

Removal of Selenium from Industrial Waste Water
by Ferrous-Ferric Salt

MS Thesis Report submitted towards the partial fulfillment for
the award of

Integrated BS MS degree program

By

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20121020

To

DEPARTMENT OF CHEMISTRY



Indian Institute of Science Education and Research, Pune

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30th March 2017

CERTIFICATE

This is to certify that this dissertation entitled "**Removal of selenium from industrial waste water by ferrous-ferric salt**" towards the partial fulfilment of the BS MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents original research carried out by "**Lipi Jain at Shell New Technology Center, Bangalore**" under the supervision of "**Dr. Tarakranjan Gupta, Project Activity Lead, Shell New Technology Centre Bangalore and Dr. Srinivas Hotha, Associate Professor, Department of Chemistry, IISER Pune**" during the academic year 2016-2017.

Date 26/03/2017


Place Bangalore



Signature of the Student

Date 26/03/2017

Place Bangalore



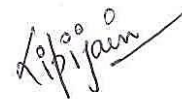
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DECLARATION

I hereby declare that the matter embodied in the report entitled "**Removal of selenium from industrial waste water by ferrous-ferric salt**" are the results of the investigations carried out by me at **Shell New Technology Center Bangalore**, under the supervision of **Dr. Tarakranjan Gupta** and the same has not been submitted elsewhere for any other degree.

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Date 26/03/2017

Place Bangalore



Signature of the Supervisor

ACKNOWLEDGEMENTS

I would first like to express my honest and profound gratitude towards my supervisor **Dr. Tarakranjan Gupta** for his constant support, guidance and providing me a better direction to work whenever needed. I must express my sincere regards towards my line manager **Dr. Albert Janssen** for providing exceptional facilities at **Shell New Technology Center, Bangalore**. Without their consistent support, this accomplishment would have never been achieved.

I would especially like to thank **Mehak Singla** for her continuous encouragement during lab experiments and her efforts to make the lab environment comfortable and friendly. I would like to acknowledge the work of **Manigandan Parthasarathi** and the entire analytical team of **Shell New Technology Center, Bangalore** for providing analytical support to the project.

I must be thankful to **Dr. Srinivas Hotha** for helping me to communicate with IISER Pune and keep the record of my work throughout the year.

I would also like to thank my teammates Dr. Anupom Sabhapondit, Dr. Prashant Sinha, Dr. Anal Chavan, Dr. Jitendra Kadam and Sathya Narayan for making me comfortable in the team to work freely.

At the end, I would like to thank my family and friends for supporting me continuously in all the good and bad circumstances throughout the year.

-Lipi

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1. Abstract

Natural water bodies are continuously facing excessive selenium discharge from chemical industries, refineries and various treatment plants in US. Selenium is a naturally occurring element which is soluble in water in the form of inorganic oxyacids i.e. selenate (SeO_4^{-2}) and selenite (SeO_3^{-2}). Both selenate and selenite have tendency to accumulate in few parts of animal/human body. Selenium has essential roles in mammalian metabolism but it is considered as dietary supplement at <4ppb concentration. Selenium discharge at higher concentration into natural water bodies can cause adverse effects on aquatic and aquatic dependent wild life. Under Clean Water Act (1977) Section 304 (a), Environmental Protection Agency US regulates discharge of selenium and other toxic pollutants into natural water bodies for the protection of aquatic life. Current EPA Regulation for selenium discharge is 5 ppb on a daily average and 4 ppb on a monthly average and expected to get stricter in future. Best Available Technology (BAT) suggested by US EPA can remove only selenite from industrial waste water. Hence, it is difficult to meet EPA freshwater criteria using BAT when both selenate and selenite are present in industrial waste water. Currently, there is no such process available which can constantly meet EPA regulation related to selenium discharge. In this study, a new process comprising addition of ferrous and ferric salt has been developed for synthetic waste water prepared in laboratory. The process has been tested in batch as well as in continuous experiments. The newly developed process is able to remove both selenate and selenite from synthetic waste water to <5ppb total selenium; therefore, it has potential to meet forthcoming stringent EPA regulations.

2. Introduction

2.1 Environmental Cycle & Toxicology of Selenium:

Selenium is a naturally occurring element which is mostly found in metal sulfide ores, where it replaces sulfur due to their similar properties. Selenium is released into the environment by natural sources such as weathering, runoff of selenium rich soil into rivers and anthropogenic sources such as refining of metal sulfide ores, coal burning, irrigated agriculture, mining industries, metallurgical industries and, oil and gas industries [1, 2]. These sources are attributed for major selenium transport to water via rocks, soil and sediments where it enters animals due to consumption of selenium contaminated water and sediments; and plants by adsorption through soil and sediments. Transport of selenium continues via food chain from one species to other and finally to humans. This transportation cycle terminates with degradation of animal/human/plant body while restoring selenium back in the environment. Selenium has a tendency to accumulate in few parts of human/animal body [1, 2, 3, 4].

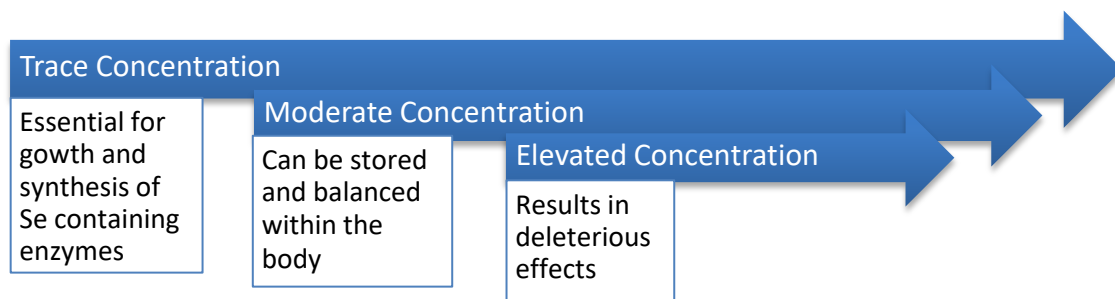


Fig. 1: Effect of varying concentration of selenium

Selenium has an essential role in cellular functioning in many organisms; it is present in few enzymes e.g. glutathione peroxidase, thyrodoxin reductase and deiodinase enzymes [1, 3]. Therefore, a trace amount of selenium is necessary for the synthesis of Se-containing enzymes. Although, Se is an important dietary supplement and deficiency of the same can cause deleterious effects; however, in most cases, food e.g. grains, cereal, and meat provide a substantial amount of selenium to combat its deficiency. Excess selenium can substitute sulfur present in methionine and form selenomethionine, an analogue of methionine. Human or animal body doesn't synthesize selenomethionine; hence, it can't distinguish

selenomethionine from methionine [1, 3]. As a result, it gets incorporated into a variety of methionine containing enzymes and interferes with their functioning [1, 3]. The two-edged sword nature of selenium with a narrow window between essential and toxic doses (40 to 400 µg per day on an average) justifies the need for strict regulations on selenium uptake. The US Food and Drug administration (US FDA) has recommended 55 micrograms per day as a dietary allowance for selenium. Exceeding this limit can result in severe selenium poisoning and lead to selenosis, reproductive failure, hair and fingernail loss (due to dis-functioning of Keratin, an enzyme rich in sulfur content), and birth defects (e.g. larval deformity and mortality in aquatic invertebrates) [1, 2, 3, 4].

2.2 Current EPA (Environmental Protection Agency) Regulations for Selenium Discharge:

In US chemical industries, oil refineries, coal liquification plants and power plants, discharge of selenium into natural water bodies is regulated at 5 ppb total Se on a daily average and 4 ppb total selenium on a monthly average by Environmental Protection Agency (EPA) [4, 5]. EPA requests local regulatory boards (e.g. California water board) to propose and implement their own regulatory limits which are compliant with EPA's safe water disposal criteria. In order to meet these regulations, some industries in California are given dilution credits by California water board to dilute selenium contaminated stream with a non-selenium contaminated stream. For example, Chevron USA (Richmond Refinery) has got a dilution credit of 7D, ConocoPhillips (San Francisco Refinery), Shell US (Martinez Refinery) and Tesoro (Golden Eagle Refinery) have received a dilution credit of 9D. A dilution credit of 9D (1:9) will allow the industry to discharge 50 ppb of total selenium on a daily average and 40 ppb of total selenium on a monthly average. If an industry fails to meet discharge limits set by the local authorities, it can put their license for operation at risk [4].

Under Clean Water Act (CWA, 1977) Section 304 (a), Environmental protection agency (EPA) evaluates and revises ambient water quality criteria (AWQC) time to time, to keep it consistent with CWA. Ambient water quality criteria express an acceptable numeric value of different pollutants in water for the protection of aquatic life and their designated uses. Under CWA, EPA published

AWQC in 1999 for the protection of aquatic life and aquatic-dependent wildlife. EPA periodically updated and released the criterion for public comments and the final update has been released in 2016 using the latest scientific knowledge of the relationship between the concentration of different pollutants and their harmful effects [4].

The 1999 selenium criterion was expressed in terms of selenium toxicity due to dissolved selenium in water. The final 2016 AWQC includes four elements:

- Fish eggs-ovary element
- Fish whole body/muscle element
- Water column monthly effect (long-term exposure)
- Water column intermittent effect (short-term exposure)

The first two elements are expressed in terms of metabolic transfer of selenium to fish eggs and body; the other two elements are expressed in terms of concentration of dissolved selenium in the water body. All four elements take care of both long-term and short-term exposure to selenium. Since EPA has published a new and stricter AWQC for estimating the maximum limit of selenium for the protection of aquatic life, it is anticipated that these regulatory limits and therefore, the dilution criteria will become more stringent in future, providing a maximum limit of 10 ppb (after dilution) total selenium for discharge [4].

2.3 Selenium Chemistry:

Selenium is a group 16 element with atomic number 34 and belongs to Chalcogen family of the periodic table. It exhibits properties of both metal and non-metal; therefore, it's a metalloid. Selenium was accidentally discovered by a Swedish chemist Jons Jacob Berzelius in 1817 when he encountered the contamination of a red-brown precipitate in Sulfuric acid. Initially, he believed that it was Tellurium due to their similar smell but continued to analyze it further. Ultimately, he put an end to the discussion and declared that the impurity contained an undiscovered element which shared similar properties to both sulfur and Tellurium. This new element was named after Greek word for 'Moon', Selene [1].

Selenium exists in different allotropic forms i.e. red amorphous powder, red crystalline material and a grey crystalline form called metallic selenium. Most Se forms are insulators but the grey crystalline form is a semiconductor. Moreover, the presence of light enhances its electrical conductivity; for that reason, it is extensively used in photovoltaic cells, solar cells and photocopiers [1]. One more important application of selenium is in glass industries. It is added to the glass for two major effects. First, a small amount of selenium can neutralize the green color of the glass due to the presence of iron compounds. Second, a large amount of selenium can add a sheer red color to the glass. Aside from this, selenium is used in rectifiers, anti-dandruff shampoo, coloring agent in paint industries, stainless steel, vulcanization of rubber, and alloy formation [1].

Selenium has 20 different isotopes; however, only 6 of them are stable i.e. ^{74}Se , ^{76}Se , ^{77}Se , ^{78}Se , ^{80}Se and ^{82}Se . This rare element is pretty reactive in nature and mostly combines with hydrogen, oxygen, and halogens. It exists in various oxidation states such as -2, 0, +4, +6 [1, 6].

- -2 as H_2Se , HSe^- , metal selenides, alkyl selenides, seleno-amino acids.
- 0 as Se^0 including trigonal (grey) and monoclinic (red) crystalline forms.
- +4 as SeO_3^{-2} , HSeO_3^- , H_2SeO_3 .
- +6 as SeO_4^{-2} and HSeO_4^- .

Selenium exists in the environment in both organic and inorganic forms. Organic forms such as dimethyl selenide (Me_2Se), dimethyl diselenide (Me_2Se_2) and selenoaminoacids. Naturally occurring inorganic forms include selenite (SeO_3^{-2}), selenate (SeO_4^{-2}) and selenides (Se^{-2}). The most common aqueous forms of selenium at moderate pH and temperature are oxyacid salts i.e. selenite and selenate. Selenium (IV) species are much more reactive compared to selenium (VI) species and has more tendency to reduce to elemental selenium [7, 8]. Additionally, selenate salts exhibit better solubility in water compared to selenite salt. On the other hand, elemental selenium has relatively less solubility in water and exists in both crystalline and amorphous form. These facts indicate that removal of selenate from water is a wearying affair [7, 8].

2.4 Source, Fate and Transport of Se in Industrial Waste Water:

Waste water originating from oil and gas industries is one of the sources of selenium release in the environment. Generally, crude oil which contains seleniferous marine shales is rich in selenium and the major source of selenium in industrial waste water. During various refining steps of crude oil, selenium and other pollutants (e.g. oil residues, benzene, phenol, arsenic, chromium etc.) are transferred from oil to waste water [9, 10].

Crude oil contains both sulfur and selenium compounds in the form of organosulfides and organoselenides. In hydrotreaters, these compounds are converted to H_2S and H_2Se respectively. During processing of crude oil, Se follows transport of sulfur due to similar chemistry till sour water stripper, where H_2S is stripped because of its volatile nature but H_2Se remains as it is. Thiocyanate present in the sour water stripper reacts with some H_2Se and forms selenocyanate ($SeCN^-$). Se mostly appears as selenocyanate ($SeCN^-$) and selenium hydride (H_2Se) in stripped sour water with concentration ranging from 700-5000 ppb. Further, stripped sour water is transferred to the waste water treatment system where in the biotreater, these selenium compounds are oxidized to oxyacids i.e. selenite (SeO_3^{-2}) and selenate (SeO_4^{-2}); both the forms are soluble in water. The concentration of soluble selenium in post bio-treated water varies from 100-200 ppb. The ratio of selenate to selenite can vary drastically between industries and sometimes within different treatment plants of the same industries depending on the units in the operation, process and type of treatment they are performing. Therefore, every industrial waste water is unique and affects the environment differently depending on its composition [9, 10].

This is how selenium is transferred from crude oil to waste water in the form of SeO_3^{-2} and SeO_4^{-2} . After bio-treatment, waste water is discharged into natural water bodies which results in selenium contamination and adverse effects on aquatic and aquatic dependent wild life. Taking this into account, Environmental Protection Agency (EPA) sets mandates to remove selenium compounds from industrial waste water before outfall into natural water bodies. The treatment technology will depend on the temperature, pH of industrial waste water at outfall and form of selenium species in industrial waste water. The challenge is to find appropriate technology that

is feasible, economical, deployable, fast and provides an eco-friendly way of selenium removal.

2.5 Existing Se Removal Methods & their Limitations:

Over the years, mainly three types of methods have been studied and developed for removal of selenium from Industrial waste water i.e. a) Physical treatment, b) Chemical treatment and c) Biological treatment. Physical treatment includes processes like ion-exchange, reverse osmosis and membrane filtration. So far, there is no report on pilot scale studies of membrane filtration but reverse osmosis has been implemented for treatment of mining wastewater in Barrick's Richmond Hill Mine and gold mine closure in California, USA. A pilot scale reactor for ion-exchange has been successfully established in Elk Valley, British Columbia. The major drawback of reverse osmosis and membrane filtration is the high cost for operation and maintenance. On the contrary, ion-exchange is comparatively cost effective process but the success rate for selenium removal is very less [1, 11, 12].

Biological treatment deals with organic carbon sources e.g. aerobic and anaerobic bacteria, algae, fungus etc. for conversion of soluble selenium species (SeO_3^{-2} and SeO_4^{-2}) to insoluble species (Se^0). Biological treatment is a low-cost alternative which is adaptable to diversification of industry specific wastewater. Having said that, it's a slow process and removal efficiency will extensively depend on temperature, pH and climate for the bacteria to grow. Moreover, interfering anions (e.g. sulfate and nitrate) and atmospheric re-oxidation of reduced Se will also have a detrimental effect on removal efficiency [1].

Chemical treatment includes adsorption, redox transformation, electrocoagulation and precipitation of insoluble selenium species. Adsorption of selenium oxyanions onto ferrihydrite is the best available technology (BAT) by USEPA [11, 12]. This process has been deployed at Shell refineries since 1998. Ferrihydrite is amorphous in nature and has excellent adsorbent properties. This process offers selenium removal in a two-step fashion; first, addition of ferric salt to industrial waste water at neutral to slight alkaline pH will generate ferric oxyhydroxide precipitate (ferrihydrite) and second, selenium oxyanions will adsorb on ferrihydrite precipitate (1).



It is expected that both selenium oxyanions (SeO_3^{-2} and SeO_4^{-2}) will adsorb on ferrihydrite surface. Unsuccessfully, this method can remove only selenite from industrial waste water. Selenate doesn't adsorb on ferrihydrite surface and remains unremoved. The reason behind this phenomenon is presence of SO_4^{-2} in industrial waste water. Both sulfur and selenium analogues appear in crude oil and during bio-treatment they are oxidized to corresponding oxyacids i.e. SO_4^{-2} and $\text{SeO}_4^{-2}/\text{SeO}_3^{-2}$. Due to structural similarity, SO_4^{-2} and SeO_4^{-2} compete for adsorption sites on ferrihydrite and unfortunately SO_4^{-2} is preferably adsorbed over SeO_4^{-2} . Consequently, this process succeeds to remove only one component of selenium (SeO_3^{-2}) from industrial waste water and thus, fails to meet regulatory limits [6, 11, 13].

2.6 Objective & Project Planning:

Despite the advances in removal technologies, at present, no process is available which has potential to meet current EPA regulations for safe water disposal. Implementation of stringent regulation, excessive selenium discharge at US industries and harmful effects of selenium compounds on environment clearly indicate the urgent need of a cost effective, eco-friendly, feasible, fast and deployable technology which can remove total Se below 5 ppb. The main objective of carrying this investigation is as follows:

- Development of a new method or modification of the existing ferric addition method (BAT) in batch process at laboratory scale to remove both SeO_4^{-2} and SeO_3^{-2} from industrial waste water to <5 ppb in presence of interfering anions (e.g. sulfate and nitrate) while minimizing the changes in existing facilities at industries.
- Demonstration of the developed method in a continuous process on a laboratory scale chemical reactor to verify the process window, identify the hazards and success rate.
- Studying the effect of pH variation and chemical dosing on selenium removal to obtain a process window and minimize the dosing, therefore, the cost.

- Inspecting the limitations of the developed method in continuous process i.e. sludge production and pH dependence, in comparison with the existing ferric addition method.

3. Experimental Methods

3.1 Development of the Concept:

As discussed in *section 2.5*, the Best Available Technology (BAT) by USEPA i.e. addition of ferric salt to industrial waste water (at pH 7-7.5) is unable to remove selenate (SeO_4^{-2}) below 5 ppb. Removal of both selenate and selenite is indispensable to meet waste water discharge regulations set by EPA. Predominant reason behind difficulty in removal of SeO_4^{-2} is unavailability of ferrihydrite adsorption site due to antagonistic behaviour of SO_4^{-2} . In order to combat this antagonism, SeO_4^{-2} can be first converted to SeO_3^{-2} using an appropriate reducing agent followed by adsorption of total SeO_3^{-2} present in waste water on a solid surface. In this manner, negative effect of SO_4^{-2} interference on SeO_4^{-2} removal can be forestalled by using a combination of adsorption and redox reaction as an alternate approach. Moreover, the determining factors to consider during development of a new technology for selenium removal are following:

- Scalable, safe and easily deployable
- Provides a process window for easy implementation
- Potential to reach <5 ppb total selenium
- Fast removal

If the BAT can be improved and modified in a manner such that it removes both SeO_4^{-2} & SeO_3^{-2} from industrial waste water to <5 ppb then deployment of the new developed process will become a lot easier, since it won't require major changes in the existing facilities at industries. However, selection of an appropriate reducing agent and adsorbent was the biggest challenge. A number of reasons pointed in the direction of using ferrous salt as the reducing agent.

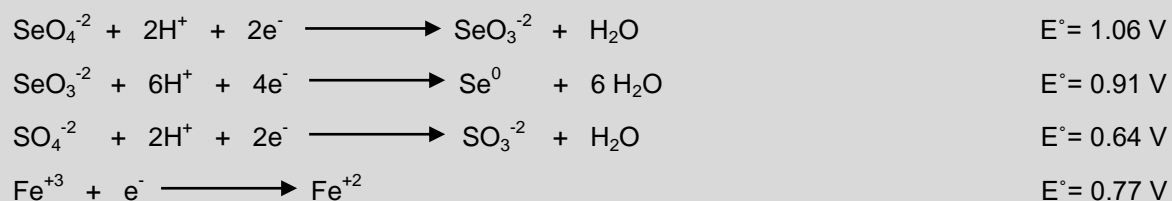


Fig. 2: Reaction potentials for determining suitable reagent for reduction of SeO_4^{-2} to SeO_3^{-2}

First, as shown in **Fig. 2**, Fe^{+2} has lower reduction potential than SeO_4^{-2} . Theoretically, SeO_4^{-2} and Fe^{+2} will form a redox couple with $\Delta G < 0$; resultantly, SeO_4^{-2} will preferentially get reduced and Fe^{+2} will get oxidized. Second, SO_4^{-2} has lesser reduction potential than SeO_4^{-2} , so SO_4^{-2} will not be able to interfere in redox conversion of SeO_4^{-2} to SeO_3^{-2} by ferrous salt. Third, this method will not require huge changes in the already existing facilities since we are still using iron for the treatment.

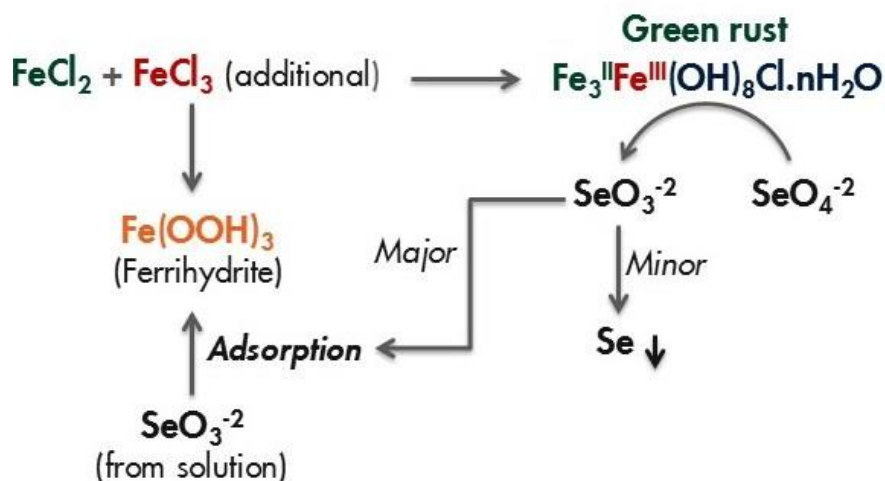


Fig. 3: Reaction mechanism of the proposed hypothesis
**Chloride salts of Fe^{+2} and Fe^{+3} were used for the experiments*

According to the reaction mechanism of this process shown in **Fig. 3**, oxidation of Fe^{+2} generates Fe^{+3} . As soon as Fe^{+3} ions arrive in the system, formation of a mixed oxide of Fe^{+2} and Fe^{+3} called "Green rust" takes place. This mixed complex is the key agent for reduction of SeO_4^{-2} to SeO_3^{-2} and further to elemental Se. Remaining Fe^{+3} ions produce an amorphous ferric oxide called "Ferrihydrite". This amorphous oxide has excellent adsorption properties and is responsible for adsorption of total SeO_3^{-2} present in the system [14, 15, 16]. We proposed that in order to improve the efficiency of the process, additional Fe^{+3} salt could be added to the system alongwith Fe^{+2} salt. As a result, we arrived at a conclusion to study three different methods for Se removal (i) using Fe^{+2} salt, (ii) using a mixture of Fe^{+2} and Fe^{+3} salt and (iii) using Fe^{+3} salt (to compare with the existing technology). According to the literature studies, both formation of Green rust and adsorption of SeO_3^{-2} onto ferrihydrite are pH dependent processes; therefore, possible challenges to this method are pH dependence of the reaction, formation of

toxic sludge and interference of the other redox couples present in the industrial waste water [11, 12].

3.2 Experimental Planning:

The entire study is divided in following sections:

- Characterization of waste water i.e. pH, TDS (total dissolved solid), presence and concentration of various anions e.g. SeO_4^{-2} , SeO_3^{-2} , SO_4^{-2} , NO_3^- , HCO_3^{-2} , CO_3^{-2} .
- Preparation of synthetic waste water.
- Screening of the best method for Se removal out of ferrous salt addition, ferric salt addition and mixture of ferrous-ferric salt addition in a batch process at laboratory scale.
- Effect of pH and total iron dosing on removal efficiency in batch process at laboratory scale.
- Designing Continuous Stirred Tank Reactor (CSTR) and demonstration of the best identified method in a continuous process.
- Kinetic studies of the reaction for estimating the time required for achieving the steady state.

3.3 Materials, Standards & Waste Water Samples:

Ferrous chloride tetrahydrate (98%), ferric chloride solution (45% w/v), sodium bicarbonate (99.7%), sodium nitrate (99%), sodium sulfate (99%), ammonium citrate dibasic (99%), hydrochloric acid (37% w/w), sodium selenate, sodium selenite (99%), Sodium hydroxide (97%) and pH standards were purchased from Sigma Aldrich. Quality assurance samples for calibration check of HPLC ICP-MS and autosampler GC vials were acquired from Agilent Technologies. Waste water samples were procured from one of the Shell refinery. These waste water samples were stored in high density polyethylene (HDPE) containers (Tarsons labware) under refrigeration. The samples were filtered using 0.45 μm Millex[®] syringe filters (Merck Millipore) and collected in polypropylene centrifuge tubes (Tarsons labware) for analysis. 1000ppb stock solution of selenate and selenite were prepared using sodium selenate and sodium selenite. These stock solutions were used for

preparation of mixed calibration standards (containing both selenate and selenite) for HPLC ICP-MS. 15% w/v ferrous chloride solution and 10% w/v sodium hydroxide solution were also prepared. All the solutions were prepared in deionized water (resistance 15.0 μ S/cm) and all the purchased chemicals were of analytical grade.

3.4 Instrumentation:

Inolab[®] Multi 9310 IDS digital multiparameter benchtop meter was used for pH and TDS measurement of waste water samples. SenTix[®] 980 IDS pH electrode filled with 3 mol/L KCl solution as an electrolyte was used for pH measurement and TetraCon[®] 925 IDS conductivity measuring cell was used for TDS measurement. The pH probe was calibrated with pH standards prior to analysis. Metrohm 848 Titrino Plus volumetric titrator was used for bicarbonate/carbonate analysis in refinery effluent and for fine pH adjustment in CSTR; Metrohm 6.0259.100 unitrode filled with 3M KCl solution as an electrolyte was used as a sensor in the titrator for pH detection. Agilent 7700 Series ICP-MS hyphenated with Agilent 1200 Infinity Series HPLC was used for speciation of total selenium (SeO_4^{-2} and SeO_3^{-2}) present in untreated and treated waste water samples. Dionex ICS3000 Ion chromatography was used for analysis of various anions present in the waste water. Masterflex[®] L/S[®] Series peristaltic pumps 77202-60 were used in CSTR for efficiently dispensing ferrous chloride solution, ferric chloride solution and sodium hydroxide solution into the reactor using Masterflex[®] L/S[®] 13 Norprene[®] Precision Tubing; Masterflex[®] L/S[®] Series peristaltic pumps 77200-62 were used in CSTR for transferring feed (untreated synthetic waste water) and waste (treated synthetic waste water) using Masterflex[®] L/S 24 Tygon[®] LFL High-Performance Precision Tubing. Heidolph RZR 2102 Overhead Stirrer was used for maintaining homogeneity in CSTR reactor.

3.5 Analysis:

3.5.1 HPLC ICP-MS:

ICP-MS is an analytical instrument which offers quite sensitive and efficient detection of trace elements (in ppb) in aqueous and organic samples with wide elemental coverage. ICP-MS distinguishes ions based on their m/z ratio. A new analytical method was developed within Shell by hyphenation of ICP-MS and HPLC for speciation of selenium in refinery effluent. This method first separates SeO_4^{-2} and

SeO_3^{-2} by HPLC using Hamilton-PRP-X-100 column (25 cm length and 4.1 mm internal diameter) having polystyrene divinylbenzene (10 μm particle size and 100 \AA pore size) as packing material. 10mM ammonium citrate buffer mixed with 2% methanol was used as the mobile phase. After separation by HPLC, SeO_3^{-2} and SeO_4^{-2} will individually enter ICP-MS according to their retention time i.e. 4.00 min. and 9.26 min. respectively (**Fig. 6**). Argon was used as plasma gas and carrier gas in ICP-MS. Hyphenation of HPLC with ICP-MS provides better control over matrices and minimizes matrix interferences. Calibration of the instrument is required prior to every analysis. For calibration, two stock solutions of selenate and selenite of concentration 1000ppb were prepared in advance using sodium selenate and sodium selenite respectively. Mixed calibration standard of selenite and selenate containing 50ppb selenite and 50ppb selenate was prepared using above stock solutions. Further, this mixed standard was diluted using mobile phase and DI water to make calibration standards of total selenium concentration 2.5ppb, 5ppb, 10ppb, 20ppb and 40ppb (**Table 1**). The detection limit of the system is 0.8ppb and quantification limit is 2.5ppb.



Fig. 4: Schematic presentation of the hyphenated system of HPLC and ICP-MS

A blank solution was prepared to verify any contamination by mobile phase and DI water. At the end, quality assurance samples or certified standards were also run to ensure the calibration of the instrument. A calibration curve is obtained for both selenite Se(1) and selenate Se(2) as shown in **Fig. 5**. For analysis purpose, samples were filtered and diluted using mobile phase and DI water. Dilution factors were chosen in a manner such that concentration of selenite and selenate in the

sample lie within calibration range of the instrument. **Fig. 6** is an example of chromatogram obtained from analysis of treated synthetic waste water by HPLC ICP-MS.

S.N.	Se Conc. (ppb)	100ppb standard (g)	Ammonium citrate buffer (g)	DI Water (g)
1	0	0	1	9
2	2.5	0.25	1	8.75
3	5	0.5	1	8.5
4	10	1	1	8
5	20	2	1	7
6	40	4	1	5

Table 1: Calibration standards preparation method for HPLC ICP-MS

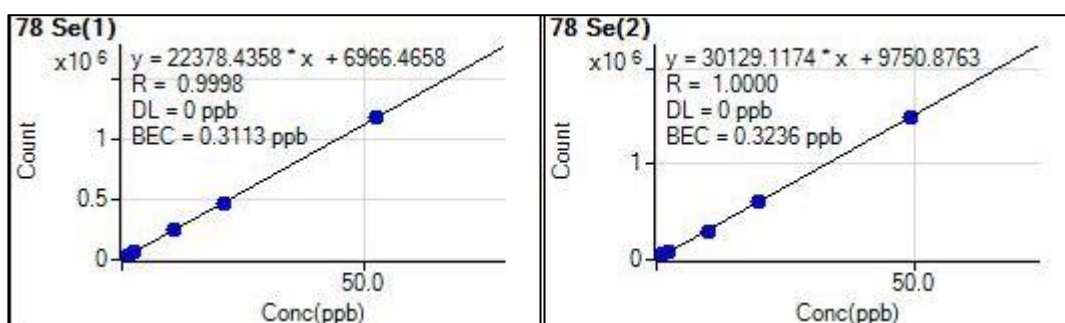


Fig. 5: Calibration curve of selenite Se(1) and selenate Se(2) by HPLC ICP-MS

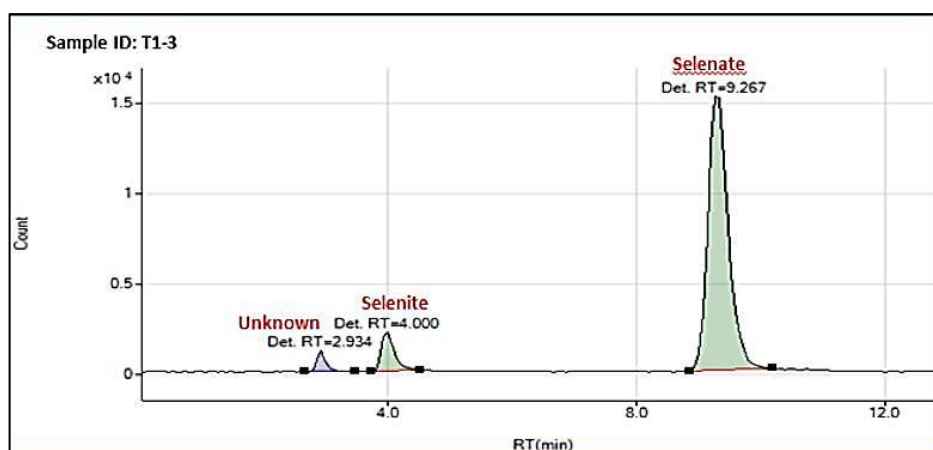


Fig. 6: Chromatographic separation of selenite Se(1) and selenate Se(2) by HPLC ICP-MS

3.5.2 Ion Chromatography:

The main objective of analysis of waste water samples by ion chromatography was to detect and quantify nitrate and sulfate present in the samples. Later on, these quantifications will help in estimating the interference of nitrate and sulfate in selenium removal process and therefore, amount of iron required to compensate the interference. For this purpose, 15ml filtered waste water sample was submitted to analytical team of Shell New Technology Center, Bangalore. This procedure uses RFIC Ionpac AS15 anion exchange column with a guard column AG15. Millipore water was used as mobile phase. Eluent flow rate was kept 1.2 ml/min. The column separates anions based on their affinity toward stationary phase and conductivity detector generates a signal depending upon their retention time. According to the chromatogram of untreated waste water generated by ion chromatography (**Fig. 7**), sulfate appears at 8.5 min. retention time and nitrate appears at 11.7 min. retention time. Concentration of sulfate and nitrate were calculated by integrating their peak area.

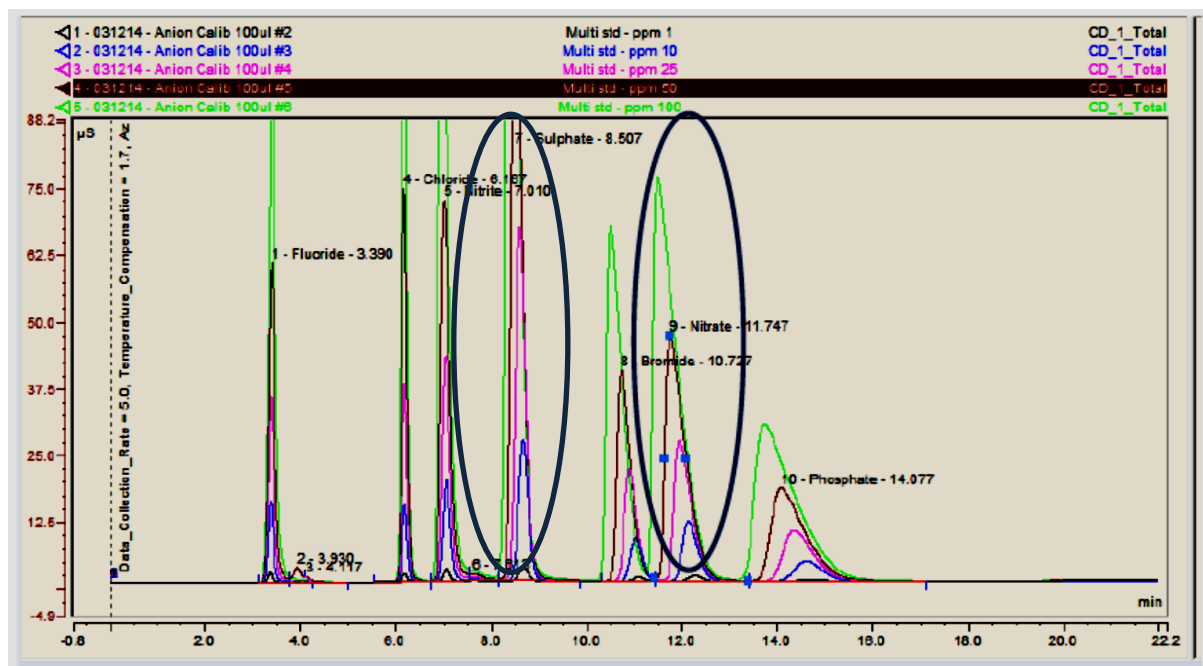


Fig. 7: Chromatographic separation of various anions present in waste water by Ion-chromatography

3.5.3 Volumetric Titrator:

Detection and quantification of $\text{HCO}_3^-/\text{CO}_3^{2-}$ in waste water was done by volumetric automated titrator. The instrument can work on various titration modes i.e. dynamic equivalence point titration, monotonic equivalence point titration and set endpoint titration. The working mechanism uses the principle of basic acid-base titration of $\text{HCO}_3^-/\text{CO}_3^{2-}$ present in the sample with NaOH. A titration curve is generated as soon as the equivalence point is reached which estimates the amount of reagent used for the titration; accordingly, amount of $\text{HCO}_3^-/\text{CO}_3^{2-}$ present in the system can be calculated. During designing of CSTR (*section 3.6.3*), we encountered the requirement of a sophisticated instrument which can control the pH of the system at a particular value for sufficiently long time. Initially, mock runs were performed using peristaltic pump which dispenses required amount of NaOH into the reactor to maintain a constant pH. The major drawback of this method was the poor control over pH since the flow rate of the pump had to be controlled manually. Moreover, maximum deviation observed was -0.5 to +0.5 which was fairly high for pH sensitive reactions.

As will be discussed in *section 3.6.3*, we came up with a thought of using SET endpoint titration mode in volumetric titrator to control pH in CSTR. Excellent control over pH with maximum deviation -0.2 to +0.2 was observed; however, the instrument can dispense only 20ml of reagent at a time and requires refilling (takes approximately 30-40 sec.) quite frequently. During the refilling period, pH of the system goes very down (pH 3-4) due to the presence of highly acidic FeCl_3 . In order to mitigate above shortcomings, we ended up with an idea to use both peristaltic

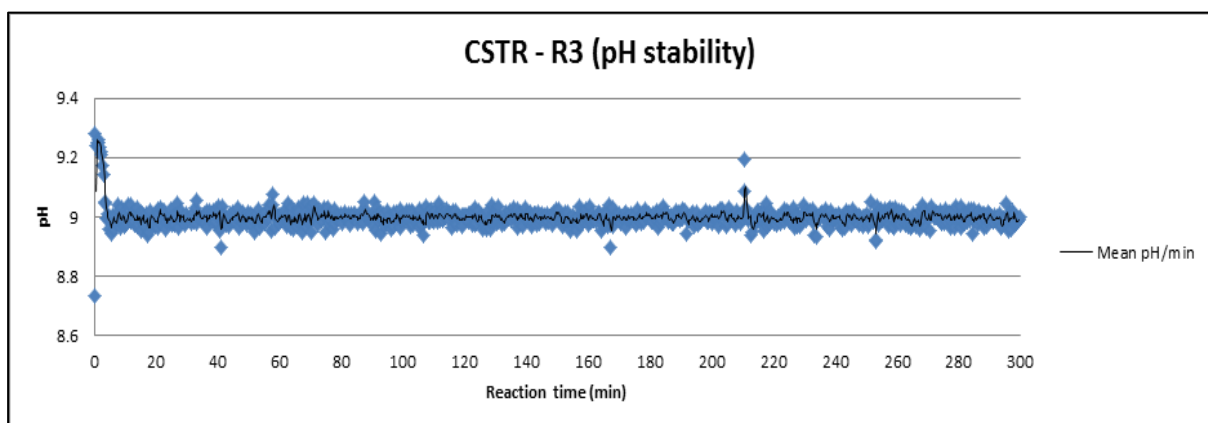


Fig. 8: Fine control over pH at 9 during CSTR run for 5 hrs

pump and volumetric titrator for pH adjustment in CSTR. Bulk pH adjustment was thought to be done by peristaltic pump and fine pH adjustment by a logical programme in volumetric titrator. In this way, we overcame the problem of frequent refilling since fine pH adjustment by titrator requires very less reagent. **Fig. 8** represents fine control over pH in one of the CSTR runs with average pH 8.999339 and standard deviation 0.032803 over 5 hours using a combination of volumetric titrator and peristaltic pump.

3.6 Experimental Procedure:

3.6.1 Preparation of Synthetic Waste Water:

According to the characterization data obtained in *section 3.5.2 and 3.5.3*, waste water sample contains 260 ppm sulfate, 250 ppm bicarbonate and 40 ppm nitrate. Due to limited availability of waste water samples, synthetic waste water will be required for mimicking the actual waste water composition during laboratory experiments. Preparation of synthetic waste water was done by dissolving required amount of sodium sulfate, sodium bicarbonate, sodium nitrate, sodium selenite, and sodium selenate in deionized water. Concentration of selenate and selenite was varied individually from 50 ppb to 160 ppb for different experiments.

S.N.	Chemical	M.Wt. (g/mol)	Conc.	Amount to be added for 1L solution
1	DI Water			1000 g
2	Sod. selenite*	172.94	80 ppb	175.22 µg
3	Sod. selenate*	188.94	80 ppb	191.43 µg
4	Sod. bicarbonate	84.01	250 ppm	344.30 mg
5	Sod. nitrate	84.99	40 ppm	54.83 mg
6	Sod. sulfate	142.01	260 ppm	384.61 mg

Table 2: Composition of 1L synthetic waste water

*Concentration of selenite and selenate was varied for various experiments; remaining composition remains constant.

*Sodium selenite and sodium selenate were added from their 1000ppb stock solutions because of very less concentration.

3.6.2 Experiments in Batch Process:

Three methods for removal of selenium, (i) Fe⁺² salt addition, (ii) Fe⁺³ salt addition and (ii) mixture of Fe⁺² and Fe⁺³ salt addition were performed in batch

process. The first objective of executing the experiments in batch process was to understand the effect of total iron dosing on selenium removal. The second objective of batch studies was to identify the effect of pH variation on removal efficiency. As discussed in *section 3.1*, formation of Green rust and redox reaction take place at alkaline pH whereas adsorption of selenium species onto ferrihydrite occurs at neutral to slight alkaline pH. In order to maintain a balance between adsorption and redox reaction, pH range from 7 to 9 was chosen for carrying out the study. The experiments were performed at 100ml scale in synthetic waste water (containing 50ppm selenite and 50ppb selenate). For (i) and (ii), $\text{FeCl}_2/\text{FeCl}_3$ was added to synthetic waste water followed by quick adjustment to the desired pH. The mixture was stirred for 30 min. After the completion, 10ml sample was filtered for HPLC ICP-MS analysis. For (iii), the experiment was conducted in two steps. First, FeCl_3 was added to synthetic waste water and 10ml filtered sample was collected after stirring the mixture for 15 min. Then FeCl_2 was added and pH was adjusted to the desired value. The mixture was stirred for 30 min more and 10 ml sample was filtered after the completion.

3.6.3 Experiments in Continuous Process:

The next stage of the study was to conduct above experiments at larger scale in a continuous process. In chemical industries, chemical reactors are used to execute these experiments where reactants and product continuously flow in and out of the reactor with continuous stirring. In that direction, we designed a Continuous Stirred Tank Reactor (CSTR) (**Fig. 9**) at laboratory scale to imitate industrial conditions. All the experiments on CSTR were performed at 5L volume of reactor scale. The experiments were conducted in two modes; co-addition and two step addition of ferrous and ferric salts. **Fig. 9** shows Block Flow Diagram (BFD) of CSTR for two step addition. Two 5L reactors **3**, **4** were connected in series. Two peristaltic pumps, **9** for 45% FeCl_3 solution and **8** for feed (synthetic waste water) were connected to **3**. pH of untreated synthetic waste water ranges from 6.5-7.5 and presence of substantial amount of bicarbonate keeps it buffered; so, no pH adjustment was required in **3** (step 1). pH adjustment was done only in **4** (step 2). An additional pump **12** was used as a bridge for transferring half treated feed from **3** to **4**. Potentiometric titrator and three peristaltic pumps, **10** for 15% ferrous chloride

solution, **11** for 10% sodium hydroxide solution and **13** for waste (treated synthetic waste water) were attached to **4**. 100L feed **1** was prepared prior to every run. For co-addition of ferrous and ferric salts, **3** and **12** were removed from BFD and **8, 9** were connected to **4**. The entire system was kept in a secondary tray to prevent any massive injury by spillage of chemicals. **6, 7** (Acute Toxic Substance; ACT) and **5** (hazardous chemical) were kept in secondary containers; separate container which can hold volume as large as 200L was used for keeping 100L feed tank and 100L waste tank. Since we were dealing with large volume of chemicals, a safety assessment of the entire system was done by HSSE (health, safety, security and environment) department of Shell New Technology Centre, Bangalore.

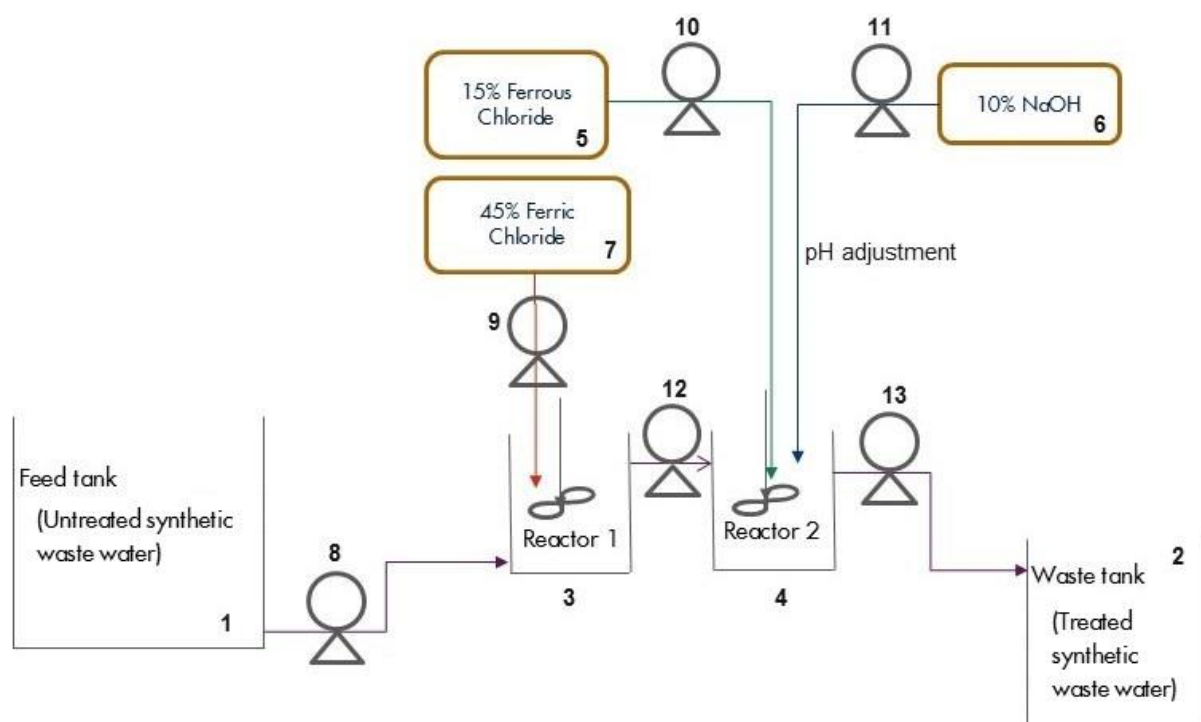


Fig. 9: Block Flow Diagram (BFD) of CSTR for two-step addition
 *8, 9, 10, 11, 12, and 13 are peristaltic pumps.

For two-step addition, the experiment starts with pumping feed and FeCl_3 into **3**. So, as soon as the level reaches 5L mark, **12** starts transferring the half treated feed from **3** to **4**. In order to maintain 5L feed in **3**, flow rate of **8** and **12** were kept same. **10** starts dispensing FeCl_2 solution into **4**. Bulk pH adjustment in **4** was done by peristaltic pump **11** and fine pH adjustment was done by potentiometric titrator. **13** will start pumping out the waste into **2** as soon as it overflows from 5L marking. For co-addition, **8, 9** and **10** will dispense feed, FeCl_3 and FeCl_2 solution respectively into

4 due to the absence of 3 and 12. The remaining procedure remains same. Every experiment was run for 5-6 hours. Following assumptions were taken during the execution of experiments on CSTR:

1. Perfect mixing; therefore, all spatial derivatives become zero.
2. Composition of material at outlet is identical to material present inside the reactor.
3. The reaction runs at steady state; therefore, all the time derivatives become zero.
4. Constant temperature
5. First order reaction
6. Irreversible reaction

Following is the mass balance equation of CSTR:

$$\left[\begin{array}{c} \text{flow of X into the} \\ \text{reactor} \end{array} \right] - \left[\begin{array}{c} \text{flow of X out of} \\ \text{the reactor} \end{array} \right] + \left[\begin{array}{c} \text{rate of} \\ \text{generation of X} \end{array} \right] = \left[\begin{array}{c} \text{rate of} \\ \text{accumulation of X} \end{array} \right] \quad (2)$$

According to assumption 1, r_A will be constant throughout the reactor and rate of accumulation over time becomes zero.

$$\Rightarrow \{Q.C_{in}\} - \{Q.C_{out}\} - \int r_A dv = 0 \quad (3)$$

$$\Rightarrow Q (C_{in} - C_{out}) = r_A.V \quad (4)$$

Where, Q = Volumetric flow of the feed (ml/min)

C_{in} = Concentration of X at the inlet ($\mu\text{g/ml}$)

C_{out} = Concentration of X at the outlet ($\mu\text{g/ml}$)

$-r_A$ = Rate of generation of X

V = volume of the reactor

$$\Rightarrow (C_{in} - C_{out}) = r_A.V/Q$$

$$\Rightarrow (C_{in} - C_{out}) = r_A.\theta_H \quad (5)$$

$V/Q = \theta_H$ is called Hydraulic Retention Time (HRT), which represents average time any species has spent inside the reactor.

$$\Rightarrow 1 - C_{out}/C_{in} = \theta_H.r_A/C_{in}$$

$$\Rightarrow 1 - C_{out}/C_{in} = \theta_H.K \quad (6)$$

For first order reaction $r_A = K.[C_{in}]$

Where K = Rate constant

$$\Rightarrow 1 - \theta_H.K = C_{out}/C_{in} \quad (7)$$

(7) is called Levenspiel equation of CSTR. According to equation (7), C_{out} and therefore, conversion of X into product will depend on θ_H . Change in the flow rate of feed will change θ_H , which can be manipulated to control conversion of the reactant into product. Sampling was done at every θ_H time interval to ensure a new batch in the reactor. Every experiment was run for 5-6 hours with continuous sampling to ensure no changes in the removal efficiency occur over time. The entire study with CSTR was performed at different pH falling in the range 7-9.

3.6.4 Kinetic Studies:

The main objective of studying kinetics for selenate and selenite removal by mixture of Fe^{+2} and Fe^{+3} salt addition method was to find out the time required to achieve steady state in a continuous process (CSTR). Later on, this will help in scaling up the technology at industries. Previous studies done in batch process suggested that the reaction is extremely fast and completes in less than a minute. Practically, it is not possible to collect substantial amount of sample for kinetic studies at various time intervals within one minute. So, we decreased the scale of the reaction from 5L to 100ml to achieve very low hydraulic retention time (calculated by Levenspiel equation of CSTR) which ensures incomplete reaction. The entire setup and procedure is similar to *section 3.6.3*. Four CSTR runs were performed at different feed flow rates to achieve a retention time as low as 24 sec (**Table 3**). The major limitation of this system is that kinetic studies by Levenspiel equation of CSTR will be valid if and only if the reaction is first order or pseudo first order.

Kinetics experiment (ferrous-ferric addition)					
	Composition	Exp 1	Exp 2	Exp 3	Exp 4
Feed	160ppb (Selenite)+ 160ppb (Selenate)	2.5 L/h	5 L/h	10 L/h	15 L/h
FeCl ₂	15%	2.11mmol Sec. ⁻¹ L ⁻¹	2.11mmol Sec. ⁻¹ L ⁻¹	2.11mmol Sec. ⁻¹ L ⁻¹	2.11mmol Sec. ⁻¹ L ⁻¹
FeCl ₃	45%	1.01mmol Sec. ⁻¹ L ⁻¹	1.01mmol Sec. ⁻¹ L ⁻¹	1.01mmol Sec. ⁻¹ L ⁻¹	1.01mmol Sec. ⁻¹ L ⁻¹
pH	10 % NaOH	9	9	9	9
θ_H^*		144 sec.	72 sec.	36 sec.	24 sec.

Table 3: Experimental planning for kinetic studies

* θ_H is the hydraulic retention time (HRT) calculated by Levenspiel equation

4. Results and Discussion

The main objective of this investigation is to find a solution to remove selenium efficiently from refinery effluent. Henceforth, the presented study will mainly focus on the development of the process and its application on industrial scale.

4.1 Selenium Removal Efficiency Analysis in Batch Process:

Current facilities available at industries (ferric addition process) are using 4.7 mmol/l iron dosing. In order to remain consistent with them, we executed batch studies at same iron dosing. Three experiments using ferrous addition, ferric addition and ferrous-ferric addition method were performed at 4.7mmol/l total iron dosing. Ferrous-ferric addition method was performed in two step manner. These experiments were carried out at pH 9. As indicated in **Fig. 10** all three methods could remove only selenite from the solution; hence, total selenium comes down from 100ppb to nearly 50ppb. One reason for such results could be lack of required dosage of iron for satisfactory removal. In that order, three more experiments with three times higher dosing i.e. 14.1mmol/l total iron were performed. Obtained results in **Fig. 10** show that ferric addition method still could not remove selenate from the solution. Ferrous addition method removed both selenite and selenate but could not go below 20ppb total selenium. Best results were obtained with ferrous-ferric addition method which removed both selenate and selenite to <5ppb total selenium. These results are consistent with the hypothesis given in *section 3.1*.

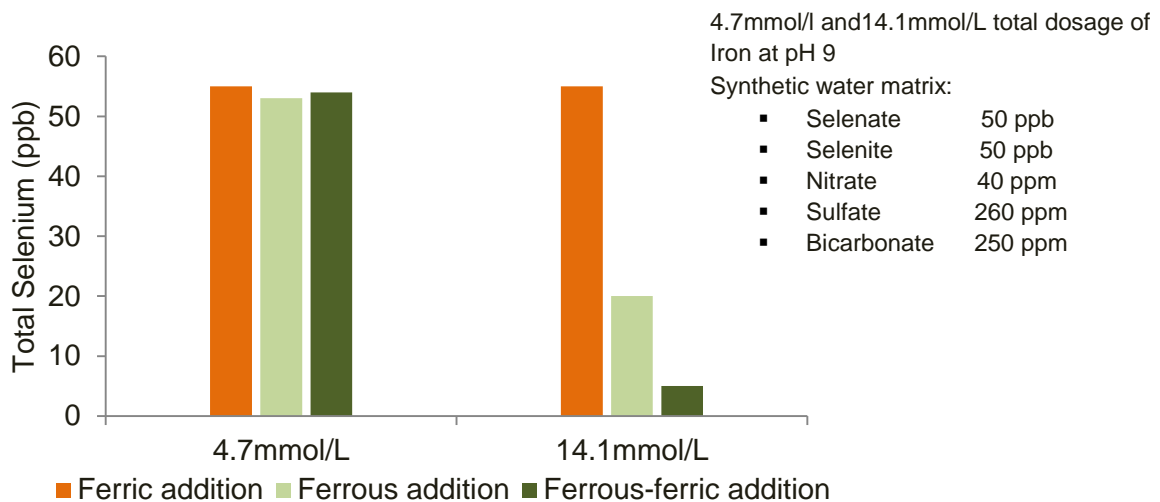


Fig. 10: Comparison of selenium removal efficiency by ferrous/ferric/ferrous-ferric addition method at pH 9

In order to find out whether <5ppb removal is happening at some intermediate concentration (between 4.7mmol/l and 14.1mmol/l), similar experiments were performed at two times higher dosing than 4.7mmol/l i.e. 9.4mmol/l total iron for ferrous-ferric addition method at pH 9. Plotted results in **Fig. 11** explain that almost linear increase in removal efficiency was observed on an increase in iron dosing. However, the method performed the best still at 14.1mmol/l. These results explain that minimum 14.1mmol/l iron dosing is required for achieving <5ppb total selenium by ferrous-ferric addition method.

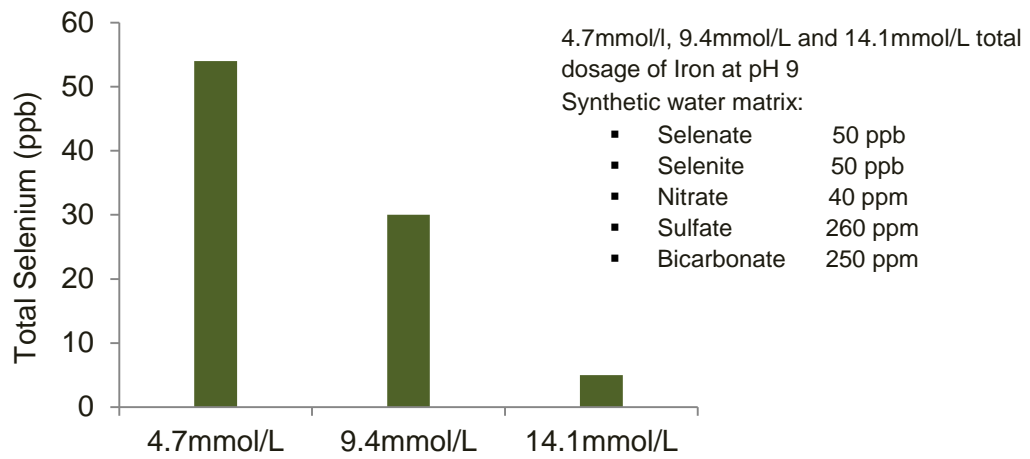


Fig. 11: Effect of iron dosing on selenium removal efficiency by ferrous-ferric addition method in at pH 9

As discussed in *section 3.1*, both generation of “Green rust” and adsorption of selenium species on “Ferrihydrite” are pH dependent phenomenon. So, next step would mainly focus on monitoring the effect of pH variation on selenium removal by the best identified technology (ferrous-ferric addition). Adsorption occurs best at neutral to slight alkaline pH and Green rust formation occurs best at alkaline pH. It’s very important to maintain a balance between adsorption and redox conversion to achieve exceptional results. So, the study was conducted at pH range 7 to 9 for ferrous-ferric addition method. **Fig. 12** shows that pH 7 could not remove selenate due to lack of formation of green rust. On the other hand, pH 8 and 9 both could remove selenate and selenite to <5ppb which indicates that at pH range 8 to 9 both redox and adsorption reactions are occurring to the desired extent.

We can conclude from batch studies that ferrous-ferric addition method performed the best and minimum 14.1mmol/l total iron dosing is required for achieving <5ppb selenate and selenite in pH range 8 to 9. Since ferrous-ferric addition method is showing considerable removal at laboratory scale, henceforth, our next aim will be focusing on development of this technique at larger scale.

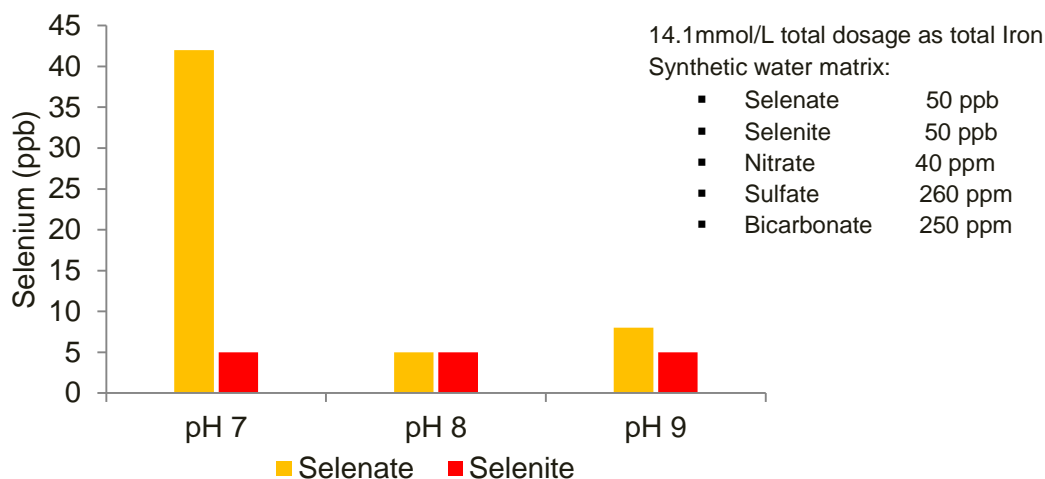


Fig. 12: Effect of pH on selenium removal efficiency by ferrous-ferric addition method

4.2 Selenium Removal Efficiency Analysis in Continuous Process:

As discussed in section 3.6.3, A Continuous Stirred Tank Reactor (CSTR) was designed to verify the validity and performance of ferrous-ferric addition technique at larger scale. The experiments on CSTR were performed in co-addition and two-step addition manner. However, Co-addition of iron salts is usually preferred by the industries since it requires fewer changes in the existing facilities. Therefore, we first demonstrated ferrous-ferric addition method on CSTR in co-addition manner. Initial concentration of selenate and selenite in synthetic waste water was kept 80ppb for each. Since selenium concentration in continuous process is almost double than batch process, we should expect considerable selenium removal at approximately 30mmol/l iron dosing (twice of 14.1mmol/l observed in batch studies). Feed flow rate was varied from 10L/h, 15L/h, 20L/h, 30L/h to 40L/h. Variation in flow rate of feed changes retention time; hence, conversion factor of reactants into product. Flow rate of ferrous chloride and ferric chloride were kept in a manner such that flow rates 10L/h, 15L/h, 20L/h, 30L/h and 40L/h represent 56.33mmol/l, 37.55mmol/l, 28.16mmol/l, 18.77mmol/l and 14.08mmol/l total iron respectively. The

experiments were performed at pH 9. **Fig. 13** clearly indicates that the technology is able to remove selenite from 80ppb to <5ppb even at the lowest iron dosing i.e. 14.08mmol/l in continuous process but it could remove selenate from 80ppb to 13ppb only at very high dosing i.e. 56.33mmol/l.

In order to compare the efficiency of Best available technology (ferric addition method) and ferrous-ferric addition method, we performed a set of runs using ferric addition method (pH 7-7.5) and ferrous-ferric addition method (pH 9) at 56.33mmol/l total iron dosing. Stacked plot of obtained results is shown in **Fig. 14**, which signifies that both methods can remove selenite from 80ppb to <5ppb but the newly developed method performed much better than BAT for removal of selenate from synthetic waste water.

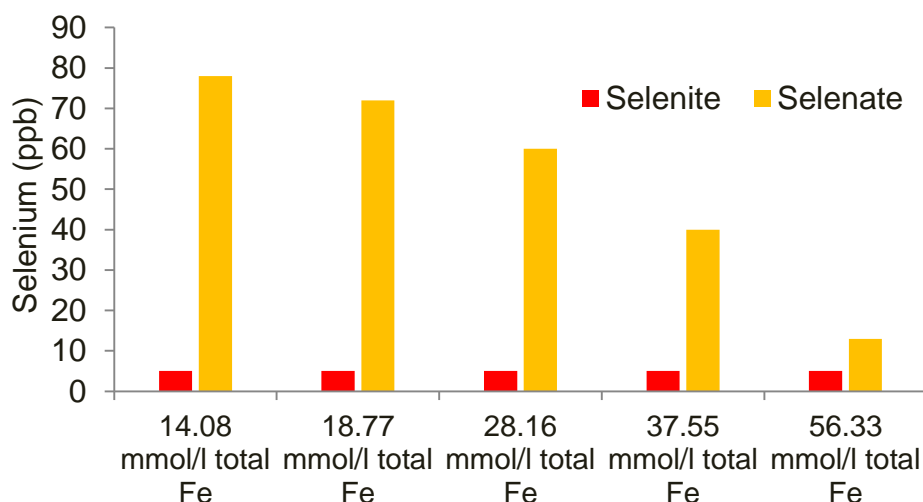


Fig. 13: Effect of iron dosing on selenium removal by ferrous-ferric co-addition method on CSTR at pH 9 (80/80 selenate/selenite) (Feed flow rate: 10L/h, 15L/h, 20L/h, 30L/h, 40L/h; run time: 6hours; Room temperature)

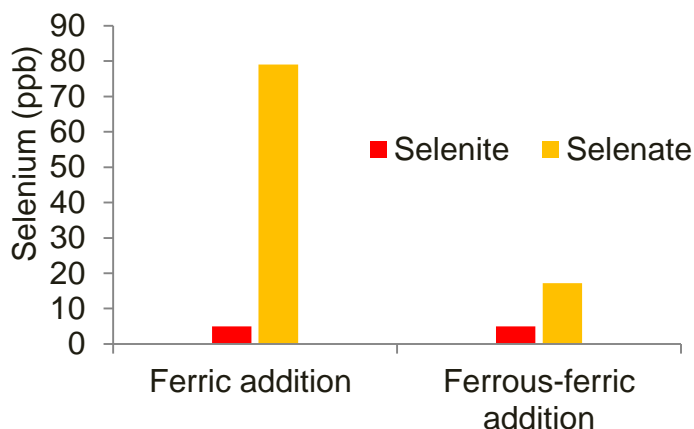


Fig. 14: Comparison of ferric addition and ferrous-ferric co-addition method on CSTR (80/80 selenate/selenite) (Feed flow rate: 10L/h; Total iron dosing: 56.33mmol/l; run time: 6hours; Room temperature)

Following the steps of batch studies, next action was to see the effect of pH on removal efficiency in continuous process. Set of experiments were performed on CSTR at 10L/h feed flow rate or 56.33mmol/l total iron dosing. The experiments were performed at four different pH 7.5, 8, 8.5 and 9. According to the results obtained from batch studies (**Fig. 12**), it was expected that selenate removal efficiency should increase with an increase in pH from 7.5 to 9 and selenite removal efficiency should remain nearly constant. As shown in **Fig. 15**, expected results were obtained for selenite removal efficiency but selenate removal efficiency decreased with an increase in pH. These results are quite inconsistent with the results obtained from batch studies. The possible reason could be that batch studies were performed in two step addition manner whereas continuous studies on CSTR were performed in co-addition manner. These results don't support co-addition of ferrous and ferric salt in CSTR; therefore, we should further concentrate on demonstration of two-step addition of ferrous and ferric salt in CSTR.

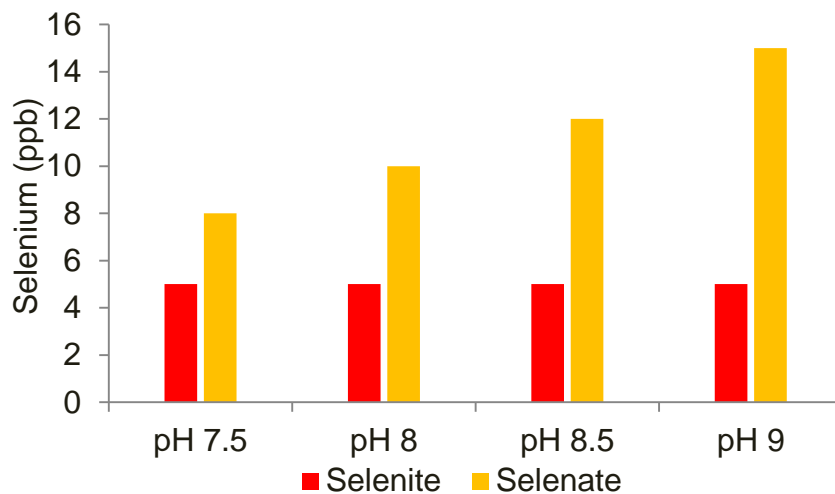


Fig. 15: Effect of pH on selenium removal efficiency at pH range 7.5 to 9 by ferrous-ferric co-addition method on CSTR (80/80 selenate/selenite) (Feed flow rate: 10L/h; Total iron dosing: 56.33mmol/l; run time: 6hours; Room temperature)

Results obtained by co-addition of ferrous and ferric salt suggested us to try two step addition of ferrous and ferric salt in CSTR. The first experiment with two step addition was performed at 10L/h feed flow rate or 56.33mmol/l total iron dosing and pH was maintained at 9. As shown in **Fig. 16**, 56.33mmol/l total iron dosing could remove both selenate and selenite to <5ppb total selenium after step 2. To see

the extent of removal at lower iron dosing, we varied the flow rate of feed over a range 10L/h, 15L/h, 20L/h, 30L/h to 40L/h and therefore, total iron dosing. As shown in **Fig. 16**, both selenate and selenite could be removed from the system to 7ppb total selenium at total iron dosing as low as 28.16mmol/l. In this case, obtained results are quite consistent with results obtained from batch studies.

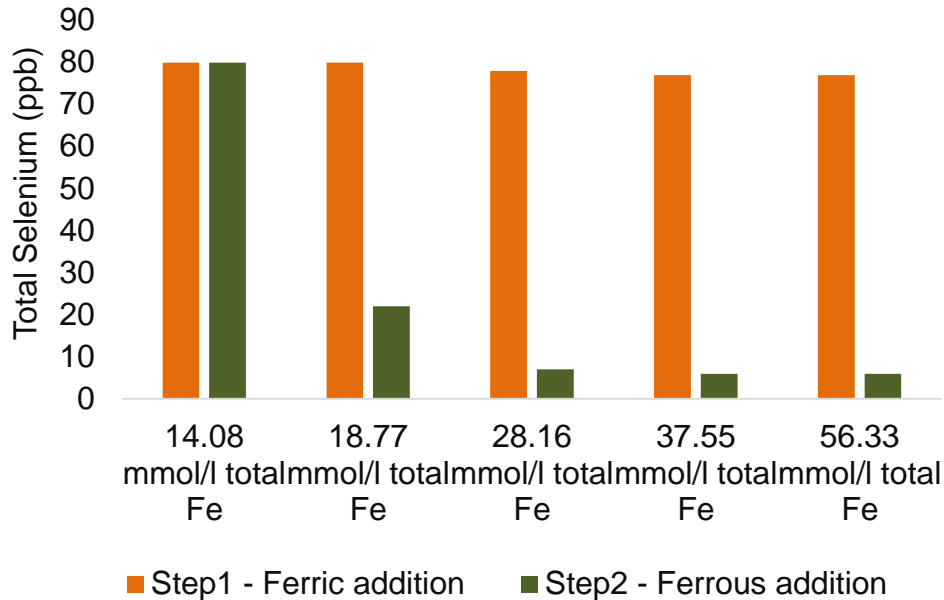


Fig. 16: Effect of iron dosing on selenium removal at pH 9 by ferrous-ferric two-step addition method on CSTR (80/80 selenate/selenite) (Feed flow rate: 10L/h, 15L/h, 20L/h, 30L/h, 40L/h; run time: 6hours; Room temperature)

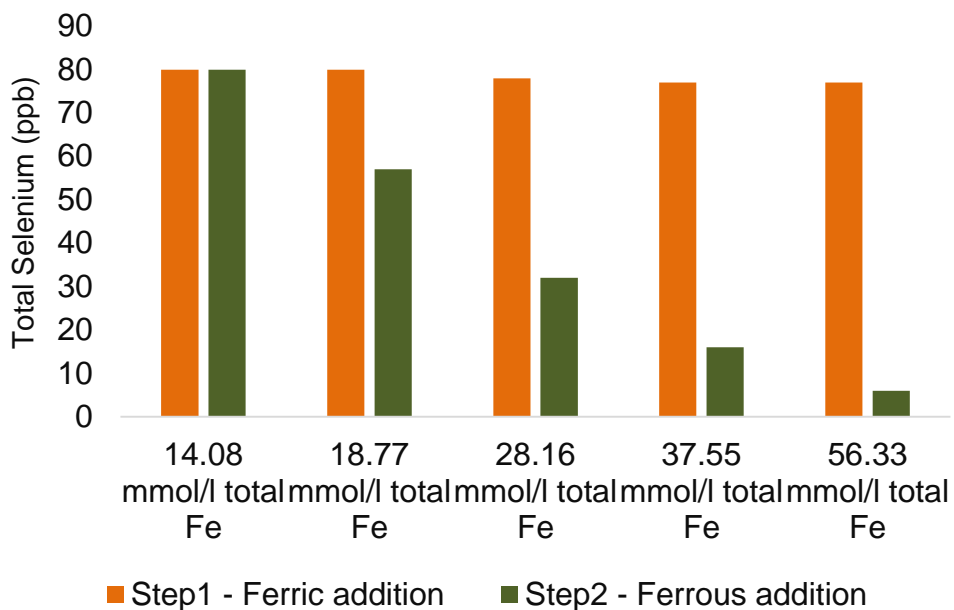


Fig. 17: Effect of iron dosing on selenium removal at pH 8 by ferrous-ferric two-step addition method on CSTR (80/80 selenate/selenite) (Feed flow rate: 10L/h, 15L/h, 20L/h, 30L/h, 40L/h; run time: 6hours; Room temperature)

To understand the effect of pH, similar experiments were performed at pH 8. Plotted results in **Fig. 17** clearly signify that pH 8 also works well for removing substantial amount of selenium but considerable results are obtained at relatively higher dosing. As a result, minimum 56.33mmol/l total iron dosing will be required for achieving 80ppb to 6ppb total selenium in treated waste water. So, at the end we can state that two-step addition of ferrous and ferric salt performed better than co-addition method in continuous process and acceptable selenium removal at lower dosing i.e. 28.16mmol/l was achieved at pH 9.

At the end of every CSTR experiment, tremendous amount of sludge (mixture of Green rust and ferrihydrite with adsorbed selenium species) is generated. For disposal of treated waste water into natural water bodies, considerably fast settling of sludge is equally important to separate treated waste water from toxic solid waste. Therefore, in the next section we focused on monitoring the settling of sludge produced by various experiments performed on CSTR in two step addition at pH 8 and pH 9 (**Fig. 16 and Fig. 17**). Settling time was kept 1 hour for every sample of sludge. **Fig. 18** represents stacked diagram of percentage sludge settled in 1 hour. Sludge settling rate will majorly depend on the iron dosing and morphology of sludge. Higher pH and lower iron dosing facilitate separation process due to less production of Green rust. We observed that approximately 80% separation of sludge from liquid phase occurs in one hour even at highest dosing. At iron dosing 28.16mmol/l, convincing separation (85%) occurs in one hour.

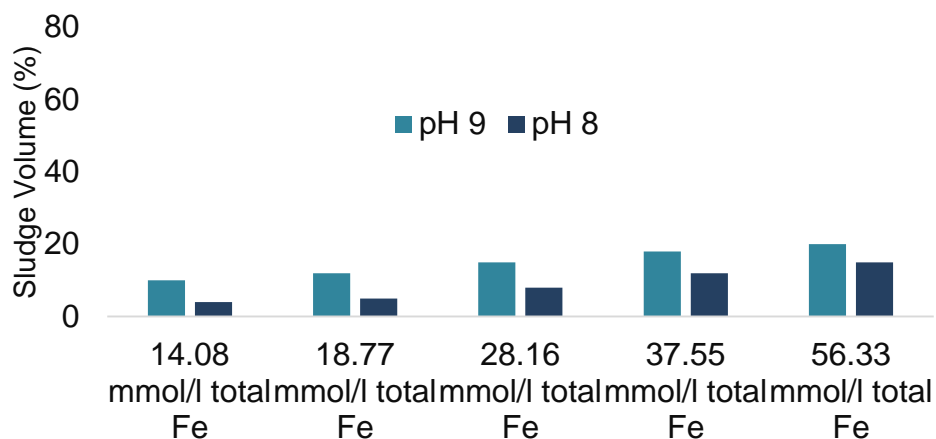


Fig. 18: Sludge settling studies at pH 8 and 9 by ferrous-ferric two-step addition method on CSTR (80/80 selenate/selenite) (Feed flow rate: 10L/h, 15L/h, 20L/h, 30L/h, 40L/h; run time: 6hours; Room temperature)

We also performed a comparison study on settling of sludge between co-addition, two step addition and ferric addition on CSTR. Sludge settling was monitored for 1 hour. We observed (**Fig. 19**) that sludge produced by ferric addition method was disperse in nature and settles very slowly. On the other hand, sludge produced by two step and co-addition of ferrous and ferric salt was compact in nature and settles quickly; however, sludge produced by two step addition of ferrous and ferric salt took least time to separate from liquid phase. These results also indicate that ferrous-ferric two-step addition process provides faster separation of toxic sludge from treated waste water compared to ferric addition process.

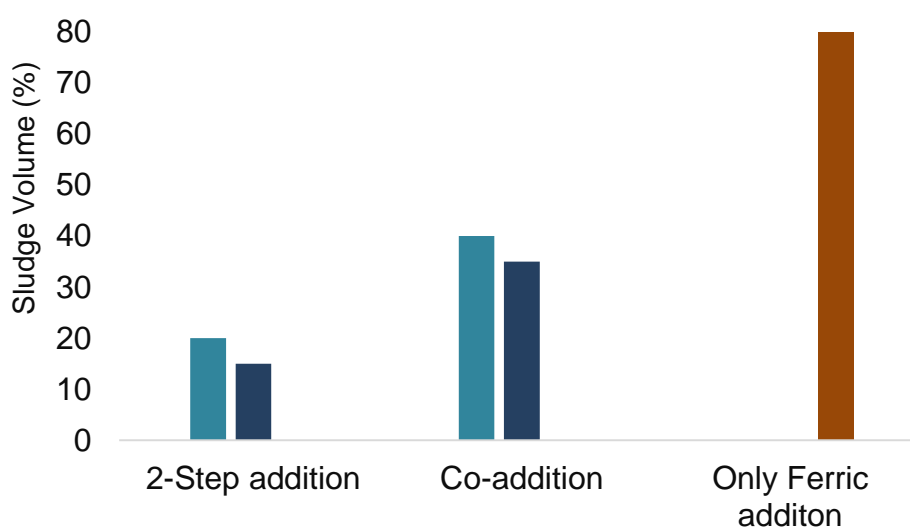


Fig. 19: Sludge settling studies by various available methods at pH 8 and pH 9 on CSTR (80/80 selenate/selenite) (Feed flow rate: 10L/h; run time: 6hours; Room temperature; total iron dosing: 56.33mmol/l)

4.3 Kinetic Studies of Selenate and Selenite Removal:

In order to study kinetic behaviour of selenate and selenite removal by ferrous-ferric addition method, ferrous chloride ($2.11\text{mmol Sec.}^{-1} \text{L}^{-1}$) and ferric chloride ($1.01\text{mmol. Sec.}^{-1} \text{L}^{-1}$) were added to 100ml reactor in a continuous process (CSTR) and pH was maintained at 9. Model refinery effluent containing 160ppb selenate and 160ppb selenite was prepared prior to the analysis. The experiment was performed at four different flow rates as shown in **Table 4** and **Table 5**. It was

observed (**Table 4**) that selenate is removed from 161.3 ppb to <10 ppb if minimum 144 seconds are provided for the reaction to occur.

Exp.	Reactor volume (ml)	Feed rate (L/h)	Selenate (ppb) conc. in feed	Selenate (ppb) conc. in reactor	Hydraulic retention time (sec)	Cout/ Cin
1	100	2.5	161.3	9.5	144	0.06
2	100	5	161.3	20.8	72	0.13
3	100	10	161.3	34.5	36	0.21
4	100	15	161.3	54.6	24	0.34

Table 4: Kinetics of Selenate removal by ferrous-ferric addition method at pH 9

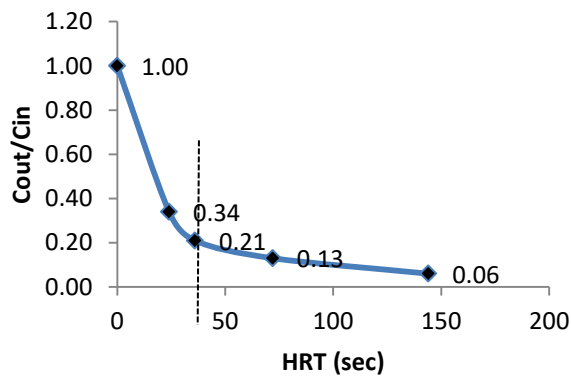


Fig. 20: C_{out}/C_{in} vs. Hydraulic retention time for Selenate removal by ferrous-ferric addition method

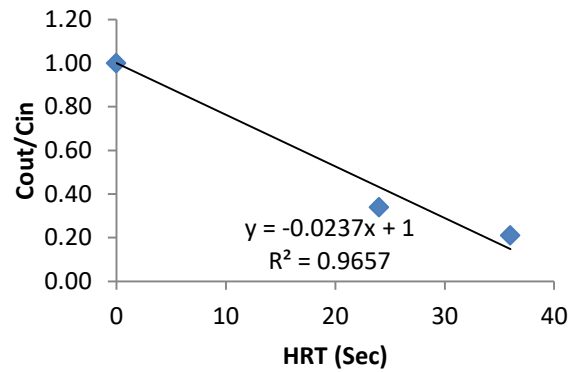


Fig. 21: Levenspiel plot for Selenate removal by ferrous-ferric addition method

According to **Fig. 20**, Selenate removal by ferrous-ferric addition method follows Levenspiel equation of CSTR (7) till 36 seconds retention time. After 36 seconds, it deviates from Levenspiel equation. So, removal of Selenate follows first order kinetics till a specific point and later the order of the reaction changes. Therefore, this reaction is a pseudo first order reaction.

$$-\frac{d(\text{SeO}_4)}{dt} = K [\text{SeO}_4^{-2}][\text{Fe}] \quad (4)$$

$$-\frac{d(\text{SeO}_4)}{dt} = K' [\text{SeO}_4^{-2}] \quad (5)$$

$$\text{Where } K' = K [\text{Fe}]$$

The Levenspiel plot of selenate removal is shown in **Fig. 21**. According to Levenspiel equation of CSTR **(7)**, magnitude of slope of the Levenspiel plot denotes rate constant of the first order reaction.

Therefore,

$$K' = 0.0237 \text{ sec}^{-1}$$

$$K [\text{Fe}] = 0.0237 \text{ sec}^{-1}$$

$$\text{Total iron dosage } [\text{Fe}] = 3.12 \text{ mmol. Sec.}^{-1} \text{ L}^{-1} (2.11+1.01 \text{ mmol Sec.}^{-1} \text{ L}^{-1})$$

So,

$$K = 0.0076 \text{ L. mmol}^{-1}$$

Removal of selenate by ferrous-ferric addition method follows pseudo first order kinetics. The possible reason behind this anomaly is that at retention time less than 36 seconds, iron doesn't play very important role in driving the reaction since the solution is flowing out from the reactor very rapidly; therefore, rate of the reaction is determined only by the retention time of selenate in the reactor.

Exp.	Reactor volume (ml)	Feed rate (L/h)	Hydraulic retention time (sec)	Selenite (ppb) conc. in feed	Selenite (ppb) conc. in reactor
1	100	2.5	144	172.1	7.2
2	100	5	72	172.1	<5
3	100	10	36	172.1	<5
4	100	15	24	172.1	<5

Table 5: Kinetics of Selenite removal by ferrous-ferric addition method at pH 9

On the other hand, results obtained for selenite removal are shown in **Table 5**, which clearly indicate that selenite is removed from 172.1 ppb to <5 ppb even at the lowest retention time 24 seconds.. Therefore, derivation of rate law and rate constant for kinetics of selenite removal is not possible by this method.

5. Conclusion

Selenium is a highly toxic element and removal of the same from Industrial waste water is necessary for the protection of aquatic and aquatic dependent wild life. We initiated this study to develop a new method which is scalable, deployable, safe, fast and offers <5ppb selenium content in treated waste water. In that direction, we developed a new method for selenium removal i.e. addition of ferrous and ferric salt to industrial waste water. Experiments using this method in batch process provided convincing selenium removal from 100ppb to <5ppb at 14.1mmol/l total iron dosing and pH range 8-9. When the technology was demonstrated on larger scale (CSTR), it showed exceptional results 160ppb to 6ppb only at pH 9 in two-step addition manner at 28.16mmol/l total iron dosing. Ferrous-ferric addition method is an up-gradation of the Best Available Technology (BAT); therefore, it doesn't require massive changes in the already existing facilities. Moreover, Results obtained from CSTR studies of this method are quite consistent with the results obtained from batch studies. This shows that the process is deployable. Kinetic studies of the method showed that the reaction is exceptionally fast and requires 144 sec. for 161.3ppb to 10ppb removal of selenate and 24 sec. for 172.1 to 5ppb removal of selenite, which shows that the process is fast and scalable. Additionally, the proposed method requires nearly one hour for 85% separation of produced sludge from treated waste water. All these results clearly indicate that ferrous-ferric addition method is a potential approach for removing both selenate and selenite from industrial waste water to <5ppb concentration.

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