Chapter 4

Conclusions and Future scopes

4. Conclusions and Future scope:

Chapter 4 embraces and articulates the conclusions of this research work and future scopes opened up by the work. This chapter is subdivided in to two sections *viz.* conclusions and future scopes.

4.1. Conclusions:

In the present systematic experimental research work, an attempt has been made to modify the OCOP method with an intention to reduce cost and to examine removal of arsenic, iron, manganese and other heavy metals simultaneously from groundwater sources. We have utilized the coexisting iron to minimize externally added $FeCl_3$ as used in the OCOP method to remove arsenic and iron from groundwater sources. We also have optimized the doses of $KMnO_4$ and $NaHCO_3$ by RSM analysis with CCD design, to remove arsenic and iron below ND and 0.03 mg/L, respectively. After reducing the cost and optimizing the doses of $NaHCO_3$ and $KMnO_4$ in modified OCOP method we also used this modified method to simultaneous removal manganese, arsenic, and iron, from groundwater sources. To study removal of manganese along with arsenic and iron we have optimized the doses of $NaHCO_3$, $KMnO_4$ and $FeCl_3$ for better removal efficiency with lower cost than the earlier modified OCOP. We also have compared four commonly used oxidants, namely, $KMnO_4$, $NaOCl$, Fenton's reagent and H_2O_2 in the OCOP method with an equivalent dose to check the removal efficiencies of arsenic by various oxidants separately and to enable to select the better oxidant for the purpose. Finally, we examined OCOP method to remove commonly found hazardous heavy metals other than As, Fe and Mn, viz., Cd, Pb, Ni, Cr, Cu and Co from the contaminated drinking water to see the effectiveness of the OCOP method in removal of heavy metals.

In a nutshell, the present study shows that the cost of the OCOP method can be reduced by utilizing the coexisting iron, the method is capable of removing manganese and other heavy metals also along with arsenic and iron, and potassium permanganate is the best choice of oxidant for removal of arsenic by OCOP method. The detail conclusion of the present work has been presented in four sections corresponding to the four different parts/sections of the present study as follows:

4.1.1. Utilization of co-existing iron for simultaneous removal of removal of As and Fe by OCOP:

- Arsenic and iron removal from groundwater sources by utilization coexisting iron in OCOP method in lieu of/adding minimum amount of externally added $FeCl_3$ dose as coagulant was found better than the existing OCOP method with lower cost.

- Cost of the OCOP method was tried to lower by using coexisting iron concentration in groundwater along with arsenic as coagulant by using the dose of $FeCl_3$ as equal to difference between dose used in OCOP and the co-existing iron concentration, i.e. (25 mg/L – $[Fe^{2+}]_o$).

- Here the dose of oxidant $KMnO_4$ was used as percentage equivalent of coexisting iron concentration, $[Fe^{2+}]_o$ in the range 5% to 100% in equivalent of $[Fe^{2+}]_0$ and $KMnO_4$ dose as 70%-95% equivalent of $[Fe^{2+}]_o$ was found necessary to remove arsenic below 2 µg/L (ND) from initial arsenic concentration of about 100 µg/L for various coexisting iron concentration.

- With increase dose of $KMnO_4$ in percentage equivalent of coexisting iron concentration, $[Fe^{2+}]_o$ and with increase in coexisting iron concentration, $[Fe^{2+}]_o$ removal of arsenic along with iron was found to increase.

- From the batch experiment we predicted the required doses of $KMnO_4$, in percentage equivalent of $[Fe^{2+}]_o$, for practical applications as: 95%, 93%, 90%, 85%, and 80% for $[Fe^{2+}]_o$ in the ranges of 0–5, >5–10, >10–15, >15–20, and >20–25 mg/L, respectively to remove arsenic and iron below ND and 0.03 mg/L, respectively.

- In this modified OCOP method the doses of $NaHCO_3$ and $KMnO_4$ were optimized by using CCD design of RSM analysis for removal of arsenic and iron below ND and 0.03 mg/L, respectively, at pH of about 7.3(±0.1).

- RSM analysis showed that if $[Fe^{2+}]_o$ present in water are 0.857, 5, 10, 15, 20, 25, and 29.14 mg/L then the required doses of $KMnO_4$ as percentage of equivalent of $[Fe^{2+}]_o$ will be 95.34%, 95%, 92.84%, 90%, 85%, 80.21%, and 78.73% respectively.

- We had added 95%, 93%, 90%, 85%, 80% for $[Fe^{2+}]_o$ as 0–5, 5–10, 10–15, 15–20 and 20–25 mg/L, respectively, for removal of arsenic from initial 100 µg/L to ND in laboratory batch experiment.

- RSM analysis also showed that if $[Fe^{2+}]_o$ present in water are 5, 10.27, 15, 20.09, 25 mg/L then the required doses of $NaHCO_3$ are 39.43, 48.03, 56, 62.20, 71.43, respectively for removal of arsenic and iron below ND and 0.03 mg/L.

- For practical purpose we rounded off the dose of $NaHCO_3$ to 40, 48, 56, 61, and 72 mg/L for initial iron concentrations of 5, 10, 15, 20, and 25 mg/L, respectively.

- From this experiment we found that there is a close correlation between the predicted and the experimental doses of $KMnO_4$ and $NaHCO_3$ with respect to $[Fe^{2+}]_o$. Accordingly we can use the RSM optimized doses of $KMnO_4$ and $NaHCO_3$ in field application to remove arsenic below ND on the basis of $[Fe^{2+}]_o$ and thereby lowering the cost of the OCOP method utilizing coexisting iron.

- In the field trial experiment of this modified OCOP method in 32 households and 8 schools of Nagaon, Mangaldoi, Lakhimpur and Jorhat in Assam, India with optimized doses by RSM furnished satisfactory arsenic removal from initial concentration of arsenic of about 284–25 µg/L and iron removal from initial concentration of about 2–23 mg/L, to below ND and 0.01 mg/L, respectively.

- In this modified OCOP method, the externally added $FeCl_3$ is not required for water with >25 mg/L coexisting iron concentration, $[Fe^{2+}]_0$. The saving for 25 g/m^{-3} $FeCl_3$ is ≈USD 0.025 per m^3 giving a total chemical cost of MOCOP as ≈USD 0.10 per m^3. Thus, with competing chemical cost with other coagulation methods, the modified OCOP method removes arsenic more efficiently to < 2µg/L (ND) along with coexisting iron. This method also saves almost 20% of the cost of OCOP for water with 25 mg/L coexisting iron through saving in terms of the $FeCl_3$ dose.

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

- A series of OCOP experiments were performed for removal of manganese, arsenic and iron from 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 with an interval concentration of 0.5 mg/L.

- Aqueous $KMnO_4$ solution was added in percentage equivalent of initial iron concentration, $[Fe^{2+}]_0$ from 30% to 100% in alkaline medium maintained by

$NaHCO_3$. Then dose of $FeCl_3$ as $[Fe^{3+}]$ was taken as equal to $(8.6 - [Fe^{2+}]_0)$ in mg/L. Final pH at $\approx 7.3(\pm 0.1)$ of the treated water was adjusted by $NaHCO_3$.

- We found an increase in the removal of arsenic with increase in $[Fe^{2+}]_0$ and $[Mn^{2+}]_0$ as well as with increase in the dose of $KMnO_4$.

- The increase in the removal of arsenic with increase in $KMnO_4$ dose is due to oxidation of As^{3+} to easily removable As^{5+}.

- The observed increase in the removal of arsenic with increasing $[Fe^{2+}]_0$ at fixed $[Mn^{2+}]_0$ indicates increased formation of iron coagulates by oxidation of Fe^{2+} in to Fe^{3+} after addition of $KMnO_4$.

- Removal of arsenic with increasing $[Mn^{2+}]_0$ at fixed $[Fe^{2+}]_0$ is ascribed to increased adsorption of arsenic on solid MnO_2 precipitates formed due to oxidation of Mn^{2+} ions by $KMnO_4$.

- It was observed that remaining total $[As]$, $[Mn^{2+}]$ and $[Fe^{2+}]$ after the treatment were below ND, 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.

- The dose of $FeCl_3$ was taken as equal to $(8.6 - [Fe^{2+}]_0)$ in mg/L. This 8.6 mg/L was the dose of $FeCl_3$ as Fe^{3+} in mg/L in OCOP and there is no need further addition of $FeCl_3$ when coexisting $[Fe^{2+}]_0$ is above 8.6 mg/L because this $[Fe^{2+}]_0$ is expected to provide Fe^{3+} ions equal to the dose of $FeCl_3$ in OCOP.

- The doses of $NaHCO_3$ in mg/L, $KMnO_4$ in % equivalent of $[Fe^{2+}]_o$ and $FeCl_3$ in mg/L to remove As, Mn, and Fe simultaneously from groundwater below ND, 0.009 mg/L, and 0.01 mg/L respectively were optimized by RSM analysis for application of modified OCOP method in laboratory as well as in field trial experiment.

- It was observed that the dose of $FeCl_3$ decreases with increase in $[Fe^{2+}]_o$ up to 8.607 mg/L as Fe beyond which, there is no need of externally added $FeCl_3$. However, required dose of $KMnO_4$ increases slightly with increase in $[Fe^{2+}]_o$ in the whole range as expected. With increase in $[Fe^{2+}]_o$ required dose of $NaHCO_3$ also decreases slightly because with increase in $[Fe^{2+}]_o$ required addition of $FeCl_3$, decreases requiring more $NaHCO_3$ to raise the pH to $7.3(\pm 0.1)$.

- Field trial of this method shows removal of Mn, As and Fe ions from initial concentrations in the range of 23–2 mg/L to less than 0.03 mg/L, 91 - 25 µg/L to ND, and 0.5-1.9 mg/L to less than 0.009 mg/L, respectively.

- An estimation of the cost of the present method has been found to be 0.326 USD per m^3 for simultaneous removal of As, Fe and Mn, slightly lower than the cost of removing As and Fe by earlier modified OCOP method, attributed to the contribution of MnO_2 in As removal in the present method.

4.1.3. Evaluation of performance of different oxidizing agents in OCOP:

- In this work a set of OCOP experiments were performed with varying quantities of oxidants, viz., $KMnO_4$, Fenton's reagent, NaOCl and H_2O_2 with fixed doses of 200 μg/L initial As^{3+} and 100 mg/L initial $NaHCO_3$ and 25 mg/L of $FeCl_3$. The dose of $KMnO_4$ was varied from 0.2 mg/L to 2 mg/L at an interval of 0.2. Dose oxidants other than $KMnO_4$ were added as same in equivalent of $KMnO_4$ dose to see the performance and compare the oxidants in removal of As by OCOP method.

- Removal of arsenic with Fenton's reagent and $KMnO_4$ were much better than that with NaOCl and H_2O_2. However, $KMnO_4$ has been found to be the best oxidizing agent, for removing As^{3+} by OCOP among all four oxidizing agents used, which closely followed by Fenton's reagent.

- For the dose 0.2 mg/L of $KMnO_4$, which is equal to an equivalent concentration of 0.632×10^{-6}, the As removal efficiency has been found to be 97.12%. It may be noted that the doses of $FeCl_3$ and $NaHCO_3$ were fixed at 25 mg/L and 100 mg/L, respectively. The doses of Fenton's reagent, NaOCl and H_2O_2 equivalent (0.632×10^{-6}) to that of 0.2 mg/L of $KMnO_4$ are 1.19 mg/L, 0.14 mg/L and 0.14 mg/L, respectively. With the equivalent dose of 0.632×10^{-6}, the As removal efficiency of Fenton's reagent, NaOCl and H_2O_2 have been found to be 95.6%, 86.7%, and 86.4%, respectively.

- The As removal efficiency was found to increase remarkably on increasing the oxidant dose. On increasing the dose, removal of As reaches 100% at a dose of 2 mg/L (Equivalent concentration of 6.327×10^{-6}) of $KMnO_4$. The equivalent dose of 6.327×10^{-6} of Fenton's reagent (11.9 mg/L), NaOCl (1.41 mg/L) and H_2O_2 (1.41 mg/L) could remove As to 98.8%, 89.0% and 88.0%, respectively.

- Among the chosen oxidants, the performance of $KMnO_4$ in removal of As has been found to be the best followed by Fenton's reagent.

- Highest removal efficiency was found in case of $KMnO_4$ because during oxidation As^{3+} to As^{5+}, $KMnO_4$ itself reduces to MnO_2 which also helps in removal of arsenic by adsorbing on its surface.

- The observed rapid and linear increase in the removal of arsenic in the acidic conditions up to about pH 4.5 may be attributed to first dissociation (pKa1 = 4.503) of H_3AsO_4 and in the pH range from about 6.5 to 7.5 may be attributed to the second dissociation (pKa2 = 7.09) of H_3AsO_4 through reaction.

- Arsenic removal by OCOP with $KMnO_4$ as oxidant method linearly increases with temperature and is highly effective between 10^oC to 45^oC indicating applicability of the method within this temperature range.

- For all $[As^{3+}]_o$ in the range, the remaining arsenic concentration was found below the WHO guideline value for drinking water, *i.e.,* 10 µg/L. The concentration of remaining arsenic was found to be a polynomial function of fourth order of initial arsenic concentration.

- Interestingly, Freundlich, Langmuir and Temkin plots showed almost equal R^2 values, indicating similar moderate fitting of the adsorption data to all three models of adsorption which is an unusual observation. We attribute this observation to the fact that the arsenic adsorption by adsorbent mixture of MnO_2 and FeOOH, formed in the present case, starts right from the nucleation of the solid entities of MnO_2 and FeOOH, which continues during the growth of the precipitate of MnO_2 and coagulates of FeOOH or a mixture of them until completion of the process.

- Here arsenic was chemisorbed on heterogeneous surface and inside the precipitates MnO_2 and FeOOH formed by $KMnO_4$ and $FeCl_3$. However, the observed high values of Temkin constants A_T and B_T suggests adsorption to be the mechanism of binding of arsenic rather than ion-exchange.

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

- A set of OCOP experiments with variation of initial concentration of the heavy metals from 2 mg/L to 10 mg/L with a fixed treatment time of 2h was verified to see the capacity of removal of heavy metals and another set of OCOP experiment with synthetic contaminated water with a fixed 5 mg/L initial concentrations of each of Cu^{2+}, Cr^{6+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, and Co^{2+}, respectively, was performed

varying residence time from 1 to 4 h to see the effect of residence time on removal efficiency.

- The percentage of removal of all heavy metals increased with decrease in the initial concentration of the heavy metals. The removal of the metals from equal initial concentration of 2 mg/L was found to increase in the order Cd (79.0%) << Co (94.8%) < Ni (94.4%) << Cu (98.0%) < Cr (98.3%) < Pb (99.5%).

- The observed low removal of Cd may be attributed to weaker binding/adsorption to oxygen of $FeOOH$ or MnO_2 formed during OCOP treatment due to its soft acidic nature and Cr, being a hard acid, was removed very well due to its strong binding $FeOOH$ and MnO_2.

- Removal of heavy metals from initial concentration of 5 mg/L was found to increase with increase in residence time. The removal levelled off above 3 h for Cd and Co which is the optimum residence time for most adsorption methods but continued to decrease up to 4 h in the case of Pb, Cr, Ni and Cu. This experiment indicates that more residence time is required for maximum removal of these heavy metal ions than that of 2 h, normally required for OCOP method to remove As and Fe.

- The concentrations of the heavy metals in the aqua-regia extracts of the solid obtained in OCOP process had showed good correlation with the initial concentrations of the heavy metals. It is interesting to note that the sums of remaining concentration in the filtrates and the concentration observed in the extract of coagulates were same with that of the initial concentrations each heavy metal ions within experimental error limits.

- The EDX estimation of the heavy metals in the solid obtained from the OCOP experiment with performed separately for individual metal ions with initial concentration of the metal ions as 5 mg/L and residence time of 2 h. The spectra obtained for each metal ion showed the presence of the respective elements.

- Powder XRD analysis of the coagulates reveals that the presence of Cd leads to formation of highly crystalline compounds of CdO_2, $Cd_{0.1}Mn_{0.9}O$ and $Cd_2Mn_3O_8$ in addition to facilitating formation of crystalline $FeOOH$, MnO_2 and Mn_3O_4. Similarly, the presence of Pb in the solid coagulates clues to formation of $Pb(Fe,Mn)_{12}O_{19}$ in addition to facilitating formation of crystalline Fe_2O_3 and $FeOOH$. Presence of Ni, Cr and Cu in the water leads to formation of some

crystalline compounds of $NiFe_2O_4$ and NiO, Cr_3O_8, and $Cu(FeO_2)$, respectively. Co being very similar to iron gave amorphous solids like that containing iron alone produced in absence of any heavy metal.

- Formation of CdO_2 may be possible due to the oxidation of Cd^{2+} to Cd^{4+} by addition $KMnO_4$ because $KMnO_4$ which is well known strong oxidizing agent. Formations of the complexes $Cd_{0.1}Mn_{0.9}O$ and $Cd_2Mn_3O_8$ are possible because in these complexes oxidation state of Cd is +2 and in water generally heavy metals precipitates as oxides and hydroxides.

- Co is removed only by adsorption onto amorphous $FeOOH$ and MnO_2, and therefore removed much more than Cd but comparatively less than the other moderately hard acid metal ions.

- Ni is removed better than Co due to formation of come crystalline $NiFe_2O_4$ and NiO in addition to adsorption. In water heavy metals like Ni^{2+} form hydroxide or oxide at higher pH. The formation of $NiFe_2O_4$ may result from conversion of NiO due during heating and drying of the coagulates before analysis.

- The removal of Cu^{2+}, Pb^{2+}, and Cd^{2+} may also be facilitated by co-precipitations with the iron hydroxides or oxide such as $FeOOH$ and Fe_2O_3. Cu is probably adsorbed stronger than Co and Ni due to its smaller size. Cr is adsorbed very strongly due to its hard acidic nature as mentioned earlier. The highest removal of Pb may be attributed to co-precipitation along with precipitation of highly crystalline $Pb(Fe,Mn)_{12}O_{19}$ in addition to moderate adsorption as a moderately hard acid.

4.2. Future scopes:

The outcomes of the present work open up a spectrum of scopes for future research and development works for the water researcher, engineers and water treatment personnel, as mentioned below:

- *viz.,* developing a compact automated OCOP units and field trial of the technique at large community water supply unit for removal of the heavy metals along with arsenic, iron and manganese.

- The OCOP method also has a prospect in removal of turbidity and clays from river water which may be very helpful during water crisis in flood time.

- One has to examine the microbial contamination in river water for using the method for purification of flood water for drinking during flood time in future.

- Biological stability of the treated water by OCOP and activity of the treated water on human cell can also be another scope of future research.

- It is also possible to recover some chemicals like arsenic and iron from the solid sludge.

- This work also upshots possible future research work on complexation of arsenic and other heavy metals such as Mn, Fe, Cd, Pb, Ni, Cr, Cu, and Co with ferric coagulant and MnO_2 in removal of them.

- Relations and influences of the heavy metals with each other can also be studied in details.