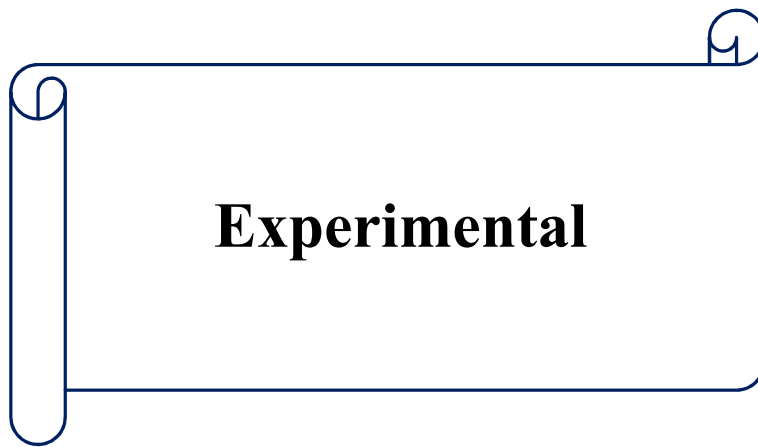


*Chapter 2*



**Experimental**



## 2. Experimental:

### 2.1. Materials:

#### 2.1.1. Chemicals:

Sodium bicarbonate ( $\text{NaHCO}_3$ ), Potassium permanganate ( $\text{KMnO}_4$ ), Ferric chloride ( $\text{FeCl}_3$ ), Ferrous sulfate ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ ), Manganous sulfate ( $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ), Sodium hypochlorite ( $\text{NaOCl}$ ), Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), Fenton's reagent, Copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), Cadmium chloride ( $\text{CdCl}_2$ ), Chromium sulfate ( $\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ ), Cobalt chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ), Nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) and Lead sulfate ( $\text{PbSO}_4$ ) were obtained from Merck, India. Sodium arsenite ( $\text{NaAsO}_2$ ) was purchased from Sigma-Aldrich. All chemicals were of analytical grade and were used without further purification.

#### 2.1.2. Stock solutions:

Stock solution of  $\text{As}^{3+}$  with concentration of 100 mg/L was prepared by spiking tap water with  $\text{NaAsO}_2$ , from which we can obtain synthetic experimental water of 100  $\mu\text{g/L}$  of initial  $\text{As}^{3+}$  concentration by diluting. The stock solutions of 500 mg/L [as  $\text{Fe}^{2+}$ ] of  $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$  as a source of coexisting iron,  $\text{Fe}^{2+}$ , 500 mg/L of  $\text{FeCl}_3$  as a source of  $\text{Fe}^{3+}$  used as coagulant, 500 mg/L  $\text{KMnO}_4$  used as oxidant and 9.0 g/L of  $\text{NaHCO}_3$  for pH adjustment were prepared in doubly distilled water. Stock solutions of 1.0 g/L of  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Pb}^{2+}$  solution were prepared by spiking tap water with  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{CdCl}_2$ ,  $\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{PbSO}_4$ , respectively. Fenton's reagent, a mixture of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$ , was prepared by adding 14.29 mg of  $\text{Fe}^{2+}$  and 33.003 mg of  $\text{H}_2\text{O}_2$  per litre as stock solution in doubly distilled water.

#### 2.1.3. Analytical tools:

Atomic Absorption Spectrophotometer (AAS, Perkin Elmer, model Analyst 200 Thermo iCE 3000 series, USA) coupled with a hydride vapour generator (model VP100) and an Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES, Perkin Elmer, model Optima 2100 DV, USA) were used for determination of concentrations of As, Fe and other heavy metal ion such as Mn, Cd, Pb, Ni, Cr, Cu, and Co in water samples of contaminated areas and in treated water. The detection limit of this AAS for

arsenic concentration is 2 µg/L and the observed arsenic concentrations below this have been considered as not detectable (ND). AAS determination of concentrations of As and other heavy metals are validated by preparing standard curve which is taken as reference with excellent regression coefficient of 0.999. Fe concentrations in treated as well as in field water samples were sometimes determined also by 1, 10-phenanthroline method using a UV-visible Spectrophotometer (Shimadzu, model UV -2500). Validation of this UV-visible spectrophotometer was done by the wavelength accuracy in the range 400 nm to 800 nm with baseline correction. The pH of water was measured using a multi parameter kit (Orion, model 5 Star pH.ISE.Cond.DO Benchtop, USA) fitted with a temperature sensor. The calibration of the pH meter was done with standard buffer solutions of pH 4.00, 7.00 and pH 10.00. Other water quality parameters such as F<sup>-</sup>, Cl<sup>-</sup> are measured by an Orion Multiparameter Kit (Orion, 4-Star pH.ISE Laboratorytop) using the respective Ion Selective Electrode (ISE) electrodes. Concentration of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> in the treated and untreated water samples was measured by a Flame Photometer (Systronic, model 128, India). Full scale sensitivity of Na, K, Ca, and Mg are 2 ppm, 1 ppm, 30 ppm and 10 ppm respectively. Favourable detection range of Flame Photometer (Systronic, model 128, India), are 10-100, 10-100, 100-300 and 50-250, respectively.

The field water samples were preserved in dilute HCl of final concentration of 0.15% and pH < 2 for determination of various metal ions [258]. pH of the water samples were maintained to less than 2 because at lower pH the metal ions do not get oxidised to form their respective hydroxides or any insoluble compounds. In the field experiments As and pH were determined using a mobile As detection kit, (Merck, Model Merckoquant 1.17927.0001, Germany. and a pocket sized pH meter (Hanna Instruments, Model HI96107, USA), respectively, to get the instant information.

The surface micrographs of coagulates or precipitates were obtained from a Scanning Electron Microscope (SEM, Jeol, model JSM-6390LV, Japan) with Energy Dispersive X-ray Spectra (EDS) at an accelerating voltage of 15.0 kV. Resolution of 3.0 nm, accuracy voltage of 0.5 to 30 KV and magnification of 5-300000 is the key feature for validation of SEM-EDS results.

#### 2.1.4. Water:

Preparation of As and all other metal ion solutions for the laboratory experiments was done by using doubly distilled water. Groundwater, collected from tap water of connected with the laboratory, used during the experiments was drawn from a shallow tube well. Some relevant chemical parameters of the groundwater are mentioned in the following **Table 2.1**. Concentration of F<sup>-</sup> and Cl<sup>-</sup> were determined using Ion Selective Electrode (ISE). Concentration of Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> were determined by flame photometer. Sulphate and phosphate were determined by standard turbidimetric method of the sample by UV-visible spectrophotometer.

**Table 2.1:** Compositions of tap water used in the laboratory experiments

Parameter	mg/L
Chloride	6.00
Fluoride	0.01
Sulphate	6.42
Sodium	11.34
Potassium	7.71
Manganese	0.002
Calcium	0.73
Arsenic	ND
Iron	0.006
Magnesium	0.87
Dissolved solid	96.0
pH	6.72
Phosphate as P	<0.003
Oxygen Saturation	82.50%

\*(Average % error = 1.08 %), \*\*ND=Not Detected

#### 2.1.5. Response surface methodology:

Response surface methodology (RSM) is a method which explores the relationships between several explanatory variables and one or more response variables [257]. The method was introduced by Box and Wilson in 1951 [259]. The main idea of RSM is to use a sequence of designed experiments to obtain an optimal response. Box and Wilson suggest using a second degree polynomial model to do this. They suggested that RSM is

one of the methods to determine the optimum conditions in a limited number of experiments [105, 257]. Statistical approaches such as RSM can be conveniently employed to maximize the production of a special substance by optimization of operational factors.

## 2.2. Experimental Methods:

The experimental methods used in this study have been presented in four sub-sections (from 2.2.1 to 2.2.4), each corresponding to one of four major works of the study:

### 2.2.1. Methods for utilization of co-existing iron for simultaneous removal of removal of As and Fe by OCOP:

#### 2.2.1.1. Batch experiment:

A series of oxidation-coagulation-adsorption experiment was performed in five 1 L beakers containing tap water amended to initial concentrations of ferrous iron ( $[\text{Fe}^{2+}]_0$ ) varied as 5, 10, 15, 20, and 25 mg/L respectively, which was considered as the coexisting iron. Each beaker is also amended with a fixed initial  $\text{As}^{3+}$  concentration of 100  $\mu\text{g/L}$  along with the coexisting, Fe. These solutions of initial arsenic ( $[\text{As}^{3+}]_0$ ) and  $[\text{Fe}^{2+}]_0$  were prepared by diluting the required volume of stock solutions to 1 L. After that 2 or 3 drops of pH conditioner of 9%  $\text{NaHCO}_3$  solution were added to each beaker to increase the pH to 8 to 9. Then,  $\text{KMnO}_4$  solution was added to get varying  $\text{KMnO}_4$  concentrations from 5% to 100% equivalent of  $[\text{Fe}^{2+}]_0$  with an interval of 5%. Then, aqueous  $\text{FeCl}_3$  solution was added to the solutions. The  $\text{FeCl}_3$  dose was taken as equal to the difference between the coagulant dose (25 mg/L) of the OCOP method and the coexisting iron concentration,  $[\text{Fe}^{2+}]_0$ , i.e., as  $(25 \text{ mg/L} - [\text{Fe}^{2+}]_0)$ . As  $\text{FeCl}_3$  lowers the pH, more  $\text{NaHCO}_3$  was then added drop-wise to adjust the final pH in the range of 7.0–7.3, a favourable range for arsenic removal [218, 248]. The water was stirred gently with a glass rod during dosing and allowed to coagulate and settle down for 2 h. The samples were then filtered using Whatman filter paper grade 42 and the filtrates were stored for analysis. 60 mL of the filtrate water of each experiment was first mixed with 2 mL mixture of (5%) KI and (5%) ascorbic acid, and 1 mL HCl (10%) and kept for 30 min at dark place to pre-reduce  $\text{As}^{5+}$  to  $\text{As}^{3+}$  before the determination of total arsenic concentration in the filtrate [218, 258].

### 2.2.1.2. Optimization of the doses:

General optimization method requires changing one variable at a time, keeping the other variables at a certain level. This is not always practically feasible because performing all the possible factorial combinations of the test variables require a large number of experiments to be done. So in this work, the effects of major operating variables ( $\text{NaHCO}_3$  and  $\text{KMnO}_4$ ) on arsenic removal from groundwater were weighed by Response Surface Methodology (RSM) using central composite design, (CCD) [257]. Design-Expert, version 9 software (DX9), software was used to develop the statistical model. CCD gave surface areas which we used to get the optimum concentrations of externally added  $\text{KMnO}_4$ ,  $\text{NaHCO}_3$ . The experimental data were analysed using quadratic model validated by statistical analysis. Here two design factors, A and B, were taken as the independent variables and their effect on the response (Y) was optimized [105, 257].

In the present modified OCOP method major operating parameters such as the coexisting  $[\text{Fe}^{2+}]_0$ , dose of  $\text{KMnO}_4$  and the dose of  $\text{NaHCO}_3$  were chosen as the independent variables. Three types of 3D plots were prepared from CCD of RSM, by selecting two independent variables out of these three independent variables with the remaining As concentration as the response. As a whole twelve, 3D plots were prepared because three type of 3D plots for each % of  $\text{KMnO}_4$  (80%, 85%, 90% and 93%) in equivalent of  $[\text{Fe}^{2+}]_0$  were selected for 3D plots from RSM analysis. Two more type of plots was also prepared as follows:

- (a) in which, independent variables were  $[\text{Fe}^{2+}]_0$  and  $[\text{NaHCO}_3]$ , and the response was the dose of  $\text{KMnO}_4$  in percentage equivalent of  $[\text{Fe}^{2+}]_0$  to obtain the optimum doses of  $\text{KMnO}_4$  for removal of arsenic to less than  $1 \mu\text{g/L}$ .
- (b) in which, independent variables were  $[\text{Fe}^{2+}]_0$  and dose of  $\text{KMnO}_4$  in percentage equivalent of  $[\text{Fe}^{2+}]_0$ , and the response was  $[\text{NaHCO}_3]$  to optimize the doses of  $\text{NaHCO}_3$  with respect to  $[\text{Fe}^{2+}]_0$  and dose of  $\text{KMnO}_4$ .

#### 2.2.1.2.1 Experimental design:

In the CCD of RSM experimental design selection of the two parameters (A and B), each at two levels coded -1 and +1 for low and high concentrations, respectively was involved. The response was studied in the ranges of  $[\text{Fe}^{2+}]_0$  concentration from 5 to 25

mg/L. The variables  $\text{KMnO}_4$  and  $\text{NaHCO}_3$  doses were based on the results of laboratory experiments on arsenic removal on varying the dose of  $\text{KMnO}_4$  at different fixed  $[\text{Fe}^{2+}]_0$ .

The number of trials (N) relates with the number of the design factors (k) and the replicate number according to the **Equation 2.1** [257, 260].

$$N = 2^k + 2k + 5 \quad (2.1)$$

Replicate number of 5 represents five levels, viz.,  $-\alpha$ ,  $-1$ ,  $0$ ,  $+1$  and  $+\alpha$ ; with which all factors were studied. The value of ' $\alpha$ ' depend on the number of variables and can be calculated by using the **Equation 2.2** [257].

$$\alpha = 2^{(k-p)/4} \quad (2.2)$$

where, ' $p$ ' denotes the number of coefficients of the mathematical model and its value for two, three and four variables are 1.41, 1.68 and 2.00, respectively. The trial number, N is 13 when ' $k$ ' is equal to 2. Therefore, the data were analysed for two variables with two levels consisting of 13 experimental runs. Based on the CCD matrix, an attempt was then made to fit the data of the major operating variables in removal of arsenic according to the following polynomial **Equation 2.3** including individual and cross effects of each variable:

$$Y = a_0 + a_1 \times A + a_2 \times B + a_3 (A \times B) + a_4 \times A^2 + a_5 \times B^2 \quad (2.3)$$

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

#### 2.2.1.2.2. ANOVA analysis:

The mathematical model (obtained from CCD of RSM) after fitting the function with the data sometime may not adequately describe the experimental data obtained. So, the quality of the model fitted can be evaluated by using analysis of variance (ANOVA). Analysis of variance (ANOVA) is a collection of statistical models and their associated estimation procedures used to analyse the differences among group. In this analysis validity of the model was determined by coefficient  $R^2$ , adjusted coefficient (adjusted  $R^2$ ), lack of fit and Fisher's F-test.

In ANOVA analysis, the terms with Prob > F values of  $<0.05$  suggests its statistical significance in the model and a term Prob>F values of  $>0.1$  are not significant. The terms



with Prob > F values of >0.1 were eliminated in order to achieve a refined surface model. The  $R^2$  statistic indicates the percentage of variability of the optimized parameters that is explained by the model [260].

### 2.2.1.3. Field experiment:

The arsenic contaminated field water samples of some selective districts of Assam were collected and preserved with 1 ml of 50 % diluted concentrated HCl (final concentration of HCl in the sample was 0.1 M) for determination of arsenic and coexisting iron concentrations in the samples. The water samples (60 mL) are also 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 concentration in the sample [258, 218].

In the field trial of OCOP method, two 20 L plastic buckets with taps fitted towards the bottom were used for making a household unit in some As contaminated villages in Assam as shown in **Figure 2.1**. The upper bucket was used for dosing and sedimentation. A tap was fitted with this bucket 2 cm above the bottom of the bucket to prevent the flow of coagulates along with treated water. A sand gravel filter was made with the other bucket with a 5 cm layer of 2–3 cm size gravel at the bottom, a nylon net cloth over it and 20 cm layer of sand at the top. Twenty six such household units were installed at Sariyahtali village of Nagaon district, six units at Namkhola of Mangaldoi district of Assam, India. For a small community unit, two 200 L plastic drums were used instead of the buckets as shown in **Figure 2.2**. They were installed at 8 schools at different places of Lakhimpur, Mangaldoi and Jorhat district in Assam, India.

The field trial was carried out with groundwater from tube well sources contaminated with both arsenic and iron at 32 rural households and 8 schools in some arsenic affected areas spread over four districts, viz., Nagaon, Mangaldoi, Lakhimpur and Jorhat in Assam, India. The initial concentrations of As and Fe in the groundwater from tube well sources were in the ranges of 284–12 mg/L and 2.9–23.0 mg/L, respectively. As and Fe removal efficiency by these units were determined by analysis the filtrate water obtained from the units for at least three times and plots for removal of As, Fe and Mn against their initial concentration were prepared. The pH of treated waters

was also determined to check whether the final pH was in the acceptable range for drinking water or not.



**Figure 2.1:** Photo of one domestic OCOP unit installed in Sariyahtali village of Nagaon district, Assam, India.



**Figure 2.2:** One small 200 L community unit installed at Tipomia Bagodia L. P. School, Titabar, Jorhat, Assam.

The field trial was carried out with groundwater from tube well sources contaminated with both As and Fe at total 32 rural households and 8 schools in some As affected areas spread over four districts, viz., Nagaon, Mangaldoi, Lakhimpur and Jorhat in Assam, India. Photographs of some 20L OCOP systems installed in different arsenic contaminated household of Sariyohtali, Nagaon, Assam are shown in **Figure 2.3**. Samples of field experiments with name of houses and schools, addresses, concentrations of initial As, and initial Fe are presented in **Table 2.2**. After the experiment the filtrate water samples were collected and preserved for analysis of remaining As and Fe concentrations and final pH of filtrate.



**Figure 2.3:** Photographs of some 20 L OCOP systems installed in different arsenic contaminated household of Sariyohtali, Nagaon, Assam.

**Table 2.2:** Sample identification water sources with concentrations of initial As ( $[As]_0$ ) and initial Fe ( $[Fe]_0$ ) of field experiments. (Average % error for triplicate experiment for  $[As]_0 = 1.05\%$  and for  $[Fe]_0 = 1.03\%$ )

SL No	Sample source identification	Address	Initial $[As]_0$ ( $\mu\text{g/L}$ )	Initial $[Fe]_0$ ( $\text{mg/L}$ )
1	H 1	Sariyohtali, Nagaon	90	7.1
2	H 2	„	38	9.0
3	H 3	„	81	9.9
4	H 4	„	69	11.7
5	H 5	„	38	12.1
6	H 6	„	37	12.2
7	H 7	„	41	12.5
8	H 8	„	56	17.3
9	H 9	„	37	22.4
10	H 10	„	65	23.0
11	H 11	„	92	12.6
12	H 12	„	37	11.7
13	H 13	„	38	8.6
14	H 14	„	28	7.9
15	H 15	„	20	12.1
16	H 16	„	25	10.3
17	H 17	„	32	6.9
18	H 18	„	37	13.2
19	H 19	„	23	4.0
20	H 20	„	26	7.5
21	H 21	„	26	9.7
22	H 22	„	30	12.2

23	H 23	„	35	6.4
24	H 24	„	44	8.9
25	H 25	„	29	8.5
26	H 26	„	27	6.9
27	H 27	Namkhola, Mangaldoi	43	10.7
28	H 28	„	67	15.0
29	H 29	„	119	10.1
30	H 30	„	169	12.0
31	H 31	„	31	5.4
32	H 32	Dhalpur, Lakhimpur	132	5.2
33	Deodhoni School	„	44	7.7
34	Kadam Jatiya Vidyalaya	Kadam, Lakhimpur	284	11.9
35	Ruptali Prathamik Vidyalaya	Dhalpur, Lakhimpur	230	15.6
36	M.R.S. Higher Secondary School	Titabar, Jorhat	109	2.9
37	P.R.S. Govt. Sr. Basic School	„	139	3.2
38	Karatipar L.P. School	„	95	3.65
39	Rebakanta Boruah Public High School	Kenduguri, Jorhat	15	5.3
40	Samuguri Satra Prathamik Vidyalaya	Majuli, Jorhat	12	5.8

A one-page handout, as shown in **Figure 2.4**, describing the arsenic removal method with procedure and a brief of As contamination of drinking water and its health effects were distributed to the users for ready reference in local language, Assamese.

### আৰ্ছিবন নিলগন NCSTC

**আৰ্ছিবন নিলগননো কি?**  
আৰ্ছিবন নিলগন হৈছে ঘৰতে খোৱাপানীৰ পৰা একেলগে আৰ্ছেনিক আৰু আইৰন গুচাব পৰা এটা অতি সহজ, সৰু আৰু কম খৰচী উপায়।

**আৰ্ছেনিকনো কি?**  
আৰ্ছেনিক দুমকল আৰু দীৰ্ঘ টিউবলৰ পানীত থকা এবিধ অতি মাৰাত্মক আদুশ প্ৰাচুৰ্যক। খোৱাপানীত থকা সামান্য পৰিমাণৰ আৰ্ছেনিকেও কেঞ্চাৰকে ধৰি বিভিন্ন ধৰণৰ ৰোগৰ সৃষ্টি কৰে। বিশ্ব স্বাস্থ্য সংস্থাই খোৱা পানীৰ আৰ্ছেনিক ১০ পিপিভিৰ তলত অৰ্থাত পানীমাৰণৰ ভৰণ এটা কোটি জীৱৰ এজগৰো কৰ্মকে ধৰা উচিত বুলি কয়।

**আৰ্ছিবন নিলগন কেনেকৈ কৰে?**  
আৰ্ছিবন নিলগনৰ বাবে তিনিটা সাধাৰণ ৰসায়নিক দ্ৰব্য অতি কমকৈ এটাৰ পিছত এটাক নিৰ্দিষ্ট নিৰ্ধাৰিত পানীত যোগ কৰা হয়। সেই দ্ৰব্যকেইটা হ'ল:

- ১) খোৱা চ'জাৰ গুৰি
- ২) মানুহে দুখ কুলাকুলি কৰা পটাছিয়াম পাৰমেঙ্গানেট ৫% হ'ল আৰু
- ৩) ফেৰিক ক্ল'ৰাইড নামৰ এবিধ আইৰনৰ দ্ৰব্যৰ ২.৫% হ'ল।

**ৰসায়নকেইটাৰ নিৰ্ধাৰ:**  
ক) আইৰন নথক ২০/২০০ লিটাৰ পানীৰ বাবে

	২০ লিঃ	২০০ লিঃ
খোৱা চ'জাৰ গুৰি	২ গ্ৰাম	২০ গ্ৰাম
৫% পটাছিয়াম পাৰমেঙ্গানেটৰ হ'ল	৬	টোপাল মিলিলিটাৰ
২.৫% ফেৰিক ক্ল'ৰাইডৰ হ'ল	২	মিলিলিটাৰ মিলিলিটাৰ

আৰ্ছিবন নিলগনত ব্যৱহৃত ৰসায়নৰ এটা সঁজুলি

খ) পানীত যদি আইৰনো থাকে তেনেহলে পটাছিয়াম পাৰমেঙ্গানেটৰ পৰিমাণ বঢ়াই দিব। কিন্তু চাব যাতে এনে কৰোতে পানীত বেঙুনীয়া ৰং থাকি নাযায়। অথবা, আইৰন থকা পানীমাৰণি প্ৰথমতে শিল-বাৰিৰ ফিল্টাৰেৰে আইৰন গুচাই সো জৰ পিছত ওপৰৰ আঁসিকা মতে আৰ্ছেনিক গুচাব পাৰে।

গ) অধিক পানীৰ বাবে ৰসায়নকেইটাৰ পৰিমাণ সামান্যপাৰিক ভাৱে বঢ়াই দিব।

**ৰসায়নিক দ্ৰব্যকেইটা কেনেকৈ পাব?**  
খোৱা চ'জাৰ গুৰি পেপা মাৰাৰ দোকানত ফোলাকৈ আৰু ১ কিলোগ্ৰামৰ পেকেট বা ২৫ কিলোগ্ৰামৰ বস্ত্ৰত পায়। পটাছিয়াম পাৰমেঙ্গানেট আৰু ফেৰিক ক্ল'ৰাইড ৰসায়নিক দ্ৰব্যৰ দোকানত আথবা, এক আৰু আতকৈও জড়ৰ বটলত পায়।

আৰ্ছিবন নিলগনৰ দ্ৰব্যসমূহ আপোনাৰ ওচৰৰ দোকানতে সুবিধাজনক ভাৱে পাব পাৰে। খৰচ কৰক।

৫% (ভৰ/আৱতন) পটাছিয়াম পাৰমেঙ্গানেটৰ হ'ল পাবলৈ ৫০ গ্ৰাম পটাছিয়াম পাৰমেঙ্গানেটৰ গুৰি ১ পৰিমাণ পানীত গুলি এক লিটাৰ কৰি লওক। ২.৫% (ভৰ/আৱতন) ফেৰিক ক্ল'ৰাইডৰ হ'ল পাবলৈ ২৫০ গ্ৰাম ফেৰিক ক্ল'ৰাইডৰ গুৰি পানীত পানীত (distilled water) গুলি এক লিটাৰ লওক।

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### আৰ্ছিবন নিলগন NCSTC




ঘৰত ব্যৱহাৰ কৰা এটা আৰ্ছিবন নিলগনৰ যন্ত্ৰ

ভুলত ব্যৱহাৰ কৰা এটা আৰ্ছিবন নিলগনৰ ব্যৱস্থা

**সেউখিনি কি কৰিব ?**  
সেউখিনি এটা সৰু সাধাৰণ শিল-বাৰিৰ ফিল্টাৰত চালি দিয়ক। জুতেই সেউখিনি ৰৈ যাব। এনেকৈ সময় সেউখিনি জমা কৰি থাকিব। জৰ্তি হ'লে সেউখিনি নিৰাপদ স্ট্ৰাইট, যেনে, ঘৰৰ ভেটিৰ তলত বা নগৰৰ আৱৰ্তন শ্বেলোৱা ঠাই আদিত পেলাব পাৰে। এই ফিল্টাৰটোৰ পৰা ওলোৱা পানীমাৰণিত আৰ্ছেনিক নাথাকে আৰু সেউখিনি বাসিচত দিব পাৰে।  
এটা মাটিৰ টেকেলিত গেড ৰখাৰ ব্যৱস্থা কাষৰ চিত্ৰত দেখা গৈছে।

আৰ্ছিবন নিলগন পদ্ধতিটো তেজপুৰ বিশ্ববিদ্যালয়ৰ ৰসায়ন বিজ্ঞান বিভাগৰ অধ্যাপক ড॰ বৰিন কুমাৰ দত্তৰ নেতৃত্বত এটি গৱেষকৰ দলে উদ্ভাৱন কৰা। পদ্ধতিটোৰ বিষয়ে বিশদ বৈজ্ঞানিক ব্যাখ্যাৰ বাবে তলত উল্লিখিত গৱেষনা পত্ৰখিনি চাব পাৰে-  
S. Bordoloi, S.K. Nath, S. Gogoi, R.K. Dutta\*, J. Hazard. Mater., 260 (2014) 618-626.

আৰ্ছিবন নিলগনৰ বিষয়ে যিকোনো ক্ৰুখা জ্ঞানিবৰ বাবে বা এই পদ্ধতিৰে পানীৰ পৰা ক্ল'ৰাইড নিলগন কৰোতে কিবা অসুবিধা পালে তলৰ ঠিকনাত যোগাযোগ কৰক:

শ্ৰী অনুপ জ্যোতি বৰা - ৯৩৯৯৯ ২০১৯৪, শ্ৰী বাজকমল মহন - ৮৮৭৬১ ৬৬৫৭১, ড॰ বৰিন কুমাৰ দত্ত - ৯৪৩৫০ ০৬৬৭৪; ৰসায়ন বিজ্ঞান বিভাগ, তেজপুৰ বিশ্ববিদ্যালয়, নপাম, তেজপুৰ - ৭৮৪০২৮

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Figure 2.4: One-page handout of OCOP method in local language, Assamese, distributed to the users.

### 2.2.2. Simultaneous removal of As, Fe and Mn by OCOP:

#### 2.2.2.1. Pilot scale experiment:

A series of OCOP experiments for RSM optimization of the doses of  $\text{NaHCO}_3$ ,  $\text{FeCl}_3$  and  $\text{KMnO}_4$  was performed in 1 L mugs containing synthetically prepared contaminated water with a fixed initial arsenite ion concentration ( $[\text{As}^{3+}]_0$ ) of  $100 \mu\text{g/L}$ , varying initial ferrous ion concentrations ( $[\text{Fe}^{2+}]_0$ ) from  $1 \text{ mg/L}$  to  $8 \text{ mg/L}$  and varying initial manganous ion concentrations ( $[\text{Mn}^{2+}]_0$ ) from  $0.5 \text{ mg/L}$  to  $5.0 \text{ mg/L}$  with an interval of  $0.5 \text{ mg/L}$ . Accordingly, a total of 288 experiments were done. Aqueous 9%  $\text{NaHCO}_3$  solution was added dropwise to each solution to increase the pH of the water to  $\approx 8.5$ . After that, aqueous  $\text{KMnO}_4$  solution was added in percentage equivalent of  $[\text{Fe}^{2+}]_0$  from 30% to 100%. Then dose of  $\text{FeCl}_3$  as  $[\text{Fe}^{3+}]$  was added as equal to  $(8.6 \text{ mg/L} - [\text{Fe}^{2+}]_0)$ . This empirical equation used for deciding the doses of  $\text{FeCl}_3$  for the design experiment in  $\text{mg/L}$  because the dose of  $8.6 \text{ mg/L}$  was the optimised dose of  $\text{Fe}^{3+}$  for arsenic removal in the original OCOP method [218]. There is no need of addition of  $\text{FeCl}_3$  when  $[\text{Fe}^{2+}]_0$  is above  $8.6 \text{ mg/L}$  because this  $[\text{Fe}^{2+}]_0$  is expected to provide  $\text{Fe}^{3+}$  ions equal to the dose

of  $\text{FeCl}_3$  in OCOP after oxidation of the  $\text{Fe}^{2+}$  ions. Accordingly, with  $[\text{Fe}^{2+}]_0 = 1, 2, 3, 4, 5, 6, 7$  and  $8$  mg/L, the externally added  $\text{FeCl}_3$  as  $[\text{Fe}^{3+}]$  will be  $7.6, 6.6, 5.6, 4.6, 3.6, 2.6, 1.6$  and  $0.6$  mg/L, respectively. Then, aqueous  $\text{NaHCO}_3$  was added again to adjust the final pH at  $\approx 7.3$ . The amount of total added  $\text{NaHCO}_3$  in mg/L was noted. The water was stirred gently with a glass rod during addition of  $\text{NaHCO}_3$ ,  $\text{KMnO}_4$  and  $\text{FeCl}_3$ . Then, the water was allowed to coagulate and settle down for two hour. The water samples were then filtered through Whatman 42 filter paper and used for further analysis by AAS.

#### 2.2.2.2. Optimization of the doses:

RSM, using central composite design (CCD) was applied in this work also to optimize the doses of  $\text{NaHCO}_3$ ,  $\text{KMnO}_4$  and  $\text{FeCl}_3$  for simultaneous removal of As, Fe and Mn from groundwater sources. Here, 'A' and 'B' are the two design factors, taken as the independent variables and their effect on the response (Y) was optimized. Variables  $[\text{Fe}^{2+}]_0$  and  $[\text{Mn}^{2+}]_0$  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 were  $[\text{Fe}^{2+}]_0$  and  $[\text{Mn}^{2+}]_0$ , respectively, and 'Y' for plot (a), (b), and (c) was  $[\text{Mn}^{7+}]$ ,  $[\text{NaHCO}_3]$ , and  $[\text{Fe}^{3+}]$ , respectively, to obtain the optimum doses of  $\text{KMnO}_4$ ,  $\text{NaHCO}_3$  and  $\text{FeCl}_3$ , respectively, for removal of arsenic in presence of Mn and Fe ions to less than  $1 \mu\text{g/L}$ . The data were examined for two variables with 13 experimental runs similarly as stated in section 2.2.1.2.1. Based on the CCD of RSM, the data were made to fit with 3D plot of surface area for the major operating variables in removal of arsenic in presence of Mn and Fe according to the similar polynomial **Equation 2.3**. The quality of the model fitted with the 3D surface areas is also evaluated using analysis of variance, ANOVA as described earlier (2.2.1.2.1).

#### 2.2.2.3. Field trial:

A field trial of the present OCOP method with this RSM optimized doses was done in eleven household hand tube well spot sources at Sariyohtali village, in Nagaon district of Assam, India, where, water contains arsenic with coexisting iron as well as manganese. Each unit consisting of two 20 L plastic buckets fitted with a plastic tap as described earlier in section 2.2.1.3. The RSM optimised doses of  $\text{NaHCO}_3$ ,  $\text{KMnO}_4$  and  $\text{FeCl}_3$  were added one after another as solid powder, 5% solution and 25% solution, respectively, to 20 L water taken in the top bucket with mild stirring after each addition. The coagulates



settle down at the bottom of the 1st bucket and after two hours the clear water was transferred through the tap to the sand-gravel filter in the 2nd bucket for filtering. The filtered water was used for analysis of water quality parameters including As, Fe and Mn.

### **2.2.3. Evaluation of performance of different oxidizing agents in OCOP:**

#### *2.2.3.1. Comparison of oxidants:*

OCOP experiments were performed in 1 L plastic mugs using tap water separately with varying quantities of oxidants, viz.,  $\text{KMnO}_4$ , Fenton's reagent,  $\text{NaOCl}$  and  $\text{H}_2\text{O}_2$  with fixed 200  $\mu\text{g/L}$  of initial  $\text{As}^{3+}$  and 100  $\text{mg/L}$  of initial  $\text{NaHCO}_3$  concentration. These concentrations are made by addition of required volume from stock solution of 100  $\text{mg/L}$  of  $\text{As}^{3+}$  and 9% of  $\text{NaHCO}_3$ , respectively. The dose of  $\text{KMnO}_4$  was varied from 0.2  $\text{mg/L}$  to 2  $\text{mg/L}$  at an interval of 0.2  $\text{mg/L}$ . The doses of the other oxidants were also taken in equivalent of the dose of  $\text{KMnO}_4$ . The different ranges of dose of  $\text{NaOCl}$ , Fenton's reagent and  $\text{H}_2\text{O}_2$  used as equivalent concentration of the dose of  $\text{KMnO}_4$  were 0.14  $\text{mg/L}$  to 1.41  $\text{mg/L}$ , 1.19  $\text{mg/L}$  to 11.9  $\text{mg/L}$ , and 0.14  $\text{mg/L}$  to 1.41  $\text{mg/L}$ , respectively. At last, 25  $\text{mg/L}$  of  $\text{FeCl}_3$  was added to the mugs. After dosing, the water was stirred gently at an rpm of 30-40 for about 10 s and coagulate was allowed to settle for two hour. The supernatant treated water was then filtered with Whatman 42 filter paper for analysis.

The effect of pH on removal of As by the oxidant was examined by varying the dose of  $\text{NaHCO}_3$  keeping the oxidant and coagulant doses fixed in the OCOP experiments. An OCOP experiment with  $[\text{As}^{3+}]_0$  of 200  $\mu\text{g/L}$  was carried out at fixed doses of  $\text{NaHCO}_3$ , the oxidant and  $\text{FeCl}_3$  at varying temperatures from 10°C to 45°C with an interval of 5°C. OCOP experiments were also performed with varying  $[\text{As}^{3+}]_0$  from 100  $\mu\text{g/L}$  to 500  $\mu\text{g/L}$  in an interval of 50  $\mu\text{g/L}$  with fixed doses of  $\text{NaHCO}_3$ , the oxidant and  $\text{FeCl}_3$ .

#### *2.2.3.2. Adsorption isotherm:*

The study on adsorption of As on the coagulates/precipitates were conducted with varying  $[\text{As}^{3+}]_0$  between 100 and 500  $\mu\text{g/L}$  and fixed doses of 2  $\text{mg/L}$   $\text{KMnO}_4$  and 25  $\text{mg/L}$   $\text{FeCl}_3$ . Here, the fixed initial dose of the adsorbent was taken as the sum of the

quantities in mg/L of MnO<sub>2</sub> and FeOOH produced at the chosen doses of KMnO<sub>4</sub> and FeCl<sub>3</sub> assuming the adsorbent to consist of solid MnO<sub>2</sub> and FeOOH [218]. The total quantity of the so-formed adsorbent has been calculated as 14.8 mg/L with a ratio of MnO<sub>2</sub>: FeOOH as 1.2:13.7. The equilibration time was 2 h [218].

Adsorption data were fitted to Freundlich, Langmuir and Temkin adsorption isotherms [230,231]. The Linear form of Freundlich isotherm can be represented by **Equation 2.4**:

$$\ln(Q_e) = \ln(K_F) + 1/n \ln(C_e) \quad (2.4)$$

where,  $Q_e$ ,  $C_e$ ,  $K_F$  and  $n$  are the amount of arsenic adsorbed at equilibrium (mg/g), the arsenite concentration at equilibrium (mg/L), the Freundlich adsorption capacity (mg/g) and adsorption intensity, respectively. The values of  $K_F$  and  $n$  were determined from the intercept and slope of the linear plot of  $\ln(Q_e)$  vs.  $\ln(C_e)$ .

The Langmuir isotherm can be written as **Equation 2.5**:

$$C_e/q_e = C_e/Q_0 + 1/bQ_0 \quad (2.5)$$

where,  $Q_0$  and  $b$  are the adsorption capacity (mg/g) based on Langmuir isotherm and the Langmuir isotherm constant (L/mg) related to the affinity of the binding sites, respectively. The  $Q_0$  and  $b$  values were calculated from slope and intercept of the plot of  $C_e/Q_e$  vs.  $C_e$ .

The Temkin isotherm equation can be written as **Equation 2.6**.

$$Q_e = B_T \ln(A_T) + B_T \ln(C_e) \quad (2.6)$$

where,  $A_T$  (L/g) is the binding constant that represents the maximum binding energy and  $B_T = (RT)/b$  is the Temkin constant related to heat of sorption. These constants have been evaluated from the plots of  $Q_e$  vs.  $\ln(C_e)$ . From these adsorptions isotherm study we evaluated the types of adsorption taking place during OCOP on adsorbent MnO<sub>2</sub> and FeOOH and adsorption capacity of the adsorbent.

### **2.2.4. Removal of some metals: Cd, Pb, Ni, Cr, Cu and Co by OCOP:**

#### *2.2.4.1. Batch experiment:*

In this study a series of OCOP experiments with fixed doses 100 mg, 0.5 mg and 25 mg of aqueous 9% NaHCO<sub>3</sub>, 5% KMnO<sub>4</sub> and 25% FeCl<sub>3</sub>, respectively, were carried out in 1.5 L mugs. A set of experiments with variation of initial concentration of the heavy metals is verified to see the capacity of removal of heavy metals by OCOP. The initial concentrations of the heavy metals were examined in the range from 2 mg/L to 10 mg/L with an interval of 2 mg/L for a fixed treatment time of 2 h. To each mug, 100 mg, 0.5mg and 25 mg of aqueous 9% NaHCO<sub>3</sub>, 5% KMnO<sub>4</sub> and 25% FeCl<sub>3</sub>, respectively, were added with mild stirring. After that, coagulates were allowed to settle down for 2 h. The clear water at top was filtered through Whatman 42 filter paper. Another set of OCOP experiment with mug containing 1.5 L synthetic water with a fixed 5 mg/L initial concentrations of each of Cu<sup>2+</sup>, Cr<sup>6+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Co<sup>2+</sup>, respectively, in separate mugs with same dosing as stated above were performed by varying residence time from 1 h to 4 h with an interval of 1 h. All the filtrates obtained after the experiments were analysed by AAS to determine remaining concentrations of the heavy metals.

#### *2.2.4.2. Analysis of the coagulates or precipitates:*

For confirmation of the results obtained from AAS analysis of the filtrates obtained by OCOP experiment for heavy metal removal the coagulates/precipitates formed during experiment were also analysed by AAS, EDX and XRD to see the presence of heavy metal concentrations in the coagulates for each experiment separately. The collected coagulates/precipitates were dried in oven a 70°C for 2 h and stored for further study.

##### *2.2.4.2.1. Analysis of coagulates by AAS:*

For AAS analysis of the heavy metals present in the coagulates of OCOP, the solid obtained from the OCOP experiment was dissolved in aqua Regia (mixture of nitric acid and hydrochloric acid, optimally in a molar ratio of 1:3). The volume of each solution was adjusted to 1L with dilution by distilled water. Sums of remaining concentration of heavy metals found in the filtrate of OCOP experiment and the concentration observed in the extract were checked to see the actual removal of the heavy metals within

experimental error limits. This also indicates whether there is any loss of the metal ions during preparation of the extracts.

#### *2.2.4.2.2. Analysis of coagulates by EDX:*

The energy disperse X-ray spectroscopy, EDX of the solid coagulates obtained from the OCOP experiment performed separately for individual metal ions with initial concentration of the metal ions as 5 mg/L and residence time of 2h was done to see the presence of the respective heavy metal. From EDX analysis we can also determine the percentage composition of heavy metals with respect to other elements present in the coagulates/precipitates.

#### *2.2.4.2.3. Analysis of coagulates by XRD:*

Powder X-ray diffraction pattern was used to characterise the solid coagulates/precipitates. The solid coagulates obtained from OCOP experiments in the absence of the heavy metals and in presence of six heavy metals *viz* Cd, Pb, Ni, Cr, Cu, and Co, separately, were analysed by powder XRD pattern to see the presence of heavy metals and what types of complexes were formed.

