Simultaneous removal of arsenic, iron and manganese from groundwater by oxidation-coagulation-adsorption at optimized pH
Anup J. Bora, Rajkamal Mohan and Robin K. Dutta

ABSTRACT
The method based on oxidation-coagulation-adsorption at optimized pH (OCOP) using NaHCO₃, KMnO₄ and FeCl₃ as pH conditioner, oxidant and coagulant, respectively, is an efficient and low-cost method for removal of arsenic from groundwater that has been gaining popularity in India. In a recent modification of OCOP, coexisting ferrous iron of water was utilized in order to lower the dose of FeCl₃ and hence to lower the cost of the treatment of water containing both arsenic and iron. Here we present how the OCOP method can be effectively and economically used for simultaneous removal of arsenic, iron and manganese ions from water containing all three contaminants. For this we have optimized the required doses of NaHCO₃, KMnO₄ and FeCl₃ by response surface methodology and used the optimized doses in a field trial with 11 domestic units of 20 L capacity in batch mode. Arsenic, iron and manganese were removed simultaneously by the present modification of the OCOP method to below 1 μg/L, 0.03 mg/L and 0.009 mg/L from initial concentrations of 100 μg/L, 1–8 mg/L and 0.5–5.0 mg/L, respectively, with a reduced cost.

Key words | arsenic removal, coexisting iron, iron removal, manganese removal, oxidation-coagulation-adsorption, response surface methodology

INTRODUCTION

Millions of households in different parts of the world are currently using arsenic-rich groundwater as drinking water. India (Assam, West Bengal, Bihar, etc.), Bangladesh, USA, Mexico, New Zealand, Argentina, Mongolia, China, Taiwan, Vietnam, etc., have been reported to be highly affected countries of the world with arsenic concentrations as high as 2000 μg/L (Murcott 2012). Chronic arsenic exposure in drinking water can lead to severe health problems such as arsenicosis, skin lesions, hyperkeratosis, vitiligo, melanosis, skin cancer and cancer of internal organs. The World Health Organization has prescribed a provisional guideline value for arsenic in drinking water as 10 μg/L (WHO 2011). The most common species of arsenic in groundwater are arsenite (As³⁺) and arsenate (As⁵⁺), with the former generally accounting for about 90% of the total arsenic (Smalley & Kinniburgh 2002).

In recent years, brisk research activities have reported on development of low cost methods based on reverse osmosis, electro-dialysis, adsorption, oxidation, coagulation, etc., for removal of arsenic and other hazardous elements from groundwater. Among those technologies, oxidation, adsorption and coagulation-adsorption are the most prominent methods with low-cost, green and easy operations (Shannon et al. 2008). Different adsorbents such as alumina/silica oxide hydrate, carbon composite electrodes using capacitive deionization, granular ferric oxide, laterite, iron oxy-hydroxide, manganese oxide, sand, zero-valent iron, zero-valent aluminum, activated carbon, activated alumina, TiO₂, ferric hydroxide, iron containing nanoparticles, etc., have been used for arsenic removal (Mohan & Pittman 2007; Sazakli et al. 2015; Lee et al. 2016; Zhang et al. 2016). Different iron and aluminum salts, viz., FeCl₃, FeSO₄, FeCISO₄
et al. Bora iron. As the presence of iron ($\text{Fe}^{2+}$) in groundwater inhibits oxidation of $\text{As}^{3+}$, it is necessary to use an additional oxidising agent like $\text{KMnO}_4$, NaOCl, etc., sufficient to oxidise the $\text{As}^{3+}$ ions after completely oxidising the $\text{Fe}^{2+}$ ions (Bordoloi et al. 2015). Air, chlorine, hypochlorite, ozone, permanganate, hydrogen peroxide, Fenton’s reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$), manganese dioxide, etc. can be used as the oxidising agent (Bordoloi et al. 2015). Efficient removal of $\text{Fe}^{2+}$, $\text{Mn}^{2+}$ and $\text{NH}_4^+$ has been reported using biofilm coupled with aeration and $\text{MnO}_2$ coated quartz bed requiring a long adaptation period, e.g., 3–4 weeks (Śtembał et al. 2005; Cheng 2016). Efficient removal of iron, manganese and arsenic has also been reported using $\text{Fe}^{2+}$ and $\text{Mn}^{2+}$ – oxidising bacteria for oxidation of $\text{As}^{3+}$ (Katsoyiannis & Zouboulis 2006).

Oxidation-coagulation-adsorption at optimized pH (OCOP) using $\text{NaHCO}_3$, $\text{KMnO}_4$ and $\text{FeCl}_3$ as pH conditioner, oxidant and coagulant, developed by our research group, has been gaining popularity in domestic and small community (20–500 L batch units) as well as large scale community application (110,000 L/day) as Arsiron Nilogon (Arsenic + iron removal) (Bordoloi et al. 2013, 2015; DST 2015) in India, especially in Assam. The recommended doses of $\text{NaHCO}_3$, $\text{KMnO}_4$ and $\text{FeCl}_3$ in OCOP in the absence of coexisting iron are $100 \text{mg/L}$, $4 \text{mg/L}$ and $25 \text{mg/L}$, respectively. In the presence of coexisting ferrous iron, however, more $\text{KMnO}_4$ is to be added until the water gives light purple coloration to completely oxidize the dissolved $\text{Fe}^{2+}$ to $\text{Fe}^{3+}$ along with oxidation of $\text{As}^{3+}$ to $\text{As}^{5+}$. Recently we reported a modification of the OCOP method in which the coexisting ferrous iron of groundwater is made to act as coagulant reducing the dose of $\text{FeCl}_3$ for removing both arsenic and iron simultaneously (Bora et al. 2016). Here, the doses of $\text{KMnO}_4$ and $\text{NaHCO}_3$ were optimized through response surface methodology (RSM) while the dose of $\text{FeCl}_3$ was taken as equal to the difference between the coagulant dose of OCOP ($25 \text{mg/L}$ of $\text{FeCl}_3$) and the concentration of the coexisting ferrous iron ($[\text{Fe}^{2+}]_0$) in mg/L.

Very often, manganese ($\text{Mn}^{2+}$) ions, in excess of the WHO guideline value 0.1 mg/L for drinking water, is also present along with arsenic and iron in groundwater (WHO 2011). Epidemiological studies in different countries have showed adverse effects in humans for consuming manganese dissolved in drinking-water in addition to aesthetic problems due to dissolved manganese ions. The Eh-pH diagram indicates that the dominant dissolved species of manganese in natural waters is $\text{Mn}^{2+}$ (Jensen et al. 1998).

Activated carbon, granular activated carbon, sugar cane bagasse and beet pulp, dissolved organic carbon; Groundnut shells, coconut shell charcoal, kaolinite, polysaccharide-based material, carbon aerogel, etc., are some common adsorbents of $\text{Mn}^{2+}$ (Cvetković et al. 2010). Ferric salts are also given preference as coagulant for removal of manganese (Katsoyiannis & Zouboulis 2006). Chlorine dioxide ($\text{ClO}_2$), Ferrate (VI) salt, chlorine, potassium permanganate, ozone and $\text{H}_2\text{O}_2$ are used also for oxidation $\text{Mn}^{2+}$ to $\text{Mn}^{4+}$ to remove manganese from groundwater (Khadse et al. 2015). Nano-$\text{MnO}_2$, $\text{MnO}_2$ coated sand, alumina, etc., also are reported to contribute to removal of arsenic through adsorption (Con et al. 2015). $\text{MnO}_2$ formed in groundwater containing arsenic and manganese absorbs arsenic in the subsurface and also adsorbs $\text{Mn}^{3+}$ to catalyses its oxidation, thus increasing the overall removal of both arsenic and manganese (Bissen & Frimmel 2005). Moreover, $\text{MnO}_2$ is also reported to catalyse oxidation of arsenite to arsenate (AWWA 1993).

Considering the coexistence of iron and manganese ions along with arsenic in groundwater and the roles of iron ions, $\text{KMnO}_4$ and $\text{MnO}_2$ in removal of the three contaminants, it was thought worthwhile to investigate the simultaneous removal of arsenic, iron and manganese by the OCOP method. For this we have optimised the doses of OCOP, viz., $\text{NaHCO}_3$, $\text{KMnO}_4$ and $\text{FeCl}_3$ through RSM (Bezerra et al. 2008) and examined the performance of the method with the optimized doses for simultaneous removal of arsenic, iron and manganese from contaminated water in the field.

**MATERIALS AND METHODS**

**Reagents**

$\text{NaHCO}_3$, $\text{FeCl}_3$, $\text{KMnO}_4$, $\text{FeSO}_4\cdot7\text{H}_2\text{O}$, $\text{MnSO}_4\cdot\text{H}_2\text{O}$ were obtained from Merck, India. Sodium arsenite ($\text{NaAsO}_2$)
was purchased from Sigma-Aldrich. All chemicals were of analytical grade and used without further purification. Stock solutions of 0.10 g/L As$^{3+}$, 1.0 g/L Fe$^{2+}$ and 1.0 g/L Mn$^{2+}$ were prepared by spiking tap water with NaAsO$_2$, FeSO$_4$.7H$_2$O and MnSO$_4$.H$_2$O, respectively. Synthetic groundwater containing these three ions was prepared by mixing these freshly prepared stock solutions with groundwater. The major water quality parameters of the tap water were: chloride = 2.3, fluoride = 0.13, sulphate = 6.4, sodium = 4.71, potassium = 7.7, manganese = 0.002, calcium = 0.72, arsenic = 0, iron = 0.006, magnesium = 0.867 and dissolved solids = 96 all in mg/L; pH = 6.7 and dissolved oxygen = 83.45% (Bora et al. 2016). The stock solutions of 1.0 g/L FeCl$_3$, 1.0 g/L KMnO$_4$ and 9.0 g/L of NaHCO$_3$ were prepared in doubly distilled water for using as coagulant, oxidant and pH conditioner, respectively.

**Instrumental analysis**

The pH of the experimental water samples were measured in the laboratory using a multi parameter kit (model 5Star pH.ISE.Cond.DO Benchtop, Orion, USA). The pH of the water samples in the field was determined using a pocket-sized pH meter (model PH-222, Lutron Electronic Enterprise CO., LTD, Taiwan). The concentrations of As, Fe, Mn and other heavy metals in influent and effluent water were determined using an atomic absorption spectrophotometer (AAS, model Analyst 200, Thermo iCE 5000 series, USA) coupled with a hydride vapour generator (model VP100).

**Initial experiments for RSM optimization**

A series of OCOP experiments for RSM optimization of the doses of NaHCO$_3$, FeCl$_3$ and KMnO$_4$ was performed in mugs each containing 1 L synthetically prepared contaminated water with a fixed initial arsenite ion concentration ([As$^{3+}$]$_0$) at 100 μg/L, varying initial iron ion concentrations ([Fe$^{2+}$]$_0$) from 1 mg/L to 8 mg/L and varying initial manganese ion concentrations ([Mn$^{2+}$]$_0$) from 0.5 mg/L to 5.0 mg/L. Aqueous NaHCO$_3$ solution was added drop-wise to increase the pH of the water to ≈8.5. Aqueous KMnO$_4$ solution was added in percentage equivalent of [Fe$^{2+}$]$_0$ from 30% to 100% followed by addition of FeCl$_3$ from 1 mg/L to 8 mg/L. Then, aqueous NaHCO$_3$ was added again to adjust the final pH at ≈7.5. The amount of total added NaHCO$_3$ in mg/L was noted. The water was stirred gently with a glass rod during addition of NaHCO$_3$, KMnO$_4$ and FeCl$_3$. Then, the water was allowed to coagulate and settle down for two hours. The water samples were then decanted and filtered through Whatman 42 filter paper.

**Statistical analysis**

RSM is a statistical method for examining the optimum conditions with a limited number of experiments (Baskan & Pala 2009). In the present case, the major operating variables, viz., NaHCO$_3$, KMnO$_4$ and FeCl$_3$ on removal of arsenic, iron and manganese simultaneously from groundwater were analysed and optimized by RSM, using central composite design (CCD). The selected model for this CCD design was the quadratic model. Design-Expert®, version 7 software (DX7), was used for the statistical analysis following the preparation of 3D surface areas for optimization of NaHCO$_3$, KMnO$_4$ and FeCl$_3$ (Bora et al. 2016). Here, ‘A’ and ‘B’ are the two design factors, taken as the independent variables, and their effect on the response (Y) was optimized. Variables such as [Fe$^{2+}$]$_0$ and [Mn$^{2+}$]$_0$ were chosen as the independent variables. In this CCD of RSM, three types of 3D plots were prepared in which ‘A’ and ‘B’ for each plot are [Fe$^{2+}$]$_0$ and [Mn$^{2+}$]$_0$, respectively and ‘Y’ for plot (a), (b) and (c) was [Mn$^{7+}$], [NaHCO$_3$], and [Fe$^{3+}$], respectively, to obtain the optimum doses of KMnO$_4$, NaHCO$_3$ and FeCl$_3$, respectively for removal of arsenic in the presence of manganese and iron to less than 1 μg/L.

The data were examined for two variables with 13 experimental runs (Bora et al. 2016). Based on the CCD of RSM, the data were made to fit with the 3D plot of surface area for the major operating variables in the removal of arsenic in the presence of manganese and iron according to the following equation:

\[ Y = a_0 + a_1 \times A + a_2 \times B + a_3(A \times B) + a_4 \times A^2 + a_5 \times B^2 \quad (1) \]

where, $a_0$, $a_1$, $a_2$, $a_3$, $a_4$ and $a_5$ are the regression coefficients.

The quality of the model fitted with the 3D surface areas is evaluated using analysis of variance (ANOVA) (Bora et al. 2016). In this analysis, the p-value (Prob > F values) of <0.05
suggests its statistical significance in the model and of > 0.1 are not significant. The terms with p-values of > 0.1 were eliminated in order to gain a superior surface model. The R-squared statistic determines the percentage of variability of the optimized parameters, explained by the selected model.

Field trial

A field trial of our RSM experiment was done in 11 domestic hand tube well spot sources in a village in Nagaon district of Assam in India, where the water contains arsenic with coexisting iron as well as manganese. Each unit consists of two 20 L plastic buckets fitted with a plastic tap. The first bucket is used for the chemical treatment and the other bucket, kept below the first one, is used as a sand-gravel filter. The RSM optimised doses of NaHCO3, KMnO4 and FeCl3 were added one after another as solid, 5% solution and 25% solution, respectively, to 20 L water kept in the first bucket, with mild stirring after each addition. The coagulates settled down at the bottom of the first bucket and after two hours the clear water was transferred through the tap to the sand-gravel filter in the second bucket for filtering. The filtered water was used for analysis of water quality parameters including As, Fe and Mn.

RESULTS AND DISCUSSION

Initial experiments for RSM optimization

Figure 1 shows the removal of arsenic from an initial 100 μg/L in arsenite form and varying concentrations of coexisting (initial) ferrous iron ions \([\text{Fe}^{2+}]_0\) and manganous ions \([\text{Mn}^{2+}]_0\) as a function of increasing KMnO4 dose of OCOP. In this experiment, approximately half of the dose of NaHCO3 was added to the water in the beginning and then the rest of the NaHCO3 was added after addition of KMnO4 and FeCl3 to adjust the pH of the treated water at \(\approx 7.3\). The dose of FeCl3 was taken as equal to (8.6 – \([\text{Fe}^{2+}]_0\)) in mg/L. This empirical equation used for deciding the doses of FeCl3 for the design experiment, viz., \([\text{Fe}^{3+}] = (8.6 – \([\text{Fe}^{2+}]_0)\) in mg/L as Fe was obtained experimentally (Bordoloi et al. 2015) and has been validated by the results of arsenic removal (Bordoloi et al. 2013; Bora et al. 2016). 8.6 mg/L was the dose of FeCl3 as Fe\(^{2+}\) in mg/L in OCOP, and there is no need for addition of FeCl3 when \([\text{Fe}^{2+}]_0\) is above 8.6 mg/L, as this \([\text{Fe}^{2+}]_0\) is expected to provide Fe\(^{3+}\) ions equal to the dose of FeCl3 in OCOP (Bordoloi et al. 2015). KMnO4 produces water-insoluble MnO2 from its reactions with Fe\(^{2+}\), Mn\(^{2+}\) and AsO\(^4\)\(^-\) in the mild alkaline conditions provided by NaHCO3 (Lihua et al. 2009):

\[
3\text{Fe}^{2+} + \text{KMnO}_4 + 7\text{H}_2\text{O} \rightarrow 3\text{Fe(OH)}_3 + \text{K}^+ + \text{MnO}_2 + 5\text{H}^+ \quad (2)
\]

\[
\text{Mn}^{2+} + \text{KMnO}_4 \rightarrow 2\text{MnO}_2 + \text{K}^+ \quad (3)
\]

\[
3\text{H}_2\text{AsO}_5 + 2\text{KMnO}_4 + 4\text{OH}^- \rightarrow 3\text{HAsO}_4^{2-} + 2\text{MnO}_2 + 5\text{H}_2\text{O} + 2\text{K}^+ \quad (4)
\]

The coagulates formed by coexisting iron (Fe\(^{2+}\)) after oxidation and by externally added FeCl3 are mainly iron oxides, namely goethite (FeOOH), ferrihydrite (5Fe\(_2\)O\(_3\)·9H\(_2\)O) and ferric hydroxide, Fe(OH)\(_3\) formed depending upon the pH (Manna et al. 2003). In a neutral pH of about 7.3 in the presence of NaHCO\(_3\), the coexisting iron Fe\(^{2+}\) and externally added FeCl3 forms coagulates, predominantly goethite (FeOOH), which adsorbs H\(_2\)AsO\(_4\) and HAsO\(_4^{2-}\) ions (Bordoloi et al. 2015).

We observed an increase in the removal of arsenic with increase in \([\text{Fe}^{2+}]_0\) and \([\text{Mn}^{2+}]_0\) as well as with increase in the dose of KMnO\(_4\) (Figure 1). The increase in the removal of arsenic with increase in KMnO\(_4\) dose can be attributed to oxidation of As\(^{3+}\) to easily adsorbed As\(^{5+}\) in addition to oxidizing Fe\(^{2+}\) to Fe\(^{3+}\) as FeCl3 alone cannot remove As\(^{3+}\) efficiently (Ouzounis et al. 2015). The observed increase in the removal of arsenic with increasing \([\text{Fe}^{2+}]_0\) at fixed \([\text{Mn}^{2+}]_0\) indicates increased formation of iron coagulates after conversion of the more and more coexisting Fe\(^{2+}\) into Fe\(^{3+}\) after addition of KMnO\(_4\). But the observed increase in the removal of arsenic with increasing \([\text{Mn}^{2+}]_0\) at fixed \([\text{Fe}^{2+}]_0\) may be attributed to increased adsorption of arsenic on MnO\(_2\) precipitates formed in the oxidation of Mn\(^{2+}\) ions by KMnO\(_4\) (Bissen & Frimmel 2003; Con et al. 2013) and catalysis of oxidation of As\(^{3+}\) to As\(^{5+}\) by MnO\(_2\) (AWWA 1993). It was observed that the remaining total [As], [Mn\(^{2+}\)] and [Fe\(^{2+}\)] after the treatment were below 1 μg/L, 0.009 mg/L and 0.03 mg/L down from their initial concentrations of 100 μg/L, 5 mg/L and 8 mg/L,
respectively. Tables 1 and 2 present the experimentally found minimum doses of KMnO₄ (in % equivalent of [Fe²⁺]₀) and NaHCO₃ (in mg/L) with which arsenic was found to be removed to below 1 μg/L from an initial 100 μg/L. These data were used for RSM analysis.

**Analysis by RSM**

The experimental results presented in Figure 1 were analysed by RSM using CCD and the quadratic model to optimize the doses of NaHCO₃, KMnO₄ and FeCl₃ required for removal of arsenic from groundwater to less than 1 μg/L in the presence of iron and manganese ions, at the same time removing iron and manganese also to less than 0.03 mg/L and 0.009 mg/L, respectively. The experimental designs for the model of the CCD involved the two independent parameters, namely, A and B, each of which has two coded levels as −1 and +1 for low and high concentrations/values, respectively. Levels of independent variables selected for the RSM analysis (low and high) of [Fe²⁺]₀ are 1 mg/L and 8 mg/L; and for [Mn²⁺]₀ are 0.5 mg/L and 5.0 mg/L, respectively. The experimental
Based on this RSM experiment we have found the optimum doses of NaHCO₃, KMnO₄ and FeCl₃ for removing arsenic, iron and manganese ions from water containing all these three contaminants.

3D Plot (a), (b) and (c) of Figure 2 for doses of KMnO₄, NaHCO₃ and FeCl₃ respectively, was prepared using Equations (5)–(7) respectively, in terms of coded factors:

\[
Y = 86.80 - 10.04 \times A - 6.46 \times B - 3.75(A \times B) - 4.83 \times A^2 + 0.56 \times B^2
\]  
(5)

\[
Y = 105.99 - 21.86 \times A - 1.69 \times B + 0.75(A \times B) + 4.57 \times A^2 - 0.013 \times B^2
\]
(6)

\[
Y = 4.14 - 3.45 \times A + 0.12 \times B + 1.25 \times 10^{-3}(A \times B) + 0.70 \times A^2 - 0.63 \times B^2
\]  
(7)

where, the factors A and B represent [Fe²⁺]₀ and [Mn²⁺]₀ in Equations (5)–(7). Validation of the model of the 3D plots of Figure 2 is obtained from diagnostics case studies (please see Supporting information, available with the online version of this paper).

### Optimized results

Table 4 represents optimized doses of KMnO₄ (as [Mn⁷⁺]) in percentage equivalent of [Fe²⁺]₀, NaHCO₃ (mg/L) and FeCl₃ (as [Fe³⁺] mg/L) predicted by the point prediction method. A comparison of Table 4 with Tables 1 and 2 shows that the doses of KMnO₄, NaHCO₃ and FeCl₃ predicted by the point prediction method show good correlation with the experimentally found doses of KMnO₄, NaHCO₃ and FeCl₃ predicted by RSM analysis.

Table 2 | The doses of NaHCO₃ (mg/L) for varying coexisting [Mn²⁺]₀ and [Fe²⁺]₀ required to remove arsenic below 1 μg/L from initial 100 μg/L.

<table>
<thead>
<tr>
<th>Coexisting [Mn²⁺]₀ (mg/L)</th>
<th>Coexisting [Fe²⁺]₀, mg/L</th>
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<tbody>
<tr>
<td>0.5</td>
<td>134 126 119 112 108 99 95 90</td>
</tr>
<tr>
<td>1.0</td>
<td>133 126 119 111 106 99 95 89</td>
</tr>
<tr>
<td>2.0</td>
<td>132 125 118 111 106 99 94 89</td>
</tr>
<tr>
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<td>131 124 118 110 105 98 94 88</td>
</tr>
<tr>
<td>4.0</td>
<td>131 124 117 110 104 98 93 88</td>
</tr>
<tr>
<td>5.0</td>
<td>130 123 114 108 104 96 93 87</td>
</tr>
</tbody>
</table>

Table 3 | The design of CCD for the dose of KMnO₄ (as [Mn⁷⁺]) in percentage equivalent of [Fe²⁺]₀, [NaHCO₃] in mg/L and FeCl₃ (as [Fe³⁺] mg/L) were taken as response, separately.

<table>
<thead>
<tr>
<th>Run</th>
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<th>Factor B</th>
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<tbody>
<tr>
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</tr>
<tr>
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<tr>
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<td>8.00</td>
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</tr>
<tr>
<td>13</td>
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</tbody>
</table>

All concentrations are in mg/L except for [Mn⁷⁺], which is in percentage equivalent of [Fe²⁺].
The doses of KMnO₄, NaHCO₃ and FeCl₃ used for the field trial as decided by the RSM analysis for various coexisting iron and manganese concentrations are presented in Figure 3. It was seen from Figure 3 that the dose of FeCl₃ decreases with the increase in coexisting iron up to 8.607 mg/L as Fe, beyond which there is no need of externally added FeCl₃. However, the required dose of KMnO₄ increases slightly with the increase in [Fe²⁺]₀ over the whole range as expected. With the increase in coexisting iron concentration, the required dose of NaHCO₃ also decreases slightly because, with the increase in coexisting iron concentration, of required addition of FeCl₃, a Lewis acid, decreases, requiring more NaHCO₃ to raise the pH to 7.3.

The field trial showed very good removal of arsenic along with removal of iron and manganese as shown in Figure 4. Arsenic was removed from initial concentrations in the range of 91–25 μg/L to less than 1 μg/L (Figure 4(a)). The removal of arsenic by the present modification of the OCOP method to such a low level is important in view of the WHO advice to remove arsenic to as low a level as possible, though it recommends a guideline value of 10 μg/L for drinking water, as groundwater with levels as low as 0.17 μg/L can cause arsenicosis if consumed over a long period of time (WHO 2011). Figure 4(b) and 4(c) show that iron and manganese ions were removed from initial concentrations in the range of 23–2 mg/L to less than 0.03 mg/L and of 0.5–1.9 mg/L to less than 0.009 mg/L, respectively. Thus, the present method simultaneously lowers the concentrations of arsenic, iron and manganese from contaminated groundwater to levels about 10 times lower than the respective guideline values of 10 μg/L, 0.3 mg/L and 0.1 mg/L prescribed by the WHO. The results of >99% As(III) removal of the present study are far better than the previously reported results of <30% As(III) removal by simple coagulation with ferric or aluminium salts (Duarte et al. 2013; Dimitrovski et al. 2012). The results of the present method are also better than the reported 85–95% As(III) removal by coagulation with FeCl₃ after pre-oxidation of As(III) with KMnO₄ (Kong et al. 2016).

Suitability of the method

Final pH of the treated water samples are also found to be in the middle of the acceptable range 7.0–7.5 for drinking (Figure 4(d)). The other relevant water quality parameters of the water before and after treatment have been found to
be well within the respective WHO guideline values (Table 5). An estimation of the cost of treatment; based on the current Indian retail price of NaHCO₃, KMnO₄ and FeCl₃; the cost of the present method has been found to be 0.326 USD per m³ for simultaneous removal of arsenic, iron and manganese. This cost is slightly lower than the cost of removing arsenic and iron simultaneously by the earlier modified form of the OCOP method, modified earlier to utilize the coexisting iron in coagulation, which has been estimated to be 0.332 USD per m³ based on the current prices. The slightly lower cost of the present method than the earlier modification can be attributed to the contribution of MnO₂ in arsenic removal in the present method. The users showed good response and expressed their satisfaction with the simplicity of the method and the results.

Table 4 | Optimized doses of KMnO₄ (as [Mn⁷⁺] in percentage equivalent (% eq.) of [Fe²⁺]₀), NaHCO₃ in mg/L and FeCl₃ (as [Fe³⁺] in mg/L) for different concentrations of coexisting [Fe²⁺]₀ and [Mn²⁺]₀ obtained from RSM

<table>
<thead>
<tr>
<th>Variables</th>
<th>Result</th>
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</thead>
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<td>[Fe²⁺]₀ mg/L</td>
<td>[Mn²⁺]₀ % eq.</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------</td>
</tr>
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Figure 3 | Plots of optimized doses of NaHCO₃, KMnO₄ and FeCl₃ for field trial of our experiment for different coexisting iron and manganese concentrations.
CONCLUSIONS

The simple OCOP method of removing arsenic and iron from contaminated groundwater has been successfully modified to remove manganese ions also, together with arsenic and iron by using RSM. The RSM fairly optimizes the doses of NaHCO₃, KMnO₄ and FeCl₃ for simultaneous removal of arsenic, iron and manganese from groundwater. The RSM analysis and experimental results for the doses of NaHCO₃, KMnO₄ and FeCl₃ correlate with each other. The field trial of our present modified OCOP method shows that arsenic, iron and manganese concentrations of contaminated water can be removed simultaneously to less than 1 μg/L, 0.03 mg/L, and 0.009 mg/L from initial concentrations of 100 μg/L, 1–8 mg/L, and 0.5–5.0 mg/L, respectively. Thus, the present modified form of the simple, efficient and low-cost OCOP method is a potential method for application for simultaneous removal of arsenic, iron and manganese from groundwater containing all these three contaminants.
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