



Utilization of co-existing iron in arsenic removal from groundwater by oxidation-coagulation at optimized pH



Anup J. Bora, Sweetey Gogoi, Gautam Baruah, Robin K. Dutta*

Department of Chemical Sciences, Tezpur University, Tezpur 784028, Assam, India

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ABSTRACT

Oxidation-coagulation at optimized pH (OCOP) using NaHCO_3 , KMnO_4 and FeCl_3 is an efficient and low-cost arsenic removal method for domestic to large community scale applications. In this method, a high dose of the oxidant is used when the groundwater contains high concentration of coexisting iron for oxidising all ferrous and arsenate ions. A fixed dose of 25 mg/L of FeCl_3 is also employed as coagulant despite the formation of ferric ions from the coexisting ferrous ions. The present study aimed at utilization of the coexisting iron for the coagulation purpose and reducing the coagulant dose. Response Surface Methodology was employed to optimize the doses of the oxidant and the pH conditioner. A field trial at various arsenic affected rural habitations has shown that the present modified OCOP method to be more efficient and economical than the OCOP method reducing both arsenic and coexisting iron concentrations to less than 2 $\mu\text{g/L}$ and 0.1 mg/L, respectively, at a lower cost. The modified OCOP method is useful especially with high concentration of coexisting iron.

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1. Introduction

Groundwater of different parts of the world such as India, Bangladesh, USA, Mexico, New Zealand, Argentina, Mongolia, China, Taiwan, etc., have been reported for contamination by toxic inorganic arsenic (As^{3+} and As^{5+} up to 2000 $\mu\text{g/L}$) [1–5]. The major sources of arsenic exposure to water are natural geological activities such as weathering of sedimentary rocks, volcanic emissions, oxidations, leaching from sulphides by carbonates and microbial mobilization, etc. [6,7]. Long-term consumption of arsenic in drinking water causes various arsenic related chronic diseases (arsenicosis) in human body hyperkeratosis; lung, kidney, prostate cancer and also produces adverse cardiovascular; neurological; haematological; renal and respiratory effects [8–14]. In India and Bangladesh alone, a population over 450 million are at a risk of arsenic poisoning [15]. The US Environmental Protection Agency (USEPA) reduced the maximum contamination level for potable water from 50 $\mu\text{g/L}$ to 10 $\mu\text{g/L}$ [16]. The World Health Organization (WHO) is also prescribing 10 $\mu\text{g L}^{-1}$ as a provisional guideline value for arsenic in drinking water [17].

Arsenic exists generally in four oxidation states (-3 , 0 , $+3$, $+5$) and the most common species of arsenic in water are arsenite (As^{3+}) and arsenate (As^{5+}). Redox potential (Eh) and pH are the most important factors controlling arsenic speciation [18]. Arsenite is the dominant species in anoxic conditions and found to be H_3AsO_3^0 ($\text{pK}_{a1}=9.1$), H_2AsO_3^- ($\text{pK}_{a2}=12.1$), HAsO_3^{2-} ($\text{pK}_{a3}=13.4$), and AsO_3^{3-} , whereas arsenate exists under oxic conditions and it is found to be H_3AsO_4^0 ($\text{pK}_{a1}=2.1$), H_2AsO_4^- ($\text{pK}_{a2}=6.7$), HAsO_4^{2-} ($\text{pK}_{a3}=11.2$), and AsO_4^{3-} [19].

In recent years, researchers have focused their work on developing low cost as well as green methods for removal of arsenic from groundwater. Among the existing arsenic removal technologies, adsorption and coagulation-adsorption are prominent methods having many advantages such as simple operation, low-cost, green and easy handling [15,20]. Different adsorbents such as iron oxy-hydroxide, iron oxide, manganese oxide, sand, zero-valent iron (ZVI) and aluminium (ZVAI), activated carbon, activated alumina, TiO_2 , granular ferric hydroxide, granular ferric oxide, manganese oxide pillared clays, and several coagulants such as FeCl_3 , FeSO_4 , $\text{Al}_2(\text{SO}_4)_3$ are generally used in these processes [21–32]. One such oxidation-coagulation-adsorption method, viz., oxidation-coagulation at optimized pH (OCOP), developed by our research group [33,34] has been gaining popularity in domestic, small community as well as large scale community applications as Arsiron Nilogon (Arsenic + iron removal) [35].

Abbreviations: S, supplementary; OCOP, oxidation coagulation at optimized pH; MOCOP, modified oxidation coagulation at optimized pH.

* Corresponding author.

E-mail address: robind@tezu.ernet.in (R.K. Dutta).

In the OCOP method NaHCO_3 , KMnO_4 and FeCl_3 are used as pH conditioner, oxidant and coagulant, respectively. Although KHCO_3 has been reported as more efficient pH conditioner than NaHCO_3 , the latter is preferred due to its familiarity as baking or cooking soda among common people [36]. KMnO_4 oxidises of As^{3+} to easily removable As^{5+} . In the presence of the pH conditioner, manganese is separated out as insoluble MnO_2 , which also adsorbs arsenic [34]. Some more advantages of KMnO_4 as oxidant are its familiarity with rural users, ease of handling, absence of harmful by-products, absence of residual Mn if used at near neutral or alkaline condition, removal of arsenic by adsorption on MnO_2 , and catalysis of oxidation of As(III) by MnO_2 [33,37]. Potassium permanganate also has higher oxidation yield compared to the other competing oxidants [38]. The most promising oxidant for removal of arsenic is KMnO_4 because it produces no harmful by-products and is easy to handling [39]. FeCl_3 is preferred in the OCOP method because it is more effective than other coagulants. The recommended doses of NaHCO_3 , KMnO_4 and FeCl_3 in OCOP in the absence of coexisting iron are 100 mg/L, 4 mg/L and 25 mg/L, respectively. In presence of coexisting iron, however, more KMnO_4 is added until the water gives light purple colouration to completely oxidise the dissolved Fe^{2+} to Fe^{3+} along with oxidising As^{3+} to As^{5+} [33,34].

As the ferric iron obtained from oxidation of the coexisting ferrous iron [40] also coagulates and is thus capable of adsorbing arsenic, it is possible to reduce the dose of FeCl_3 by utilizing the coexisting iron for coagulation and thereby to reduce the cost in the OCOP method when applied to groundwater having coexisting iron. We have examined this possibility through a strategy involving a series of laboratory experiments and modelling for optimising the doses of KMnO_4 and NaHCO_3 using response surface methodology (RSM) and finally through a field trial of the modified OCOP (MOCOP) method using the optimized doses [41,42]. The field trial was carried out at 32 households and 8 schools with 20 L and 200 L batch capacity, respectively, in some arsenic affected areas in Assam, India.

2. Materials and methods

2.1. Reagents

NaHCO_3 , FeCl_3 , KMnO_4 , $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ were obtained from Merck, India. Sodium arsenite (NaAsO_2) was purchased from Sigma-Aldrich. All chemicals were of analytical grade and used without further purification. Tap water was used to prepare stock solution of As^{3+} with concentration of 100 mg/L and for diluting it to 100 $\mu\text{g/L}$. The relevant water quality parameters of the tap water were Chloride – 6.0, Fluoride – 0.33, Nitrate < 1.0, Phosphate as P < 0.003, Silica – 4.35 and Sulphate – 6.2 etc, all in mg/L, with undetectable iron and arsenic. The dissolved oxygen was 81.4%. The stock solutions of 500 mg/L $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ as a source of Fe^{2+} , 500 mg/L FeCl_3 as a source of Fe^{3+} acting as coagulant, 500 mg/L KMnO_4 as oxidant and 9000 mg/L of NaHCO_3 were prepared in doubly distilled water.

2.2. Experimental

A series of coagulation-adsorption experiment was performed in 1 L beakers with tap water amended to a fixed initial As^{3+} concentration of 100 $\mu\text{g/L}$ and varying initial concentrations of ferrous iron ($[\text{Fe}^{2+}]_0$) of 5, 10, 15, 20 and 25 mg/L, which was considered as the coexisting iron. Then, KMnO_4 solution was added to get varying KMnO_4 concentrations from 5% to 100% equivalent of $[\text{Fe}^{2+}]_0$. The pH was adjusted to approximately 8.3 by adding 9% aqueous solution of NaHCO_3 in drop-wise manner. Then, aqueous FeCl_3 solution was added. As FeCl_3 lowers the pH, more NaHCO_3 is then added to adjust the final pH in the range of 7.0–7.3, a

favourable range for arsenic removal [36]. The FeCl_3 dose was taken as equal to the difference between the coagulant dose (25 mg/L) of the OCOP method and the coexisting iron concentration, i.e., as $(25 \text{ mg/L} - [\text{Fe}^{2+}]_0)$. The actual dose of Fe^{3+} ions was taken as approximately three times of that of the difference between the OCOP dose and $[\text{Fe}^{2+}]_0$ considering the possible seasonal fluctuation in $[\text{Fe}^{2+}]_0$ in groundwater. The water was stirred gently with glass rod during dosing and allowed to coagulate and settle down for one and half hour. The samples were then filtered with Whatman filter paper grade 42 and the filtrates were stored for analysis.

Water samples collected in the field were preserved in dilute HCl of final concentration of 0.15% and pH < 2 for determination of the metal ions [43]. The pH of the test samples in the laboratory was measured using a multi parameter kit (model 5Star pH.ISE.Cond.DO Benchtop, Orion, USA). The pH of the water samples was determined in the field using a pocket-sized pH metre (model HI96107, Hanna instruments, USA). Determination of concentrations of As, Fe, Mn and other heavy metals in influent and effluent water were measured by an Atomic Absorption Spectrophotometer (AAS, model Analyst 200, Thermo iCE 3000 series, USA) coupled with a hydride vapour generator (model VP100). The test water (60 mL) was first mixed with 2 mL mixture of KI (5%) and ascorbic acid (5%) and 1 mL HCl (10%) and kept for 30 min at dark place to pre-reduce As^{5+} to As^{3+} before the determination of total arsenic [44–46].

2.3. Statistical analysis

Usual optimization method requires changing one variable at a time, keeping the other at a certain level. This is not suitable practically because performing all of the possible factorial combinations of the test variables require a large number of experiments to be done. Response surface methodology (RSM) is one of the methods to determine the optimum conditions in a limited number of experiments [47–50]. In this work, the effects of major operating variables on arsenic removal from groundwater were assessed by RSM, using central composite design, (CCD). Surface areas obtain from this CCD were used to get the optimum concentrations of externally added KMnO_4 , NaHCO_3 . The experimental data are analysed using quadratic model validated by statistical analysis.

Design-Expert[®], version 9 software (DX9), software was used to develop the statistical model. Two design factors, A and B, were taken as the independent variables and their effect on the response (Y) was optimized. In the present MOCOP method, major operating parameters such as the concentration of the initial iron $[\text{Fe}^{2+}]_0$ (coexisting iron), the dose of KMnO_4 and the dose of NaHCO_3 were chosen as the independent variables. In this CCD of RSM, three types of 3D plots were prepared by selecting two independent variables out of these three independent variables with the remaining arsenic concentration as the response in each plot. Finally, another two type of plots was also prepared in which, (a) two independent variables were $[\text{Fe}^{2+}]_0$ and $[\text{NaHCO}_3]$, and the response was the dose of KMnO_4 in percentage equivalent of $[\text{Fe}^{2+}]_0$ to obtain the optimum doses of KMnO_4 for removal of arsenic to less than 1 $\mu\text{g/L}$ and (b) two independent variables were $[\text{Fe}^{2+}]_0$ and dose of KMnO_4 in percentage equivalent of $[\text{Fe}^{2+}]_0$, and the response was $[\text{NaHCO}_3]$ to optimize the doses of NaHCO_3 with respect to $[\text{Fe}^{2+}]_0$ and dose of KMnO_4 . The experimental designs involved selection of the two parameters (A and B), each at two levels coded –1 and +1 for low and high concentrations, respectively. The response was studied in the ranges of $[\text{Fe}^{2+}]_0$ concentration from 5 to 25 mg/L. The ranges of KMnO_4 and NaHCO_3 doses were based on the results of laboratory experiments on arsenic removal on varying the dose of KMnO_4 at different fixed $[\text{Fe}^{2+}]_0$.

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