

Studies on Removal of Some Metal Ions from Groundwater by Oxidation-Coagulation-Adsorption at Optimized pH

Abstract

This thesis describes some studies on removal of iron, manganese and other hazardous metals from water along with arsenic by oxidation-coagulation-adsorption at optimized pH (OCOP) method. The OCOP method is an efficient and low-cost method of arsenic removal from contaminated groundwater which is gaining popularity as Arsiron Nilogon in India, especially in Assam. The method uses three common chemicals, namely, NaHCO_3 , KMnO_4 , and FeCl_3 as pH conditioner, oxidant and coagulant, respectively. The present studies were aimed at modification of the method to utilize coexisting iron present in water as coagulant for simultaneous removal of arsenic and iron; simultaneous removal of arsenic, iron and manganese; a comparative study of the performance of various oxidizing agents for removal of arsenic and finally removal of the some other heavy metals from contaminated water. The metal chosen were cadmium, lead, nickel, chromium, copper and cobalt. The thesis has been organized in four chapters dealing with different aspects of the studies as follows:

- I. *Introduction*: Narrates the contextual comparative study of the literature, motivation and the choice, objectives and plan of work.
- II. *Experimental*: Describes the materials, analytical tools and the experimental methods.
- III. *Results and Discussion*: Presents the results, their interpretation, explanation and study of the mechanism involved in the removal process.
- IV. *Conclusions and future scope*: Summarizes the important findings and future scopes.

Chapter I:

Introduction:

This chapter present the introduction part of the thesis. A detail study of contamination of groundwater by inorganic metal ions, their influences on human health and mechanism of the affects, the existing remediation technologies, their merits and demerits, and scopes for this work are discussed in this chapter with reference to the literature.

Among the existing metal ion removal technologies, adsorption and coagulation-adsorption are prominent ones having many advantages including high efficiency and low-cost. Different adsorbents such as iron oxy-hydroxide, iron oxide, manganese oxide, zero-valent iron and aluminium, activated carbon, activated alumina, TiO_2 , granular ferric hydroxide, granular ferric oxide, manganese oxide pillared clays, and coagulants such as FeCl_3 , FeSO_4 , $\text{Al}_2(\text{SO}_4)_3$ are generally used in these processes.

The OCOP method, developed by our research group, which is the basis of the present work, is highly efficient, low-cost, safe, environment-friendly and simple to be operated by a layman without electricity. The filter based on this method can be made at home using easily available materials and customised as per requirement. All these factors together make the OCOP method a do-it-yourself rural technology gaining rapid popularity among arsenic affected villagers as Arsiron Nilogon in India, especially in Assam. However, based on the field experiences of the OCOP, it was observed that there were certain aspects of the method which needed further attention of researchers in order to make it more cost-effective, to improve it further and to explore more about removal of other metal contaminants from water by this method.

In this work, the coexisting iron has been used as coagulant to supplement the added FeCl_3 in OCOP method in order to reduce the dose of FeCl_3 . The required dose of FeCl_3 utilizing the existing iron was optimized along with the doses of NaHCO_3 and KMnO_4 for OCOP method by using response surface methodology (RSM). Accordingly, a set of OCOP experiment was carried out in the laboratory utilizing coexisting iron along with optimization of the doses of KMnO_4 and NaHCO_3 to remove arsenic and iron simultaneously from water. Sometimes high concentration of manganese is also found in groundwater along with arsenic and iron. Therefore it was thought worthwhile to verify the removal of manganese along with arsenic and iron from water by the OCOP method. Utilization of coexisting ferrous iron and optimization of doses by RSM was also projected to remove manganese along with arsenic and iron. There are several oxidising agents which could also be used in an arsenic removal method like OCOP, where potassium permanganate was chosen without any detail comparative study of its performance with that of other oxidising agents. Therefore, it was decided to carry out such a comparative study of the performance of KMnO_4 with that of other oxidising agents, viz., H_2O_2 , NaOCl , Fenton's reagent in the OCOP method. For this, the effects of

pH, temperature and initial arsenic concentration on the performance of the selected oxidants in removing arsenic were investigated. Finally, though, the OCOP is known to reduce the concentrations of certain metals found in water also along with removal of arsenic and iron, no detail information was available in this regard. Therefore it was also thought worthwhile to carry out a systematic study of removal of some other metals viz., Cd, Pb, Ni, Cr, Cu and Co by the OCOP method. In this work, two sets of OCOP experiment were carried out with variation of initial concentrations of the heavy metal and with variation of time.

Chapter 2:

Experimental:

Materials and analytical tools

This chapter consists of the description of the materials and the methods applied in the present study. All chemicals used in our experiments were obtained from Merck, India except Sodium arsenite (NaAsO_2) was purchased from Sigma-Aldrich. These chemicals were of analytical grade and were used without further purification. Concentration of As, Fe, Mn and other metal such as Cd, Pb, Ni, Cr, Cu, and Co, etc., were determined by using a Perkin Elmer Atomic Absorption spectrophotometer (AAS). A hydride vapor generator was used for the determination As. The pH of the solutions was measured using an Orion multi parameter kit. The characterization of coagulates/precipitate obtained after OCOP treatment was done by using XRD, EDX and AAS.

Methods:

The methods used in various studies are described in this section.

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

Here the coexisting ferrous iron was utilized as coagulant to supplement the dose of FeCl_3 in order to reduce the cost of the OCOP method. The dose of FeCl_3 was taken as equal to difference between original dose of FeCl_3 used in the OCOP and the concentration of the co-existing iron ($[\text{Fe}^{2+}]_0$), i.e., as equal to $(25 \text{ mg/L} - [\text{Fe}^{2+}]_0)$, to

remove both As and Fe from water. The doses of pH conditioner, NaHCO_3 in mg/L and oxidant KMnO_4 as percent equivalent of concentration of $[\text{Fe}^{2+}]_0$ (used in the range of 5-100%) were optimized by Response Surface Methodology (RSM). NaHCO_3 is used to adjust the pH of the treated water at 7.3. The optimized doses were verified in the field with 32 household and 8 small community Arsiron-Nilogon filters.

B. Simultaneous removal of As, Fe and Mn by OCOP

A series of OCOP experiments were performed with variation of $[\text{Fe}^{2+}]_0$ from 1 mg/L to 8 mg/L and coexisting manganous ion concentrations ($[\text{Mn}^{2+}]_0$) from 0.5 mg/L to 5.0 mg/L with an interval concentration of 0.5 mg/L. Here, aqueous 9% NaHCO_3 solution was added dropwise to each solution to adjust the final pH of the water to 7.3. After that aqueous KMnO_4 solution was added in percentage equivalent of $[\text{Fe}^{2+}]_0$ from 30% to 100%. Then, the dose of FeCl_3 as $[\text{Fe}^{3+}]$ was taken as equal to $(8.6 - [\text{Fe}^{2+}]_0)$ in mg/L. Finally, we collected the filtrates of the treated water and analysed for determination of remaining concentrations of As, Mn and Fe and other water quality parameters. The experimental doses were optimized by RSM.

C. Evaluation of performance of different oxidizing agents in OCOP

OCOP experiments were performed using tap water separately with varying doses of oxidants, viz., KMnO_4 , Fenton's reagent, NaOCl and H_2O_2 . The initial concentrations of As^{3+} and NaHCO_3 were fixed at 200 $\mu\text{g/L}$ and 100 mg/L, respectively. The dose of KMnO_4 was varied from 0.2 mg/L to 2 mg/L at an interval of 0.2. The doses of the other oxidants were also taken in equivalent of the dose of KMnO_4 . Finally, a dose of 25 mg/L of coagulant FeCl_3 was added to it. After dosing, the water was stirred gently for about 10 s and allowed to settle the coagulates for 2 hour. The supernatant treated water was then filtered preserved for AAS analysis to determine the remaining As concentrations. Effect of pH, temperature and initial arsenite concentration were examined with the best performing oxidant, i.e., KMnO_4 , found in the present OCOP experiments.

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

A set of OCOP experiments were carried out to remove heavy metals, namely, Cd, Pb, Ni, Cr, Cu and Co by varying the initial concentration of the metals in the range of 2-10 mg/L and by varying the residence time from 1h to 4h. The doses of NaHCO_3 , KMnO_4

and FeCl₃ were same as that of the OCOP method. After the experiments, filtrates were analysed by AAS and solid coagulates were analysed by EDX, XRD and aqua regia extract analysis by AAS, etc., to assess the removal efficiencies.

Chapter 3:

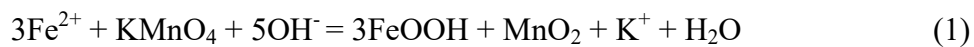
Results and discussions:

This chapter describes the results of the experiments, their interpretation, explanation and study of the mechanism involved in the removal processes. For systematic organization, this chapter has been sub-divided into four major sections corresponding to our four major works as described below.

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

Removal of arsenic was found to increase with increase in $[\text{Fe}^{2+}]_0$ and the dose of KMnO₄. There are three reasons for the increased removal arsenic with increase in $[\text{Fe}^{2+}]_0$ and the dose of KMnO₄:

- (i) KMnO₄ oxidizes difficult-to-remove As³⁺ to easily removable As⁵⁺ ions,
- (ii) KMnO₄ also oxidizes Fe²⁺ ions to Fe³⁺ ions leading to an increase in formation of coagulates on which As⁵⁺ is adsorbed and
- (iii) More the consumption of KMnO₄ the more is the formation of MnO₂ precipitate, under the prevailing mild alkaline condition, which also adsorbs As⁵⁺. The reactions can be summarised as:



Thus, the observed arsenic removal to below 2 µg/L at higher $[\text{Fe}^{2+}]_0$ and lower dose of FeCl₃ can rightly be due to increased adsorption of As⁵⁺ on MnO₂ precipitates in addition to the adsorption on the coagulates formed by FeCl₃. It was reported that at prevailing pH of about 7.3 controlled by NaHCO₃, the FeCl₃ forms coagulates consisting of predominantly amorphous goethite (FeOOH) and some amount of iron oxides such as Fe₂O₃ and Fe(OH)₃ which adsorb As⁵⁺ present in the anionic forms of H₂AsO₄⁻ and HAsO₄²⁻.

The minimum required doses of KMnO_4 for arsenic removal from $100 \mu\text{g/L}$ to less than $1 \mu\text{g/L}$ in presence of coexisting iron concentration, $[\text{Fe}^{2+}]_0$ of 5, 10, 15, 20 and 25 mg/L were assessed for practical applications as: 95%, 93%, 90%, 85%, and 80% for $[\text{Fe}^{2+}]_0$ in the ranges of 0–5, >5–10, >10–15, >15–20, and >20–25 mg/L, respectively. The gradual decrease in the minimum required KMnO_4 dose with increase in $[\text{Fe}^{2+}]_0$ may be attributed to an increasing adsorption of arsenic by MnO_2 as the precipitation of the later increases with increase in $[\text{Fe}^{2+}]_0$. RSM analysis for optimization of doses of KMnO_4 shows that if $[\text{Fe}^{2+}]_0$ 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 $[\text{Fe}^{2+}]_0$ will be 95.34%, 95%, 92.84%, 90.00%, 85.00%, 80.21%, and 78.73% respectively, which gives a good correlation with the experimental results.

The RSM analysis also shows that if $[\text{Fe}^{2+}]_0$ present in water are 5.00, 10.27, 15.00, 20.09 and 25.00 mg/L then the required doses of NaHCO_3 are 39.43, 48.03, 56.00, 62.20 and 71.43, respectively. In laboratory experiment we added 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. There is also a similarity between required doses of NaHCO_3 added in laboratory experiments with respect to coexisting iron and the doses obtained from RSM analysis to remove arsenic below $1 \mu\text{g/L}$. Therefore, our optimization of the required doses of KMnO_4 and NaHCO_3 with respect $[\text{Fe}^{2+}]_0$ is good and is also capable of predicting the doses outside the experimental range of 5 mg/L to 25 mg/L of $[\text{Fe}^{2+}]_0$. Accordingly, we can use the RSM optimized doses of KMnO_4 and NaHCO_3 in field application to remove arsenic below $1 \mu\text{g/L}$ on the basis of coexisting iron concentration and thereby lowering the cost of the OCOP method utilizing coexisting iron. Field trial of this modified OCOP method showed satisfactory results with simultaneous arsenic and iron removal from 284–25 $\mu\text{g/L}$ and 2–23 mg/L to below $1 \mu\text{g/L}$ and 0.02 mg/L, respectively.

B. Simultaneous removal of As, Fe and Mn by OCOP

We have 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 . The increase in the removal of arsenic with increase in KMnO_4 dose can be attributed to oxidation of As^{3+} to easily removable As^{5+} in addition to oxidation of Fe^{2+} to Fe^{3+} as FeCl_3 alone cannot remove As^{3+} efficiently. 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 with conversion of the more and more coexisting Fe^{2+} into Fe^{3+} after addition of KMnO_4 . But the removal of arsenic with increasing $[\text{Mn}^{2+}]_0$ at fixed $[\text{Fe}^{2+}]_0$ may be ascribed to increased adsorption of arsenic on solid MnO_2 precipitates formed due to oxidation of Mn^{2+} ions by KMnO_4 and catalysis of the oxidation of As^{3+} to As^{5+} by MnO_2 . It was observed that remaining total $[\text{As}]$, $[\text{Mn}^{2+}]$ and $[\text{Fe}^{2+}]$ after the treatment were below 1 $\mu\text{g/L}$, 0.009 mg/L and 0.03 mg/L down from their initial concentrations of 100 $\mu\text{g/L}$, 5 mg/L and 8 mg/L, respectively. In this work the doses of NaHCO_3 , KMnO_4 and FeCl_3 were also optimized by RSM with respect to coexisting iron concentration for determining the doses to remove the Mn, As and Fe below 0.009 mg/L, 1 $\mu\text{g/L}$ and 0.03 mg/L, respectively.

C. Evaluation of performance of different oxidizing agents in OCOP

In this work a set of OCOP experiment was done to remove arsenite ion from initial concentration of 200 $\mu\text{g/L}$ using equivalent dose of KMnO_4 , Fenton's reagent, NaOCl and H_2O_2 as the oxidizing agents separately with same dose of NaHCO_3 and FeCl_3 in each case. It is interesting to note that the removal of arsenic with Fenton's reagent and KMnO_4 were found 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. It may be noted here that the arsenic concentration decreased from 200 $\mu\text{g/L}$ to 27-28 $\mu\text{g/L}$ even without addition of any oxidant which may be attributed to aerial oxidation of As^{3+} to As^{5+} and adsorption As^{5+} by goethite coagulates. While the plots of remaining arsenic with respect to dose of the oxidant were found to be somewhat linear in cases of NaOCl and H_2O_2 , rapid initial decreases in remaining arsenic were observed in the cases of Fenton's reagent and KMnO_4 .

It was observed that the removal of As remarkably increases on increasing the dose of KMnO_4 and reaches 100% with a dose of 2 mg/L KMnO_4 . Under similar conditions, equivalent doses of Fenton's reagent, NaOCl and H_2O_2 could remove arsenic to approximately 98.8%, 89.0% and 88.0%, respectively. Highest removal efficiency is 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 better arsenic removal efficiencies of Fenton's reagent compared to that of NaOCl and H₂O₂, in equivalent concentration of KMnO₄, may be attributed to adsorption of arsenate ions on insoluble iron oxides formed from FeCl₃ and oxidation of ferrous iron of Fenton's reagent. An 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 ($pK_{a1} = 4.503$) of H₃AsO₄. Similarly, a rapid and linear increase in the removal of arsenic in the pH range from about 6.5 to 7.5 may be attributed to the second dissociation ($pK_{a2} = 7.09$) of H₃AsO₄. Arsenic removal by OCOP with KMnO₄ as oxidant method linearly increases with temperature and is highly effective between 10°C to 45°C indicating applicability of the method within this temperature range. Arsenic is chemisorbed on heterogeneous surface and inside the precipitates of MnO₂ and FeOOH formed by KMnO₄ and FeCl₃. 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.

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

The OCOP method has been found to be capable of removing all the six metal ions considerably well. The percentage of removal of all metals increased with decrease in the initial concentration of the 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%). In OCOP method, the mild alkaline pH provided by NaHCO₃ may favour precipitation of the heavy metals. The observed low removal of Cd may be attributed to weaker binding/adsorption to oxygen of FeOOH coagulates or MnO₂ precipitates formed during OCOP treatment due to its soft acidic nature. On the other hand Cr, being a hard acid, is removed very well due to its strong binding FeOOH and MnO₂. Removal of heavy metal was found to increase with increase in residence time. The removal levelled off above 3h for Cd and Co which is the optimum residence time for most adsorption methods but continued to decrease up to 4h in the case of Pb, Cr, Ni and Cu.

Powder XRD analysis of the solid coagulates formed in OCOP experiment for removal of heavy metals reveals that Co being very similar to iron gave XRD pattern of amorphous solids like that containing iron alone produced in absence of any heavy metal. Presence of Ni, Cr and Cu in the water leads to formation of some crystalline compounds of NiFe₂O₄ and NiO, Cr₃O₈, and Cu(FeO₂) respectively. The presence of Cd

leads to formation of highly crystalline compounds of CdO_2 and CdMnO 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 $\text{Pb}(\text{Fe}, \text{Mn})_{12}\text{O}_{19}$ in addition to facilitating formation of crystalline Fe_2O_3 and FeOOH . Literatures reveals that these selected metal concentration in natural groundwater is usually found below 2 mg/L, and therefore the OCOP method, with 94.4-99.5% of removal, is highly efficient for removal of heavy metals from groundwater.

Chapter 4:

Conclusions and future scope:

Conclusions

This is the concluding chapter of the thesis. It demarcates the final interpretations and future scope of this work. The systematic study aiming to developed a modified OCOP method utilizing co-existing iron (Fe^{2+}) in lieu of FeCl_3 as coagulant and optimizing the doses pH conditioner, oxidant and coagulant upshots a very satisfactory removal method of As and Fe simultaneously from groundwater. From this study it is pellucid that optimized doses of pH conditioner, NaHCO_3 and oxidant KMnO_4 by RSM is adequate to remove arsenic and iron from groundwater sources to below $1\mu\text{g/L}$ and 0.01mg/L respectively, which is ten times lower than the WHO guideline values. RSM recommend doses of KMnO_4 as percentage of equivalent of $[\text{Fe}^{2+}]_0$ and NaHCO_3 in mg/L gives satisfactory results in laboratory as well as in field trial experiment for removal of arsenic and iron below $1\mu\text{g/L}$ and 0.01mg/L respectively.

In the study of removal of Mn along with As and Fe we observed an increase in removal of arsenic with increase in coexisting $[\text{Fe}^{2+}]_0$ and $[\text{Mn}^{2+}]_0$ as well as with increase in the dose of KMnO_4 . Increase in the removal of arsenic with increase in KMnO_4 is because of oxidation of As^{3+} to As^{5+} in addition to formation of hydroxides of Fe^{3+} by oxidation of Fe^{2+} . The observed increase in the removal of arsenic with increasing $[\text{Fe}^{2+}]_0$ indicates increased formation of iron coagulates such as FeOOH , Fe_2O_3 and $\text{Fe}(\text{OH})_3$ etc and increase in arsenic removal with increasing $[\text{Mn}^{2+}]_0$ may be ascribed to increased formation of MnO_2 precipitates and catalysis of the oxidation of As^{3+} to As^{5+} by MnO_2 . RSM is also very useful in determining the optimized doses of NaHCO_3 ,

KMnO₄ and FeCl₃ to remove Mn, As and Fe to below 0.009 mg/L, 1 µg/L and 0.03 mg/L respectively.

OCOP experiments to remove arsenite ion from 200 µg/L using equivalent dose of KMnO₄, Fenton's reagent, NaOCl and H₂O₂ as the oxidizing agents showed that KMnO₄ was the best oxidizing agent among them. The performance of KMnO₄ was closely followed by that of Fenton's reagent. Arsenic removal efficiencies of the oxidising agents were found in order as: KMnO₄ (100%) > Fenton's reagent (98.8%) > NaOCl (89.0%) > H₂O₂ (88.0%). Highest arsenic removal observed in case of KMnO₄ is because, during oxidation As³⁺ to As⁵⁺, KMnO₄ itself reduces to MnO₂. This resulting solid MnO₂ also helps in removal of arsenic by adsorbing arsenate ions on its surface. pH and temperature did not show notable influence the performance of KMnO₄ in OCOP method.

Removal of other metals such as Cd, Pb, Ni, Cr, Cu, and Co was significant by OCOP experiment. 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%). A relatively lower removal of Cd than the other metals may be due to its soft acid nature. Cd, being a soft acid, forms weaker binding/adsorption to oxygen of FeOOH coagulates or MnO₂ precipitates formed during the OCOP treatment. On the other hand Cr, being a hard acid, is removed very well due to its strong binding with FeOOH and MnO₂.

Future scope

Finally, the outcomes of the present work open up scopes for future research and development works, viz., developing a compact automated OCOP units and field trial of the technique at large community water supply unit. The OCOP method also has a prospect in removal of turbidity, clays from river water which may be very helpful during water crisis in flood time. It is also possible to recover some chemicals like arsenic and iron from the solid sludge.