ABSTRACT: Arsenic (As) contamination in the groundwater of Bangladesh is one of the major public health concerns. It has become a challenge to remove As from groundwater and a great deal of efforts employed in this regards with limited success. Cerium oxide is one of the important medias of arsenic removal techniques. Nine units of cerium-based arsenic technology were tested with seven different well waters in five hydro-geological areas in Bangladesh. Interestingly, the same technology showed variable results in terms of As removal performance from well water. Therefore, this study aimed to investigate the reasons behind the variant performance of the As removal technology. The studied wells were contaminated with a range of 283 to 873 µg/L of arsenic, 0.35 to 10.4 mg/L of iron, 0.29 to 6.83 mg/L of phosphate, 32.5 to 49.5 mg/L of silicate, 0.08 to 0.25 mg/L of sulfate and pH range was 7.11 to 7.65. The cerium-based As removal technology consistently produced As safe water from three wells containing more than 80% As (III) of total arsenic (As) and >3 mg/L of iron and reduced As concentration to below 50 µg/L consistently but failed at other four wells containing less than 75% As (III) of tAs and <3.6 mg/L of iron. The test results confirm that the main reason of poor performance was lower concentration of As (III) and iron in groundwater. Therefore, before choosing a technique for As removal should follow the As speciation in the water system.

Keywords: Adsorption, Verification, Performance claim, Arsenic-removal, Groundwater contamination.

INTRODUCTION
In Bangladesh, a rigorous survey on arsenic (As) in tube-well water was conducted under a national project entitled 'Bangladesh Arsenic Mitigation Water Supply Project (BAMWSP)' covering 57,482 villages located in 271 upazillas in 2003. They found that out of 4.95 million tube-wells about 1.44 million tube-wells were contaminated by varying degree of As. Later on, several recent studies reported that about 70 million people are exposed to As risk in Bangladesh and out of 64 district 59 district experienced As contaminated groundwater having substantial health risk (Chakraborti et al., 2010; Rahman et al., 2016; Rahman et al., 2018). Arsenicosis from As has occurred as a result of drinking
water contaminated with arsenic in some regions and countries such as Bangladesh, Taiwan, Chile, and India (Jekel et al., 1994; Chakraborti et al., 2010). Approximately 30% Bangladesh shallow tube wells contaminated with arsenic (As) are at concentrations above the Bangladesh drinking water standard of 50 µg/L. In arsenic contaminated areas, groundwater is the only source of drinking water for about 25 to 35 million people in Bangladesh. Therefore, meeting their need for safe drinking water in these areas is a serious problem. Production of arsenic safe drinking water from arsenic contaminated groundwater is one of the different options for providing safe drinking water to our rural people in arsenic contaminated areas. Stakeholders came up with a good number of technologies for production of arsenic safe drinking having various advantages. The performance of arsenic removal technology (ARTs) varies depending on the type of media, pre- and post-treatment processes, groundwater quality parameters, etc.

Arsenic dissolved in water exists in two states, trivalent arsenite and pentavalent arsenate. Arsenic in groundwater is mostly in the trivalent state (Rasul et al., 2002). Removal of As from groundwater by adsorption is one of the most effective methods, having high removal efficiency without yielding harmful byproducts, and has been given wide attention recently (Gencu et al., 2004). Coagulation and adsorption (Jiang et al., 2001; Sikder et al., 2019) have been employed for arsenic removal from water. The adsorption process appears to be the most promising one. Some species of the iron oxides, as cheap adsorbents, have been reported to be partially effective with limitations such as low arsenic adsorption capacities, slow adsorption processes, and narrow optimum pH ranges (Munoz et al., 2002). Like the iron oxides, the activated alumina has long been the most often used adsorbent for arsenic removal with some limitations as well. However, adsorbent selection is a complex decision due to numerous critical factors. The choice depends on the oxidation state of arsenic and the many factors (Pankaj Verma et al., 2014). Arsenic removal by passive treatment depends on iron in sample (Linda C. et al., 2004). Removal efficiency of iron and arsenic (III) depends on initial concentration of iron and (Rashmi R. Devi et al. 2014). Cerium oxide is one of the important media of ARTs. Cerium (IV) oxide, also known as ceric oxide, ceria, cerium dioxide is an oxide of the rare earth metal of cerium. It is a pale yellow-white powder with the chemical formula CeO₂. Cerium oxide used as a granulated polymer suitable for adsorbing arsenic, which is a 0.7 mm spherical particle in average diameter. Adsorption of arsenic occurs on the surface of the resin grains. Cerium hydroxide has a high selective adsorption against negative ions, such as oxoanion arsenic species, fluoride, and boron. Cerium hydroxide possesses the lowest solubility against acid among the rare earth elements. An adsorbent does not elute when harmful ions in water is removed. And since it is safe to use, cerium hydroxide has been tested for arsenic removal in Bangladesh at field scale to ensure arsenic-free drinking water. But the success is significantly lower in some cases than the desired performance. Therefore, the present work aims to find out the potential reason/s behind the failure of the cerium-based technology in aquifer water to remove arsenic.

MATERIALS AND METHODS
The Arsenic Removal technologies were deployed in Dohar, Chandina, Begumgonj, Ishwardi, and Chapainababganj in Bangladesh. The field tests were conducted on seven wells in five hydrogeologically different areas of Bangladesh and tested seven months. These areas were chosen on
the basis of their groundwater quality parameters, e.g. arsenic, iron, phosphate and some other parameters. The technology was operated and closely monitored and analyzed raw and treated water for different water quality parameters by using field test kits following strict QA/QC protocols and also collected samples of raw and treated water at regular intervals and delivered these to designated laboratories for testing As (trivalent & pentavalent), Fe, Mn, PO₄, SO₄, Cl⁻ etc. Raw and treated water samples were collected in 500 mL cleaned plastic bottles. Samples taken and shipped to analytical laboratories for metals were preserved with nitric acid to pH<2.

The technology contains sand and cerium oxide resin. The technology was operated in flow through mode and it processed as much as 178 liters of well water in an hour. When contaminated tube well water passed through the sand bed, all suspended particles in the well water were arrested by sand. Ferrous ions are oxidized by the air, to ferric ions. Under circumneutral pH conditions, the ferric ion is insoluble in water and hydrolyses rapidly, forming ferric hydroxide. The latter in turn coagulates and flocs and precipitates as hydrous ferric oxide (HFO).

\[
2 \text{Fe(OH)}_2 + O_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{Fe(OH)}_3 + \text{H}_2\text{O}_2 \tag{1}
\]

The dissolved arsenite and arsenate ions are either trapped within the HFO flocs during the floc formation, or adsorbed to the floc surfaces and reacted with the active surface sites, via a ligand exchange mechanism. (Husam et. al., 2007), have shown that HFO is an excellent adsorbent for arsenic.

The adsorption reactions for arsenite and arsenate, respectively, on hydroxy ferric oxide flocs proceed as follows:

\[
\text{=Fe-OH} + \text{H}^+ + \text{H}_2\text{AsO}_4^- \rightarrow \text{=Fe-H}_2\text{AsO}_4^- + \text{HOH} \tag{2}
\]

\[
\text{=Fe-OH} + \text{H}_3\text{AsO}_4 \rightarrow \text{=Fe-H}_2\text{AsO}_3^- + \text{HOH} \tag{4}
\]

where =Fe-OH represents the active hydroxyl group (sorption site) associated with hydroxy ferric oxide flocks \(\text{H}_2\text{AsO}_3^-\) and \(\text{H}_4\text{AsO}_4^-\) are the ionized forms of arsenate. In groundwater (pH= 6.5-7.5) arsenic is present in two oxidation states (Hussam et. al., 2007) (As (III), \(\text{H}_3\text{AsO}_3\) and As (V), \(\text{H}_3\text{AsO}_4\)).

After passing through the sand bed, water then passes through the resin (cerium oxide impregnated ethylene-vinyl alcohol). The following adsorption mechanism is involved for removing arsenic (III) and arsenic (V)

During the oxidation step of the process of the invention, arsenite in the aqueous feed is oxidized to arsenate according to the following equation:

\[
2 \text{CeO}_2 + \text{H}_3\text{AsO}_3 \rightarrow \text{Ce}_2\text{O}_3 + \text{H}_2\text{AsO}_4^- + \text{H}^+ \tag{5}
\]

As the cerium +4 oxidizes the arsenite, it is reduced to cerium in the +3 oxidation state, which then reacts with the arsenate formed during the oxidation step to produce insoluble cerium arsenate as shown in the following equation:

\[
\text{Ce}_2\text{O}_3 + 2 \text{H}_2\text{AsO}_4^- + 2 \text{H}^+ \rightarrow 2\text{CeAsO}_4 + 3 \text{H}_2\text{O} \tag{6}
\]

Water or other aqueous liquid containing dissolved arsenic in the +3 and +5 oxidation states is contacted with cerium dioxide to oxidize arsenic in the +3 oxidation state to arsenic in the +5 oxidation state, and the arsenic in the +5 oxidation state is removed from the aqueous liquid by contacting the liquid with a precipitating agent that reacts with the arsenic in the +5 oxidation state to produce insoluble arsenic compounds and an aqueous liquid of reduced arsenic content.
Adsorption kinetics models are used to investigate the mechanism of adsorption. Two models are adopted and they are pseudo-first order model given as:

\[ q_t = q_e \left(1 - \exp\left(-k_1t\right)\right) \]

and pseudo-second order model represented by the following equations:

\[ q_t = \frac{q_e^2k_2t}{1 + q_ek_2t} \]

where \( q_e \) and \( q_t \) are the amount of adsorbate at equilibrium and time \( t \) (both in mg/g); \( k_1 \) is the first-order rate constant of sorption (min\(^{-1}\)); \( k_2 \) is the second-order rate constant of sorption (g/mg/min) and \( t \) is the time (min). Previous studies found that Ce based adsorbents shows chemisorption mechanism by following the pseudo-second order reaction kinetics (Yu et al., 2015; Zhang et al., 2003; Deng et al., 2010).

In this study the volume of water that can be treated by the technology over an approximately eight (8) hours period in a day and the cumulative volume of potable water produced during the testing period were recorded during field testing. Raw and treated water samples were collected at regular intervals and analyzed for concentrations of dissolved arsenate and arsenite, iron, phosphate and other water quality parameters. Arsenic and iron were measured using Hydride Generation Atomic Absorption Spectrophotometry (HGAAS) and Flame Atomic Absorption Spectrophotometry (FAAS) respectively and further confirmed with ICP-MS technique. Metal Scan using ICP-MS and Anion scan using Ion Chromatograph (IC) for both influent & effluent water samples were also performed to check weather any metal any contaminant added or removed from this treatment technology. All data were analysed using MINITAB 18 software.

**RESULTS AND DISCUSSION**

Nine units of this arsenic removal technology were field tested on seven wells in five different locations; five single units were installed and tested on five wells – at least one unit per well per region – in Ishwardi (Is), Dohar (Do), Chandina (Cd) and Chapai (Ch) regions and two sets of duplicate units were installed and tested on two wells in Chapai and Begumgonj (Bg) regions. A summary of the well water quality parameters along with their corresponding 95% CI (confidence intervals) is provided in Table 1.

The volume of arsenic-safe water produced by each unit and the mean concentrations of arsenic in the treated water are presented in Table 2.

The data presented in Table 2 shows that replicate units installed on the same wells occur breakthrough consistently from a given water matrix, indicating the uniformity and reproducibility of the technology manufacturing process.

**Table 1. Summary of the well water quality parameters**

<table>
<thead>
<tr>
<th>Location / Well No</th>
<th>[As] µg/L; Mean ± CI</th>
<th>[As(III)]/[As]T</th>
<th>[Fe] mg/L; Mean ± CI</th>
<th>[PO4] mg/L; Mean ± CI</th>
<th>pH Mean ± CI</th>
<th>SiO(_2^2^-) mg/L</th>
<th>SO(_4^2-) mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bg/W16</td>
<td>283 ± 13</td>
<td>0.85</td>
<td>5.58 ± 0.32</td>
<td>6.76 ± 0.22</td>
<td>7.25 ± 0.02</td>
<td>46.75</td>
<td>0.17</td>
</tr>
<tr>
<td>Cd/W21</td>
<td>294 ± 35</td>
<td>0.90</td>
<td>3.38 ± 0.87</td>
<td>5.04 ± 1.24</td>
<td>7.46 ± 0.04</td>
<td>36.59</td>
<td>0.08</td>
</tr>
<tr>
<td>Cd/W36</td>
<td>495 ± 22</td>
<td>0.75</td>
<td>1.19 ± 0.48</td>
<td>6.83 ± 3.87</td>
<td>7.65 ± 0.04</td>
<td>32.52</td>
<td>0.25</td>
</tr>
<tr>
<td>Ch/W21</td>
<td>669 ± 38</td>
<td>0.83</td>
<td>6.70 ± 0.28</td>
<td>1.25 ± 0.37</td>
<td>7.15 ± 0.07</td>
<td>39.30</td>
<td>0.17</td>
</tr>
<tr>
<td>Ch/W29</td>
<td>647 ± 78</td>
<td>0.60</td>
<td>0.35 ± 0.11</td>
<td>0.29 ± 0.23</td>
<td>7.11 ± 0.11</td>
<td>40.65</td>
<td>--</td>
</tr>
<tr>
<td>Do/W33</td>
<td>546 ± 16</td>
<td>0.84</td>
<td>10.40 ± 1.03</td>
<td>6.09 ± 0.49</td>
<td>7.15 ± 0.17</td>
<td>49.46</td>
<td>0.13</td>
</tr>
<tr>
<td>Is/W63</td>
<td>873 ± 131</td>
<td>0.63</td>
<td>3.60 ± 1.23</td>
<td>1.13 ± 0.61</td>
<td>7.17 ± 0.16</td>
<td>37.26</td>
<td>0.12</td>
</tr>
</tbody>
</table>
Table 2. Summary of statistical analysis (t-statistic) of arsenic concentrations in this technology treated water samples in different locations

<table>
<thead>
<tr>
<th>Location/Well/Unit</th>
<th>N^1</th>
<th>Mean effluent [As]±CI/µg/L</th>
<th>Vol. of Potable Water (L) Produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bg/W16/U4</td>
<td>14</td>
<td>30 ± 17</td>
<td>93534</td>
</tr>
<tr>
<td>Bg/W16/U7</td>
<td>17</td>
<td>32 ± 12</td>
<td>87394</td>
</tr>
<tr>
<td>Cd/W36/U5</td>
<td>7</td>
<td>29 ± 31</td>
<td>43388</td>
</tr>
<tr>
<td>Cd/W21/U9</td>
<td>16</td>
<td>13 ± 4</td>
<td>57367</td>
</tr>
<tr>
<td>Ch/W29/U01</td>
<td>8</td>
<td>48 ± 28</td>
<td>68258</td>
</tr>
<tr>
<td>Ch/W29/U06</td>
<td>8</td>
<td>41 ± 28</td>
<td>74450</td>
</tr>
<tr>
<td>Ch/W21/U08</td>
<td>17</td>
<td>7 ± 3</td>
<td>98758</td>
</tr>
<tr>
<td>Do/W33/U03</td>
<td>18</td>
<td>14 ± 3</td>
<td>150500</td>
</tr>
<tr>
<td>Is/W63/U02</td>
<td>15</td>
<td>38 ± 16</td>
<td>126739</td>
</tr>
</tbody>
</table>

Fig. 1. Shows plots of effluent arsenic concentrations as a function of cumulative volume of potable water produced by the technology, the effluent arsenic data has been analyzed statistically using t-statistic.

The data appears to be randomly distributed around a mean value, and Treated arsenic level of three units at three testing sites (Chapai, Chandina and Dohar) is found less than 50 µg/L where the well water contains iron from 3.38 mg/L to 10.4 mg/L and arsenic (III) from 83 % to 90 %. Treated arsenic level of 6 units, including replicate units, exceed 50 µg/L at four sites (Chandina, Ishwardi and Chapai) where well water contains low concentration of iron from 0.35 mg/L to 3.36 mg/L and arsenic (III) from 60 % to 75 %. Except Begumganj where well water iron concentration is 5.58 mg/L and arsenic (III) is 85 %. This technology might have failed due to operation and maintenance problem. Since cerium oxide is impregnated in ethylene-vinyl alcohol, if the HFO flocs accumulated on the media, the dissolved arsenic in water cannot pass through the media to adsorb on cerium oxide and ultimately the technology does not perform well. If well water contains high iron then media will be covered with the HFO flocs frequently. So, proper media washing is needed otherwise media will unable to produce proponents claimed volume of arsenic-safe. Cerium based adsorbent either alone or forming composite adsorbent have using to remove arsenic in previous

1. Number of data points used for statistical analysis
literatures with varying degree of success. However, the field based bulk experiments are very limited in tube-well water. For instance, cerium oxide-graphene composite produced maximum capacity of 41.31 mg-As/g at pH 7.0 in laboratories (Yu et al., 2015). While, hydrous cerium oxide nanoparticles showed exceptional arsenic removal capability with pH 7 which was 170 mg/g (As:III), and 107 mg/g (As:V) (Li et al., 2012). In addition, Fe-Ce hydroxide showed As removal capacity of 18.2 mg/g following Freundlich adsorption mechanism (Zhang et al., 2010). These all are laboratory scale study which might have different output for field experiments as the pH and other field parameters can be certainly varied. It was reported that depending on the As speciation the pH plays important role in the removal techniques. For instance Ce-Ti adsorbent showed excellent As(III) removal performance at neutral pH whereas, As(V) removed successfully at a pH below 7 (Li et al., 2010). The As mobilization in the aquifer is somehow governed by the iron-oxy hydroxide therefore, the role of Fe in both mobilization and speciation are considerable (Bose & Sharma, 2002). This study also found interference of Fe and As speciation in the removal of As from aquifer in field scale study in Bangladesh.

![Graph showing cumulative volume of arsenic safe treated water (y = 0.0759x + 2.6282, R² = 0.5902)](image)

**CONCLUSION**

Thus, the evidence obtained from the above studies, it can be concluded that cerium adsorbent based arsenic removal technology can produce arsenic safe water and performance depends on well water iron, arsenic contents and operation and maintenance. If well water contains high iron, arsenic and proper operation and maintenance protocols are correctly followed then this technology expected to meet the proponent’s claim and produce arsenic safe water. Otherwise this technology is unable to produce proponent’s claimed volume of arsenic-safe water.

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**CONFLICT OF INTEREST**

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/ or submission, and redundancy has been completely observed by the authors.
**LIFE SCIENCE REPORTING**

No life science threat was practiced in this research.

**REFERENCES**


