlier studies [32–34]. Low reaction rates during second half of the experiment might be associated with decrease in dissolved As and Fe(III) concentrations in the solution and thereby less likely to form Fe(III)-complexes.

Table 2a
SORAS experimental result showing As removal efficiency in synthetic solutions dosed with lemon juices as a natural citrate source.

Set no.	Initial				Lemon juice (mL/L)	Time of exposure	Final		% of As removal	% of As removal (mean)	Standard error of mean
	As (mg/L)	Fe (mg/L)	As/Fe molar ratio				As (mg/L)	Fe (mg/L)			
1	0.5	6	0.062	0.5	2 h		0.18	0.16	63.4	67.6	2.6
2	0.25	4	0.047	0.5			0.07	0.09	72.4		
3	0.1	2	0.037	0.5			0.03	0.01	67		
4	0.5	6	0.062	0.75			0.13	0.12	74.8	76.9	1.6
5	0.25	4	0.047	0.75			0.05	0.07	80		
6	0.1	2	0.037	0.75			0.02	0.01	76		
7	0.5	6	0.062	1			0.21	0.14	57.2	60	2.4
8	0.25	4	0.047	1			0.09	0.09	64.7		
9	0.1	2	0.037	1			0.04	0.01	58		
1	0.5	6	0.062	0.5	4 h		0.17	0.12	66	72.5	3.3
2	0.25	4	0.047	0.5			0.06	0.07	77		
3	0.1	2	0.037	0.5			0.03	0.01	74.5		
4	0.5	6	0.062	0.75			0.12	0.09	77	80.7	1.9
5	0.25	4	0.047	0.75			0.04	0.06	83		
6	0.1	2	0.037	0.75			0.02	0.01	82		
7	0.5	6	0.062	1			0.20	0.14	61	66.7	2.8
8	0.25	4	0.047	1			0.08	0.09	70		
9	0.1	2	0.037	1			0.03	0.01	69		

Table 2b

SORAS experimental result showing As removal efficiency in synthetic solutions dosed with tomato juices as a natural citrate source.

Set no.	Initial			Tomato juice (mL/L)	Time of exposure	Final		% of As removal	% of As removal (mean)	Standard error of mean
	As (mg/L)	Fe (mg/L)	As/Fe molar ratio			As (mg/L)	Fe (mg/L)			
1	0.5	6	0.062	0.5	2 h	0.10	0.07	80		
2	0.25	4	0.047	0.5		0.02	0.02	91.6		
3	0.1	2	0.037	0.5		0.01	0.01	88.6	86.7	3.5
4	0.5	6	0.062	0.75		0.09	0.06	82		
5	0.25	4	0.047	0.75		0.02	0.01	96.3		
6	0.1	2	0.037	0.75		0.01	0.01	90.5	89.6	4.2
7	0.5	6	0.062	1		0.15	0.11	69.4		
8	0.25	4	0.047	1		0.03	0.03	84		
9	0.1	2	0.037	1		0.02	0.01	79	77.5	4.3
1	0.5	6	0.062	0.5	4 h	0.09	0.07	82		
2	0.25	4	0.047	0.5		0.02	0.02	93.2		
3	0.1	2	0.037	0.5		0.01	0.01	89.7	88.3	3.3
4	0.5	6	0.062	0.75		0.08	0.05	84		
5	0.25	4	0.047	0.75		0.02	0.01	98.2		
6	0.1	2	0.037	0.75		0.01	0.01	92	91.4	4.1
7	0.5	6	0.062	1		0.11	0.10	78		
8	0.25	4	0.047	1		0.03	0.02	88		
9	0.1	2	0.037	1		0.01	0.01	86	84	3.1

3.2. The effect of As/Fe molar ratios

The As/Fe molar ratios showed an ‘optimized central tendency’ during the removal of As for all citrate sources (Table 2a, Table 2b, Table 2c). The removal efficiency was higher for the solutions with molar ratios of 0.047 (set nos. 2, 5 and 8) compared to the solutions with molar ratios of 0.037 (set nos. 3, 6 and 9). However, the solution (set nos. 1, 4 and 7) with higher molar ratios (0.062), the removal efficiency was the lowest for all citrate sources. Therefore, the initial As and Fe concentrations in the treated water are impor-

tant for better removal efficiency. Lara et al. [33] suggested that the ratio of As, Fe and the citrate content is important for better removal efficiency. The low removal efficiency at low As/Fe molar ratio indicates that species like Fe(IV), $O_2^{\bullet-}$ or $OH^{\bullet}$ [23,24] may not be the only oxidizing agent for As(III). There may be a possible interference from other potential oxidizing agents like HCO_3^- taking part in the cyclic reaction, which could regulate the course of the SORAS photochemical reaction [23,24,34]. Another possibility could be the acceleration of some intermediate reactions (proposed by Hug et al. [24]) in the photochemical cycles due to the presence of excess Fe

Table 2c

SORAS experimental result showing As removal efficiency in synthetic solutions with lime juices as a natural citrate source.

Set no.	Initial			Lime juice (mL/L)	Time of exposure	Final		% of As removal	% of As removal (mean)	Standard error of mean
	As (mg/L)	Fe (mg/L)	As/Fe molar ratio			As (mg/L)	Fe (mg/L)			
1	0.5	6	0.062	0.5	2 h	0.33	0.27	33.4		
2	0.25	4	0.047	0.5		0.13	0.19	50.2		
3	0.1	2	0.037	0.5		0.05	0.22	45	42.9	5.0
4	0.5	6	0.062	0.75		0.30	0.28	40		
5	0.25	4	0.047	0.75		0.09	0.19	65.6		
6	0.1	2	0.037	0.75		0.03	0.11	50.5	52	7.4
7	0.5	6	0.062	1		0.34	0.25	32.2		
8	0.25	4	0.047	1		0.14	0.21	45.2		
9	0.1	2	0.037	1		0.06	0.20	42	39.8	3.9
1	0.5	6	0.062	0.5	4 h	0.3	0.17	41		
2	0.25	4	0.047	0.5		0.11	0.16	54		
3	0.1	2	0.037	0.5		0.05	0.17	47	47.3	3.8
4	0.5	6	0.062	0.75		0.28	0.19	44		
5	0.25	4	0.047	0.75		0.08	0.16	69.2		
6	0.1	2	0.037	0.75		0.03	0.09	56	56.4	7.3
7	0.5	6	0.062	1		0.31	0.21	39		
8	0.25	4	0.047	1		0.12	0.18	52		
9	0.1	2	0.037	1		0.05	0.18	49	46.7	3.9

Table 3

SORAS experimental result showing As removal efficiency in groundwater samples dosed with lemon, tomato and lime juices as a natural citrate source.

Citrate sources	Sample ID	Initial		Initial citrate juice (mL/L)	Final citrate juice (mL/L)	Time of exposure	Final		% of As removal	% of As removal (mean)	Standard error of mean
		As (mg/L)	Fe (mg/L)				As (mg/L)	Fe (mg/L)			
Lemon	S-1	0.43	6.72	0.75	0.03	4 h	0.03	0.35	85		
	S-2	0.27	4.37	0.75	0.05		0.07	0.44	79		
	S-3	0.11	2.29	0.75	0.06		0.03	0.35	82.5	82.2	1.7
Tomato	S-1	0.43	6.72	0.75	0.03		0.01	0.29	97		
	S-2	0.27	4.37	0.75	0.03		0.03	0.45	90.2		
	S-3	0.11	2.29	0.75	0.05		0.01	0.43	94.5	93.9	2.0
Lime	S-1	0.43	6.72	0.75	0.05		0.06	0.29	70.2		
	S-2	0.27	4.37	0.75	0.06		0.12	0.37	63		
	S-3	0.11	2.29	0.75	0.03		0.05	0.36	67.8	67	2.1

Note: Control samples (i.e. with no added citrate juices) were run simultaneously during this experiment. The removal efficiency of control samples were 49%, 37% and 43%, respectively.

in the samples. Consequently, the concentration of free radicals is diminished, thereby reducing the removal efficiency. In contrast, with higher molar ratios, the removal efficiency might have lowered due to scarcity of sufficient dissolved Fe concentrations and subsequent generation of photocatalysts.

3.3. The effect of citrate doses

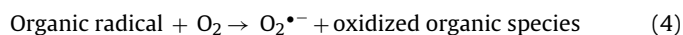
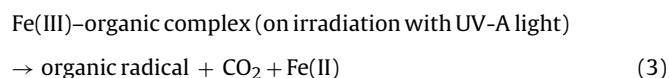
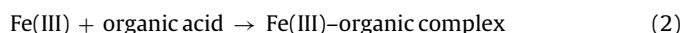
The 'optimized central tendency' was also observed for different citrate doses. The removal efficiency was higher for the 0.75 mL/L of citrate juices compared to 0.50 mL/L (Table 2a, Table 2b, Table 2c). The removal efficiency was the lowest for 1.0 mL/L of citrate juices. At low citrate doses (i.e. 0.50 mL/L of juices), the cyclic photochemical reaction [23] might not be able to generate intermediate reaction products (e.g., free radicals and Fe(III)–citrate complex) in order to provide necessary conditions for the efficient removal of As from the solution. This is mainly due to scarcity of citrates during photochemical reactions and thus unable to trigger Fenton type reactions. On the other hand, at higher citrate doses, the low removal efficiency was probably due to interference of the Fe(III)–citrate complex during the formation of Fe(III)–oxyhydroxide solids [32]. Additionally anti-oxidant composition of different citrate sources could influence the removal efficiency detailed in later section.

3.4. Arsenic removal efficiency in groundwater samples

Being the most efficient citrate level to remove As from the synthetic solutions, optimum citrate dose of 0.75 mL/L was only maintained for the experiment with the groundwater samples. The data showed that tomato juice was more efficient to remove As from groundwater samples compared to juices of lemon and lime. The sample, S-1 with As/Fe molar ratio of 0.048 has the highest removal efficiency, followed by S-3 (molar ratio of 0.036) and S-2 (molar ratio of 0.046) (Table 3). Although S-1 and S-2 have similar molar ratios, the removal percentage of As was quite different. This suggests that Fe concentrations are also critical for better removal efficiency. Additionally, high HCO_3^- concentration of S-2 groundwater sample (607 mg/L, Table 1) might have controlled the SORAS photochemical reaction. In all the samples, the consumption of citrate was almost similar (range: 92–96%) after the radiation exposure (Table 3). This indicates possible controlling factors other than the photochemical cycle of Fe(III)–citrate complex, that are promoting the citric acid from tomato juices over lemon and lime for the efficient removal of As from groundwater.

3.5. Anti-oxidant activity of the citrate juices

The citrate juices discussed here have the quantitative amount of polyphenolic anti-oxidants [35–40]. Table 4 shows that anti-oxidant activity is much lower in the case of citrate sources from tomato than lemon and lime. Therefore, the citric acids from lemon and lime juices are susceptible to oxygen radical (like superoxides or $\text{OH}^\bullet$) absorption and less conducive to photochemical oxidation, the basic requirement for the effective execution of SORAS. Hence, the reaction step (4) and the subsequent photochemical cycle (shown below) might get hindered after certain reaction time that was also proposed by Hug et al. [23]. Consequently, due to insufficient formation of superoxides (or other oxygen radicals, $\text{OH}^\bullet$), the reaction step (5) could not be able to reproduce enough Fe(III) which could again involve in the reaction with organic acids to form Fe(III)–organic complex (reaction step (2)) to continue the cyclic reaction:



Additionally, flavanones (e.g. taxifolin, naringenin, and naringin) are the major anti-oxidants found in citrus fruits like lemon and lime, whereas, hydroxycinnamic acids (e.g. p-coumaric acid and ferulic acid) are the major anti-oxidants in tomato (Fig. 3) [41,42]. Therefore, the carboxylate (R-COO^-) group of hydroxycinnamates could promote SORAS photochemical cycle, forming Fe(III)–hydroxycinnamate complexes and generating additional oxidizing radicals. On the contrary, flavanones have no such groups to form complexes with Fe(III). Therefore, tomato juice can act as a better promoter for the SORAS technique because of its ability to generate hydroxycinnamate complexes for the efficient removal of As from groundwater.

Table 4
Anti-oxidant activity of different citrate sources.

Lemon	Tomato	Lime	Estimation standard	References
93.3 ± 9.8	38.0 ± 1.7	NA	AEAC	[34]
0.69 ± 0.28	0.37 ± 0.12	NA	TDAC	[35]
NA	157 μmol TE/100 g	NA	ORAC	[36]
1225 μmol TE/100 g	367 μmol TE/100 g	823 μmol TE/100 g	ORAC	[37]
1225 μmol TE/100 g	387 μmol TE/100 g	823 μmol TE/100 g	ORAC	[38]

NA, not available; AEAC, L-ascorbic acid equivalent anti-oxidant capacity; TDAC, total anti-oxidant capacity; TE, trolox equivalent; ORAC, oxygen radical absorbance capacity.

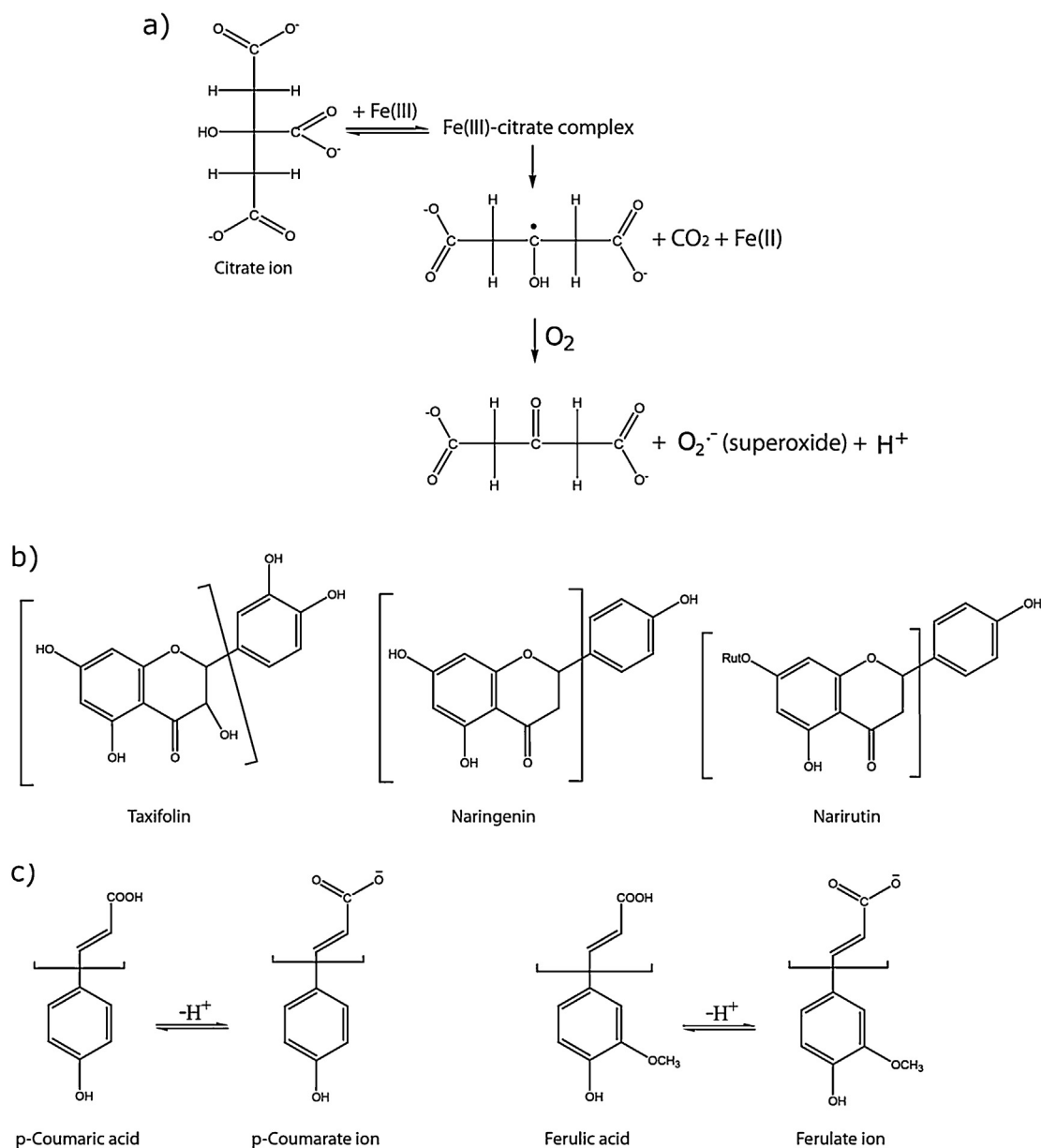


Fig. 3. (a) SORAS reaction steps (modified after Hug et al. [23]), (b) major anti-oxidants found in lemon and lime, and (c) major anti-oxidants found in tomato.

3.6. Cost analysis, availability and affordability of citrate sources

A survey was conducted in the local market of As contaminated regions in West Bengal, India for the cost analysis of different citrate sources (Table 5). The average cost of lemon and tomato (100 g in weight) is INR 4.00 (0.072 USD) whereas a lime costs INR 3.00

(0.054 USD). The average extractable juice from tomato and lime is 90 mL whereas from lemon is 70 mL (Table 5). Therefore the total citrate contents are 3.36, 3.78 and 4.12 g which can be extracted from lemon, tomato and lime weighing 100 g, respectively. Thus, apart from the effective removal of As, 100 g of tomato can produce greater volume of juices and citrate concentrations for the

Table 5Cost-estimate of different citrate sources based on the market survey.^a

Citrate sources	Availability	Price/100 g (INR) ^b	Extractable juices/100 g (mL)	Treatable volume of water/100 g of citrate sources (L)	Citrate content ^d (g)	Arsenic removal (%)
Lemon	All seasons	4.00 (0.072 USD)	70	93	3.36	82
Tomato	All seasons ^c	4.00 (0.072 USD)	90	120	3.78	94
Lime	Specific seasons	3.00 (0.054 USD)	90	120	4.12	67

^a The survey has been carried out in the local market of the study area (i.e. Chakdaha block, West Bengal, India).^b Average weight of a lemon is ~25 g, cost INR 1/-; whereas, average weight of a tomato and lime is 100 g, cost INR 4/- and 3/-, respectively. The USD value in the parenthesis is as on 29.08.2012, 1 USD = 55.6807 INR (www.xe.com).^c Modified varieties during some seasons.^d Considering citrate concentrations of 48 g/L in lemon and 45.8 g/L in lime [29] and 42 g/L in tomato [30].**Table 6**

Cost comparison of different low-cost As treatment techniques at the household levels.

Method	Required chemicals	Cost (INR/L)	Removal efficiency (%)	By products or sludge	Eco-friendliness	Reference
Candle filter fitted with plastic bucket	Bleaching powder, alum, $\text{Fe}_2(\text{SO}_4)_3$	1.2×10^{-2}	80	Hazardous sludge	No	[43]
Amal filter	Activated alumina	35×10^{-2}	80	Residual aluminium	No	[44]
CMRI filter	Chemical capsule (details are not available in public)	6×10^{-2}	<50	–	No	[45]
SORAS	Natural citric acid, as tomato juice	3.3×10^{-2}	90–97	Very little Fe-oxide precipitate	Yes	This study

treatment of large volume of As contaminated drinking water compared to lemon. We observed ~94% As removal in groundwater samples by using tomato as the citrate source. The As concentration in the treated water was ~0.1–0.5 mg/L (Table 3). Therefore, by adopting this method the concentration of As could be brought down below the WHO guideline value (0.01 mg/L) or the national safe limit of India (0.05 mg/L). We expect that this technique should work for low or high As groundwater and this requires further investigations. However, the removal efficiency would depend on the initial As and Fe concentration (i.e. molar ratios of As and Fe) in the treated water.

Table 6 showed a comparative estimate of the available low-cost household methods for As removal from groundwater. Most of the low-cost methods involve additional use of potentially hazardous chemicals and making them environmentally unacceptable due to generation of toxic wastes. On the other hand, SORAS technique with the addition of natural citric acid (as tomato juices, non-toxic) is comparatively more efficient in removing As from groundwater at the household level without producing any hazardous wastes. In rural villages tomato can be found abundantly due to its high demand and greater earnings. Hence, it would be convenient and beneficial for the rural people to cultivate tomato in their backyard and use it for the SORAS treatment. Therefore, the citrate source from tomato should be considered for the effective functioning of SORAS technique for the removal of As from drinking groundwater. The method described here is also highly cost-effective compared with other conventional treatment methods currently available in the market (Table 6). Additionally, with 100 g of tomato, 120 L of water can be treated which is much economic than use of lemon (Table 6). Most importantly, this method does not produce any hazardous chemicals, therefore, can be considered as a green chemistry approach for the effective removal of As from groundwater at household levels for drinking and cooking purposes.

The PET bottles used for the removal of As could be cleaned with cleaning soaps available in the local markets for subsequent use. The treated water should be decanted after the treatment for

drinking or cooking purposes or it can be filtered through clean, white clothes. No specific emphasis was given to monitor the precipitate formed during this experiment as an indicator for the efficiency of this method, although, higher amount of precipitates supposed to indicate greater removal on the basis of the removal mechanism detailed above.

4. Conclusion

This study reported for the first time that the citrate source from tomato can effectively remove As from groundwater compared to lemon and lime. The removal efficiency was mainly controlled by the varying As/Fe molar ratios and citrate doses, which showed an 'optimized central tendency'. The analogous citrate removal from groundwater indicates possible interference of anti-oxidants during Fe(III)-citrate photochemical cycle. Tomato, containing hydroxycinnamate as major anti-oxidants, would probably form Fe(III)–hydroxycinnamate complexes and thus favored the SORAS photochemical cycle. The market survey highlights tomato as the most cost-effective, eco-friendly, affordable, available and efficient citrate source compared to lemon and lime for the SORAS treatment at the household level. The allowance of the household filtration of the treated water makes this method more convenient for the rural villagers. The cultivation of tomato in rural backyards will additionally gain financial benefit to the rural household's in addition to treat As contaminated groundwater.

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